Physico-Chemical Studies of Uranyl Fluoride Complexes

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X-ray diffraction and IR and Raman spectroscopic characteristics of the following compounds of the $MF-UO_2F_2-H_2O$ *ternary system are presented:*

$M_3UO_2F_5$	$M = Na, K, Rb, Cs, NH_4$
$MUO_2F_3-H_2O$	$M = Cs, K;$ *for Cs:* $Cs_2(UO_2)_2F_6-2H_2O,$ *for K:* $K_3(UO_2)_3F_9-H_2O-2H_2O$
$M_2UO_2F_4-2H_2O$	$M = Cs, Rb:$ $M_4(UO_2)_2F_8-4H_2O$
$M_5(UO_2)_2F_9$	$M = K$
$M_3(UO)_2F_7-nH_2O$	$M = k, n = 2; M = Na, n = 6$
$M_2(UO_2)_3F_8-4H_2O$	$M = K, Rb, NH_4$

The condensation phenomenon observed by X-ray studies in different compounds of the series is described and the structural relationship of the ions existing in these complexes is shown. The vibrational studies concern different aspects of the above compounds, especially the influence of the cations, the solid state splittings and the variation of vibrational spectra in the condensation phenomenon.

Introduction

Presented in this report are some results obtained on alkaline halogenide uranyl complexes. Our laboratory has been working in this field for about 10 years, specifically on physico-chemical studies of uranyl fluoride complexes, and more precisely X-ray diffraction and IR and Raman spectroscopy on complexes of the ternary system $MF-UO_2F_2-H_2O$.

Fluorine is a captor of neutrons and acts as a poison in a nuclear fission reaction by lowering the neutron production. One isotopic separation method of preparing enriched uranium consists in using the gaseous diffusion of UF_6. To obtain UO_3 after this, UF_6 is made to react with a base, in this case NH_4OH, and then by pyrolysis of the precipitate, giving UO_3. Pure oxide is not obtained but it does have a very high fluorine ratio. It was thus necessary to examine the compounds formed in the reaction of neutralisation of UF_6 by the bases, such as NH_4OH, $NaOH$ or KOH. Uranium hexafluoride does not exist in solution. It is immediately hydrolysed giving UO_2^{++}

following the reaction $UF_6 + 2H_2O \rightarrow UO_2^{++} + 6F^- + 4H^+$. The precipitation of UF_6 by a base leads to the formation of compounds which are analogous to the compounds of the ternary system $MF-UO_2F_2-H_2O$. A study of such a system appeared interesting, since it would reveal the compounds formed in this system. By determining their structural characteristics in order to estimate the stability of these compounds, it helped in the comprehension of the pyrolysis reaction quoted earlier.

This paper is also concerned with the fundamental aspect of uranium for the linear uranyl ion shows very important secondary bonds in the equatorial plane. These coordination bonds are responsible for the condensation phenomenon. In one of the first experiments carried out in our laboratory, we noticed that the uranyl ion in solution is polymerised giving polynuclear ions of variable condensations.

Since the condensation phenomenon is difficult to study in solution we thought it preferable to study the polynuclear ions in the crystal state, in order to be sure of the existence of the condensed ions to make possible an examination of geometry and to foresee the consequences.

When fluoride ions are added to the previously described solution, crystallised compounds are often formed. What this implies is studying the ternary system $MF-UO_2F_2-H_2O$, finding the compounds of the system, and examining their structure in order to demonstrate the existence of the condensed ions which appear, and then studying their behaviour by a number of physico-chemical investigation methods applicable in solution.

The compounds of the ternary system $MF-UO_2F_2-H_2O$ are numerous. Table I shows the list of the compounds being studied at the present time in our laboratory.

Some of these compounds have been known for a long time. Others were found during the studies of the ternary system carried out by Sergienko and Davidovich [1]. After having checked the existence of the compounds previously discovered and studied their structure by X-ray investigation, we established other new compounds of the system. Some of these were difficult to detect because they were formed in

TABLE I. Various Compounds Studied in our Laboratory.

$M_3UO_2F_5$	M = Na, K, Rb, Cs, NH$_4$
$MUO_2F_3-H_2O$	M = Cs, K Cs$_2$[(UO$_2$)$_2$F$_6$–2H$_2$O] K$_3$[(UO$_2$)$_3$F$_9$–H$_2$O]–2H$_2$O
$M_2UO_2F_4-2H_2O$	M = Cs, Rb (M$_4$[(UO$_2$)$_2$F$_8$]–4H$_2$O)
$M_5(UO_2)_2F_9$	M = K
$K_3(UO_2)_2F_7-2H_2O$	Na$_3$(UO$_2$)$_2$F$_7$–6H$_2$O
$M_2(UO_2)_3F_8-4H_2O$	M = K, Rb, NH$_4$

a mixture with others, and again only X-ray studies of single crystals of the compounds enabled us to establish definitely formulae and properties.

A simple examination of the formulae already revealed a certain number of condensed ions in these compounds. This is the case for the compounds $Rb_2(UO_2)_2F_8-4H_2O$, $K_3(UO_2)_2F_7-2H_2O$ and $K_5(UO_2)_2F_9$. As we shall see later, this is also true for the series $MUO_2F_3-H_2O$ and $M_2UO_2F_4-H_2O$, which should more correctly be written respectively as $Cs_2(UO_2)_2F_6-2H_2O$ or $K_3[(UO_2)_3F_9-H_2O]-2H_2O$ and $M_4(UO_2)_2F_8-2H_2O$. The only series in which the uranyl ion keeps its mononuclear form is $M_3UO_2F_5$.

Structural Studies

The structure of the compound $K_3UO_2F_5$ was determined by Zachariasen [2] in 1954: it is made up of K^+ and $UO_2F_5^{-3}$ ions. This mononuclear ion was then found in the compounds $(NH_4)_3UO_2F_5$ [3–4], $Rb_3UO_2F_5$ [5] and $Cs_3UO_2F_5$ [6] whose crystal structures have been determined in our laboratory. The $UO_2F_5^{-3}$ ion has the form of a pentagonal bipyramid (Fig. 1) and the UO distance is 1.76 Å. The uranyl ion can be recognised, the U–F distance is
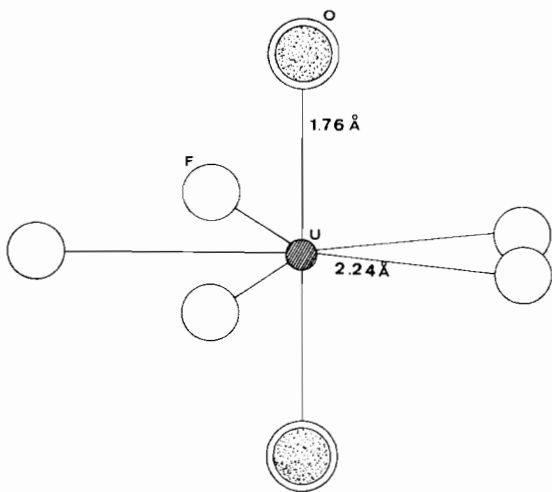

Fig. 1. The ideal structure of the $UO_2F_5^{3-}$ ion.

2.24 Å, the ion has D_{5h} symmetry. When it is placed in the unit cell and the group $UO_2F_5^{3-}$ is considered as a whole, the crystal structure of $M_3UO_2F_5$ is simple. The $UO_2F_5^{-3}$ ion is situated approximately on the corners of a c.f.c. lattice (Fig. 2). The alkaline atoms are placed on two different sites. One of the three alkaline atoms are situated on the c.f.c. sites (equivalent to the NaCl structure). The others are in the center of the 8 small cubes (equivalent to the fluorine atoms of the CaF$_2$ structure). However, the compounds of the series $M_3UO_2F_5$ (M = NH$_4$, K, Rb, Cs) are not isostructural.
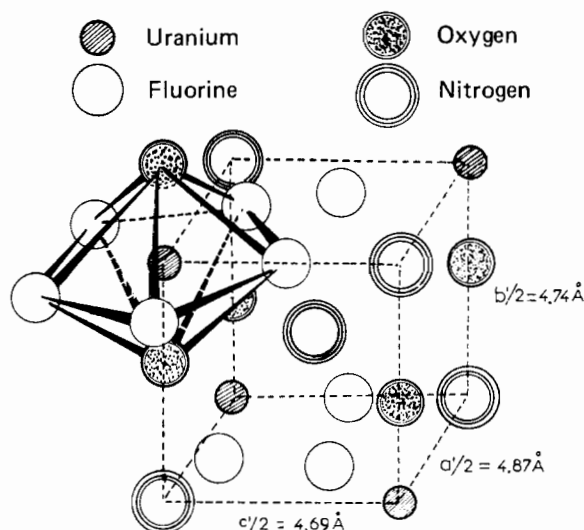
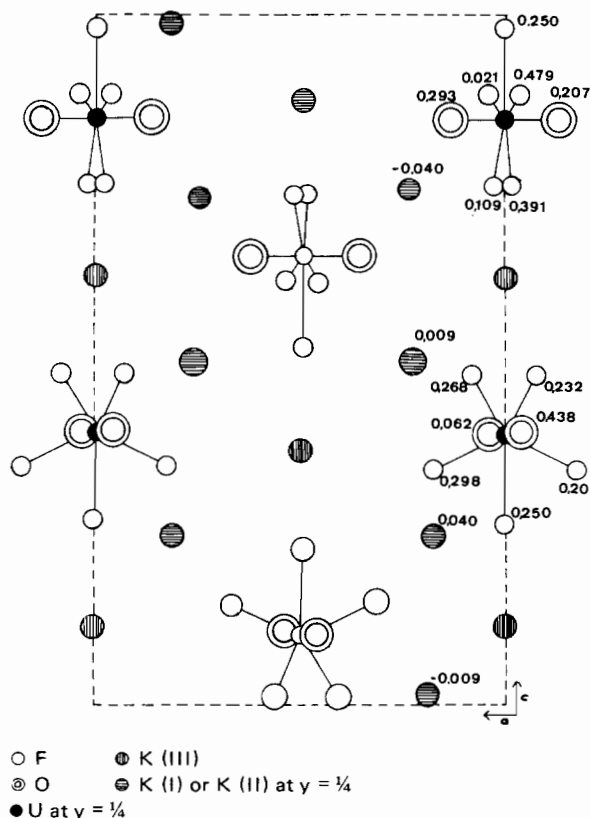Fig. 2. The eighth cell of the $M_3UO_2F_5$ structure.

In fact they do not crystallise in the same system (Table II). The ammonium compound crystallises in the monoclinic pseudo-orthorhombic, pseudo-cubic system, the potassium and rubidium compounds in the tetragonal system and the cesium compound in the cubic system. The main difference lies in the orientation of the dipyramid axis in the cell. Figure 3 shows the structure of the ammonium compound. The unit cell contains 6 formula units. It can be seen that the dipyramid axis remains parallel to the binary axis. In the potassium compound (Fig. 4), which is isomorphous with the rubidium compound, the dipyramid axis has 2 directions perpendicular to one another and forming an angle of about 10° with regard to the *a, b* axes of the unit cell. In the cesium compound a statistical structure has been observed (Fig. 5). Since it is impossible to place a D_{5h} symmetry ion in a fourfold symmetry site of the cubic system, this ion can only be found in a position of statistical disorder. The disorder concerns on the one hand the free rotation of the ion about its UO$_2$ axis, and on the other hand this axis can be oriented in a statistical manner following the 3 directions of the unit cell. This phenomenon is very important for our spectroscopic studies.

TABLE II. Crystallographic Data of the $M_3UO_2F_5$ Series.

$(NH_4)_3UO_2F_5$	$K_3UO_2F_5$	$Rb_3UO_2F_5$	$Cs_3UO_2F_5$
Pseudo-cell Orthorhombic			
$a' = 9.74$ Å	$a = b = 9.160$ Å	$a = b = 9.538$ Å	$a = 9.853$ Å
$b' = 9.48$ Å	$c = 18.167$ Å	$c = 18.573$ Å	
$c' = 9.38$ Å	$\frac{c}{2} = 9.083$ Å		
Monoclinic	Tetragonal	Tetragonal	Cubic
$Cm\ (C_s^3)$	$I4_1/a\ (C_{4h}^6)$	$I4_1/a\ (C_{4h}^6)$	$F2/m\bar{3}(T_h^3)$
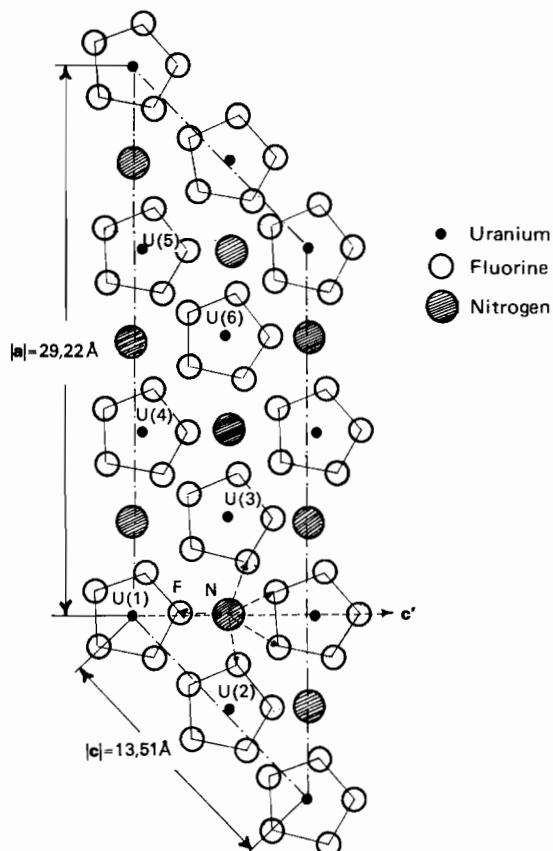
Fig. 3. The crystal structure of $(NH_4)_3UO_2F_5$.

Fig. 4. The crystal structure of $K_3UO_2F_5$ (after Zachariasen).

The compound $K_5(UO_2)_2F_9$ [7] crystallises in the monoclinic system with space group C2/c. The structure is composed of K^+ cations and $(UO_2)_2F_9^{5-}$ anions. It is a binuclear ion formed by 2 mononuclear ions sharing one fluorine atom. The dipyramid axes are not parallel but have torsion around the common fluorine atom. We have called this phenomenon condensation by a single fluorine bridge (Fig. 6). This condensation happens with a lengthening of the U—F bond which increases from 2.24 Å for a single U—F bond to about 2.33 Å for a single bridged U—F bond. When situated in the unit cell, this ion is surrounded

by 20 K atoms forming a polyhedron, which has the shape of a hexagonal prism with a trigonal pyramid at each end (Fig. 7).

The structural studies of the compounds of $M_2(UO_2)_2F_8-2H_2O$ (M = Cs, Rb) [8–9] and $Cs_2(UO_2)_2F_6-2H_2O$ [10] have shown a second kind of binuclear ion. The crystal structures of the compounds $M_2(UO_2)_2F_8-2H_2O$ are made up of binuclear ions of the formula $(UO_2)_2F_8^{4-}$, of the Rb^+ or Cs^+ cations and of crystallisation water molecules which ensure the cohesion of the structure with the hydrogen bond (Fig. 8). Figure 9 shows the structure of the
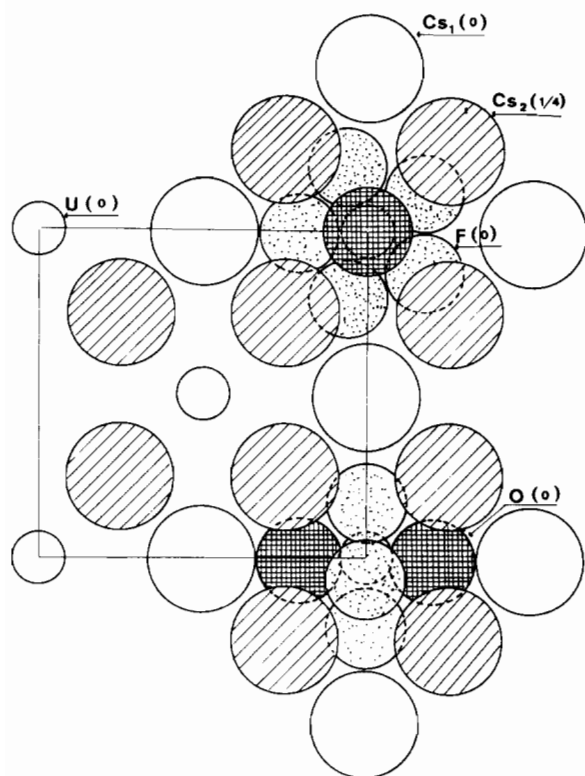
Fig. 5. The statistical crystal structure of $Cs_3UO_2F_5$.

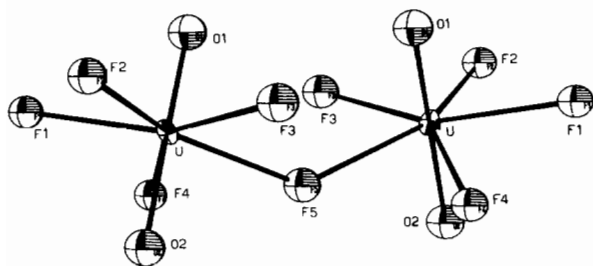Fig. 6. The geometry of the $(UO_2)_2F_9^{5-}$ ion.

Cs compound which is analogous, although the arrangement of the complex ions in the unit cell is not identical. The binuclear ion is made up of two $(UO_2)F_5^{-3}$ ions which share two common fluorine atoms. In this condensation by a double fluorine bridge, the dipyramid axes of UO_2 ions remain parallel to one another. The U—F double bridge distances are lengthened compared to the free U—F distance and are about 2.40 Å (Fig. 10).

Figure 11 shows the structure of the compounds of $Cs_2(UO_2)_2F_6-2H_2O$ projected parallel to the a axes of the monoclinic unit cell. The structure also contains binuclear ions analogous to the compounds $M_2(UO_2)_2F_8-2H_2O$, except that here the water molecules replace two missing fluorine atoms, and these molecules directly coordinate to the central
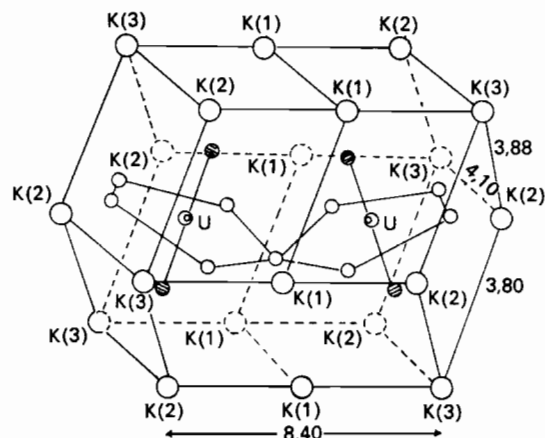

Fig. 7. Coordination polyhedron of $(UO_2)_2F_9^{5-}$ ion in the crystal $K_5(UO_2)_2F_9$.

uranium atom. This water molecule also ensures the interionic hydrogen bonds between two binuclear ions, so forming a one-dimensional chain. There are no longer crystallisation water molecules, but only coordination water. Figure 12 shows the characteristics of the $[(UO_2)_2F_6-2H_2O]^{2-}$ ion.

The polynuclear ions will be described on the basis of the two condensation modes observed on the two types of binuclear ions.

The compound $K_3(UO_2)_2F_7-2H_2O$ [11] crystallises in the monoclinic system of the $P2_1/m$ space group, and the $Na_3(UO_2)_2F_7-2H_2O$ [12] in the triclinic system of the $P\bar{1}$ space group.

The first compound is made of K^+ ions of polynuclear chains and crystallisation water molecules (Fig. 13).

The chain is made of $[(UO_2)_2F_6-F_{2/2}]^{3-}$ units identical to the ion $[(UO_2)_2F_8]^{4-}$, while the formation of the chain is made by means of a single fluorine bridge just as in the condensation already encountered in the $(UO_2)_2F_9^{5-}$ ion. It is a zig-zag chain linked by the intermediary of a fluorine atom adjacent to the double fluorine bridge. The U—F—U angle of the bridge is 137°, the same as the angle found in the binuclear ion $(UO_2)_2F_9^{5-}$. Between these chains are found the K^+ ions and the crystallisation water molecules.

Figure 14 presents the crystal structure of the compound $Na_3(UO_2)_2F_7-6H_2O$. Just as for the potassium compound, the sodium compound has chains of complex ions. This chain can still be considered as made up of binuclear units of formula $[(UO_2)_2F_6-F_{2/2}]^{3-}$. However the linking of the units is not the same for the potassium and the sodium compounds (Fig. 14). In the latter, the fluorine atom F_1 which makes the link is situated opposite the two fluorine atoms which form the double bridge of the unit, while in the potassium compound it is an adjacent fluorine atom which forms the simple
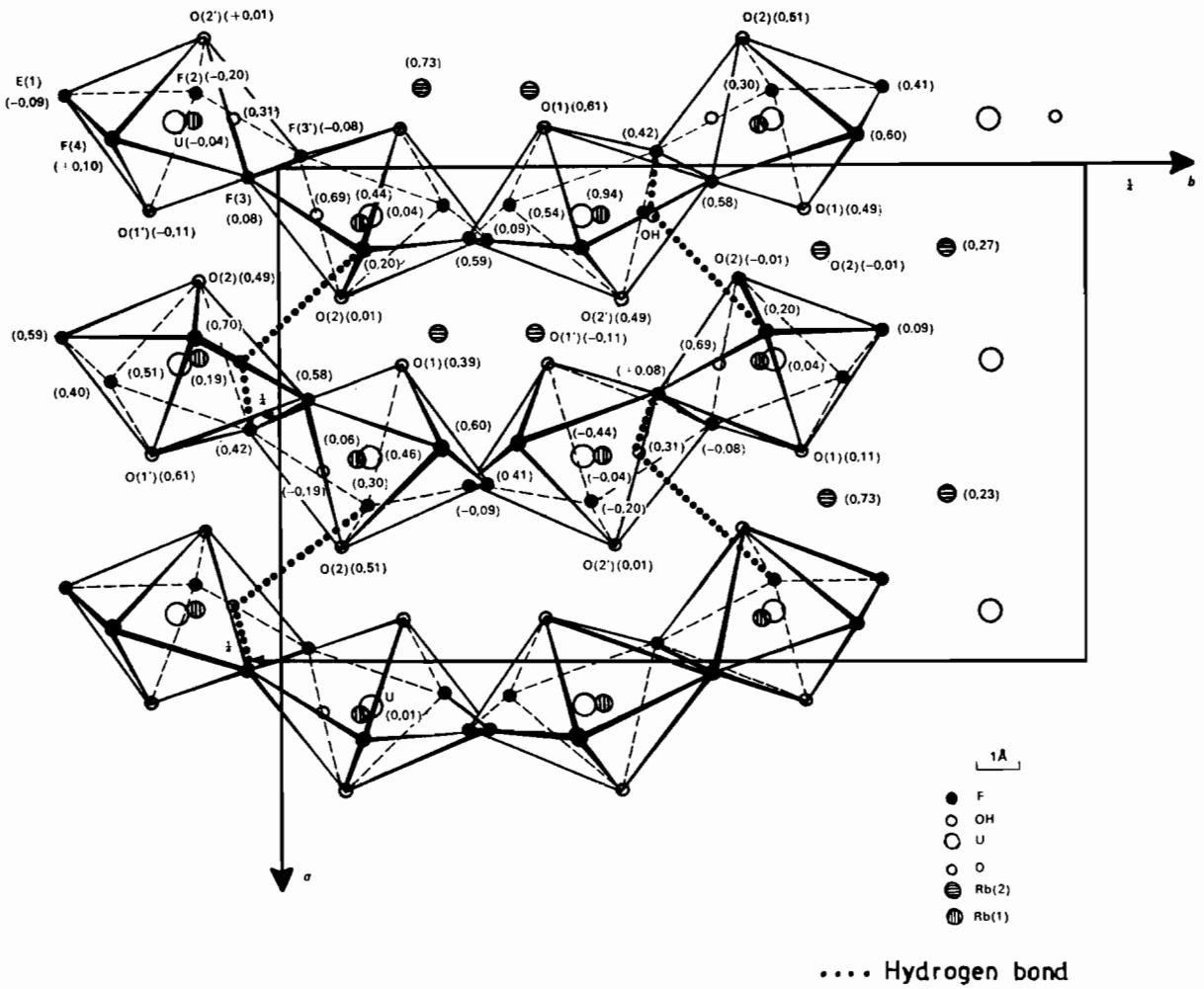
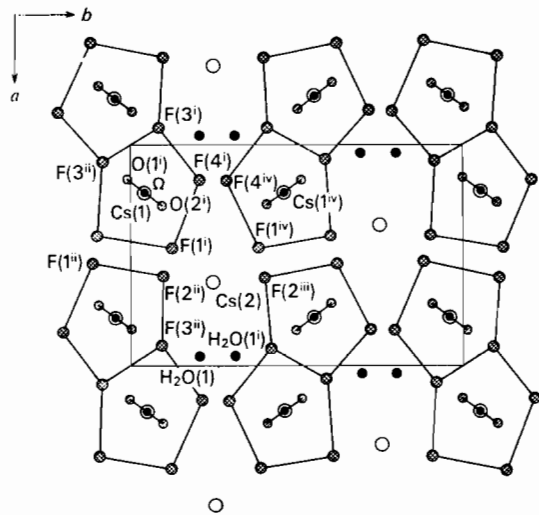Fig. 8. Crystal structure of $Rb_4(UO_2)_2F_8-2H_2O$.

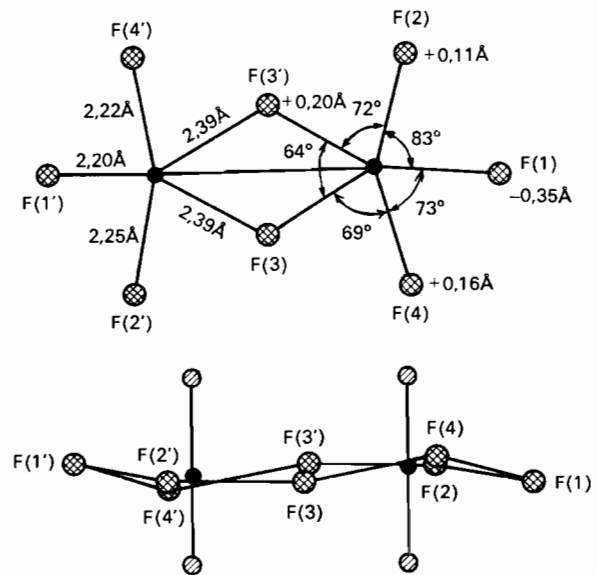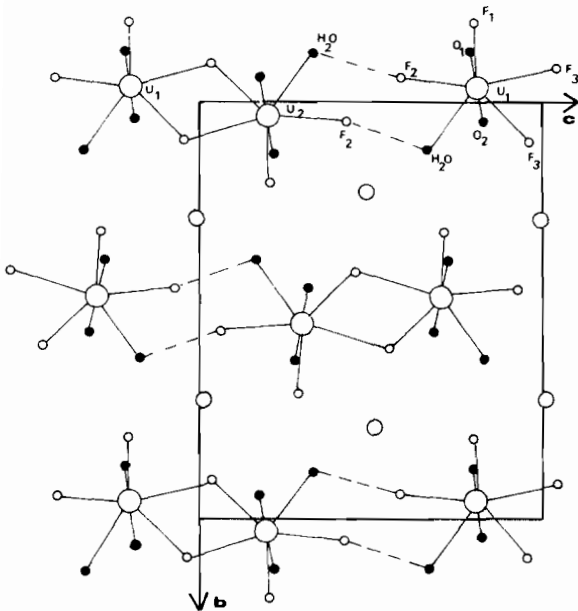Fig. 9. Crystal structure of $Cs_4(UO_2)_2F_8-2H_2O$.

Fig. 10. The characteristics of the $(UO_2)F_8^{4-}$ ion.

o Fluorine, • Oxygen, O Cesium, ◯ Uranium

Fig. 11. The crystal structure of $Cs_2(UO_2)_2F_6-2H_2O$.

Fig. 13. The crystal structure of $K_3(UO_2)_2F_7-2H_2O$.

Fig. 12. Characteristics of the binuclear $[(UO_2)_2F_6-2H_2O]^{2-}$ ion.
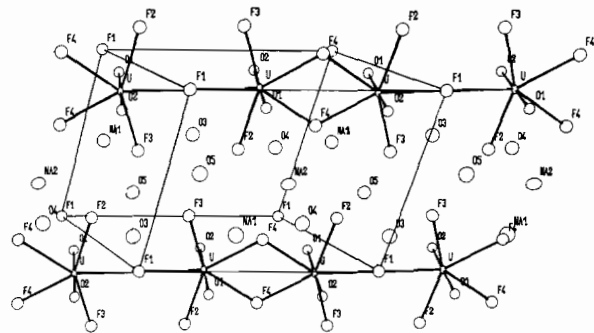
Fig. 14. The crystal structure of $Na_3(UO_2)_2F_7-6H_2O$.
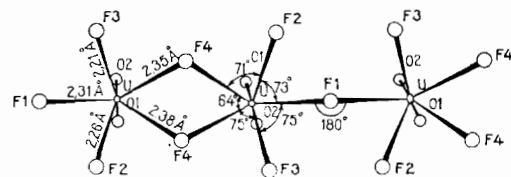
Fig. 15. Characteristics of the $[(UO_2)_2F_6-F_{2/2}]^{3-}$ chain unit.

bridge. The chain is rigorously linear. The unit is centro-symmetrical, the uranyl axes O–U–O being rigorously parallel to one another and are perpendicular to the (b, c) crystallographic plane. Moreover, because of this special position of the fluorine atom we have a very accurate measurement (that of uranium) for the U–F single bridge distance: 2.316 (5) Å. The U–F double bridge distance (U–F_4') is 2.365(9) Å on average. The U–O distance of the linear uranyl group is 1.78(1) Å.

Because of the accuracy of the refinement results we can also see a difference in the length of the U–F_3 bond (Fig. 15). When the fluorine atom is free and submitted to electrostatic attraction only (the case for the U–F_3 bond where the F_3 atom is only slightly linked to the water molecules), its distance from the uranium atom is 2.214(9) Å. When the fluorine atom is also linked to the crystallisation water
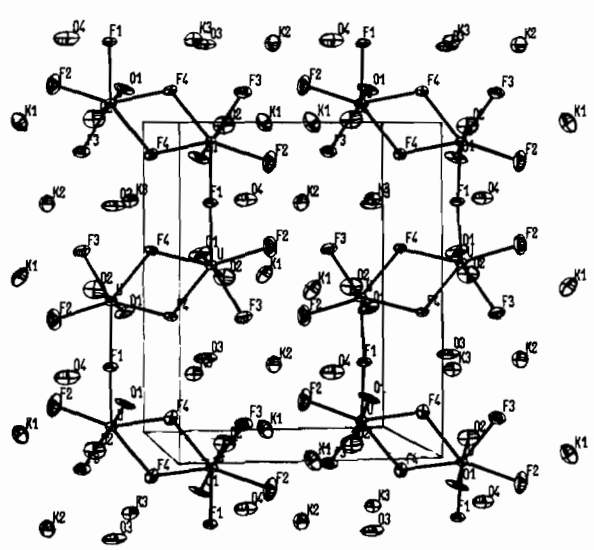
molecule (F–Na distance = 2.31 Å), the distance is 2.267(9) Å which is the case for the F_2 atom. The angles are also characteristic. The angle made by the fluorine atoms of the double bridge and the uranium atom is 64.6° (3)°. For the other fluorine atoms the angles are greater.

The structure of the compound $[K_3(UO_2)_3F_9-H_2O]-2H_2O$ [14] is made of K^+ ions, of crystallisation water molecules and of layers of complex anions. These can be considered as being formed from a double helicoïdal chain where every unit is made up of complex $UO_2F_5^{3-}$ or $(UO_2)F_4-H_2O^{2-}$ ions. The

water molecule is coordinated with the central uranium atom, as is the case for the binuclear ion $[(UO_2)_2F_6-2H_2O]^{2-}$, but here the hydrogen bond is weaker. We have also seen that the bond length is short (2.26 Å) with regard to the interatomic bond (2.35 Å). The chain formation is built up of condensation along a single fluorine bridge (UFU = 137°) which is analogous to the observation made on the $(UO_2)_2F_9{}^{5-}$ ion. There are two $UO_2F_5{}^{3-}$ and $UO_2F_4-H_2O^{2-}$ groups in one period of the helix chain and two single fluorine bridges provide the junction between two of these chains (Fig. 16) to form one layer. These different layers follow one another parallel to the crystallographic direction c, and between them are the K$^+$ ion and the remaining
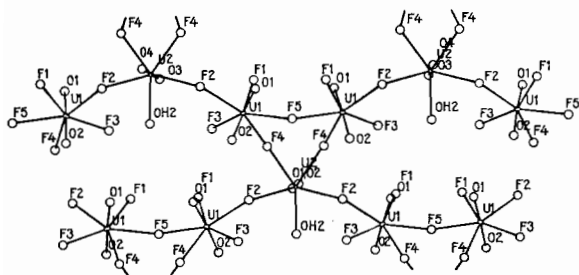

Fig. 16. The double helicoïdal chain of $[(UO_2)_3F_9-H_2O]_{\infty}{}^{3-}$ complex ion.

crystallisation water molecules. The latter provide a cohesion of the structure by H bonds between one oxygen atom of the UO_2 group of one layer and one fluorine atom of the other layer. This structure of complex ions gives rise to a trinuclear motif of the formula $[(UO_2)_3-H_2O-F_7-F_{4/2}]^{3-}$ in which the three complex mononuclear groups are linked together by means of three fluorine bridges forming a gauche cycle.

Finally, the layer of polynuclear ions has been observed in the compound $K_2[(UO_2)_3F_8-H_2O]-3H_2O$ [15]. Figure 17 presents the projection in the (a, b) plane. We can see the existence of plane layers of $UO_2F_5{}^{3-}$ or $[UO_2F_4-H_2O]^{2-}$ ions as in the preceding compound. These ions are grouped together by means of 3 single fluorine bridges. One of the 5 fluorine atoms and the coordination water molecules remain free while the 4 fluorine atoms remaining in each ion link with the neighbouring group to form a layer. Practically all the fluorine atoms and the coordination water molecules are found in the (a, b) plane.

At $z = \frac{1}{4}$, practically all the K$^+$ ions and the crystallisation water molecules are to be found. The whole structure is constituted of layers, between which exist both the attraction forces between anions and cations, and the H bonds. This structure explains the morphology of the plate crystals. The basis of the plate is perpendicular to the crystallographic axis c.
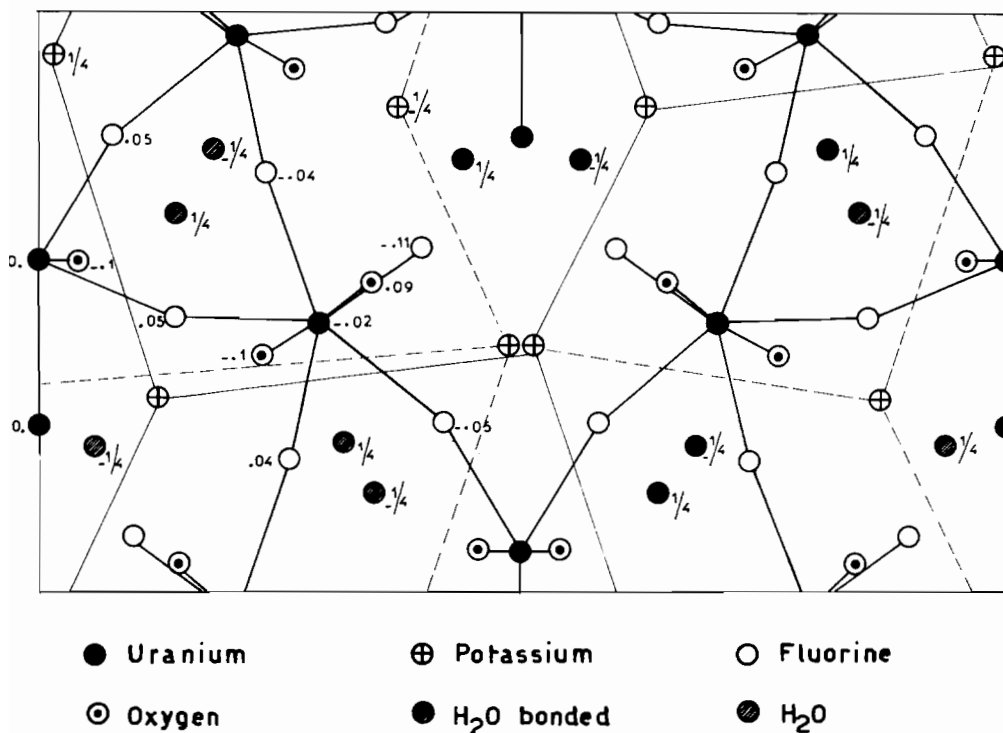

| ● Uranium | ⊕ Potassium | ○ Fluorine |
| ⊙ Oxygen | ● H$_2$O bonded | ◒ H$_2$O |

Fig. 17. Crystal structure of $K_2(UO_2)_3F_8-4H_2O$.

Vibrational Studies

In the $M_3UO_2F_5$ compounds, although the ion $UO_2F_5^{3-}$ is the same, the structures differ from one compound to another depending on the cation.

The variation of vibrational spectra in the condensation phenomenon is important.

Since we were working in the solid state, we examined the special effects caused by this state, in particular the splitting of vibrational spectra due to the lowering of the symmetry of the site effects the change of the selection rules, the change of the polarisation of the bands, *etc...*

As we have seen, the ion $UO_2F_5^{3-}$ has the form of a pentagonal dipyramid with D_{5h} symmetry. The group theory gives the vibrational structure of the ion as follows:

$$\Gamma_{vib}^{UO_2F_5} = 2A_1' + 2A_2'' + 3E_1' + 2E_2' + 1E_1'' + 1E_2''$$

The selection rules show that the A_2'' and E_1' vibrations are active in IR absorption, while A_1', E_2' and E_1'' are Raman-active. The fundamental vibration E_2'' is optically-inactive.

As for the cesium compound [6], the structure we studied showed that the $UO_2F_5^{3-}$ ion of pentagonal dipyramid form (D_{5h} symmetry) has statistical disorder. In fact, the site group T_h for the $UO_2F_5^{3-}$ ion is incompatible with the symmetry of the ion. The statistical disorder affects the rotation of the ion about its site occupied by the uranium atom, and also the axes of the pentagonal dipyramid UO_2 which can be oriented along one of the three axes $\vec{a}$, $\vec{b}$, $\vec{c}$ of the unit cell.

In these conditions, the crystal field around the ion has quasi-spherical symmetry. Consequently its influence affects only the frequency value and does not cause splitting of the bands due to the site symmetry and correlation effects. Thus there are as many vibrations of the $UO_2F_5^{3-}$ ion in the crystal as in the free ion:

$$\Gamma_{vib}^{CsUO_2F_5} = \Gamma_{vib}^{UO_2F_5^{3-}}.$$

On the non-polarised Raman spectrum of $Cs_3UO_2F_5$ (Fig. 18) five bands at 784, 423, 325, 259 and 219 cm^{-1} can be seen. To assign these bands we studied the polarised Raman spectra of the compound. Since as far as we know no polarisation study has been made of the statistical disorder phenomenon in crystals, we decided to examine this phenomenon in the compound $Cs_3UO_2F_5$. We calculated the polarisation ratio, using methods analogous to those of Wilson, Decius and Cross [16] for the case of a gas or a liquid, by adapting to the particular case of the $UO_2F_5^{3-}$ ion in the crystal $Cs_3UO_2F_5$.

According to these calculations we found that only the vibration frequencies of type E_1'' corresponds
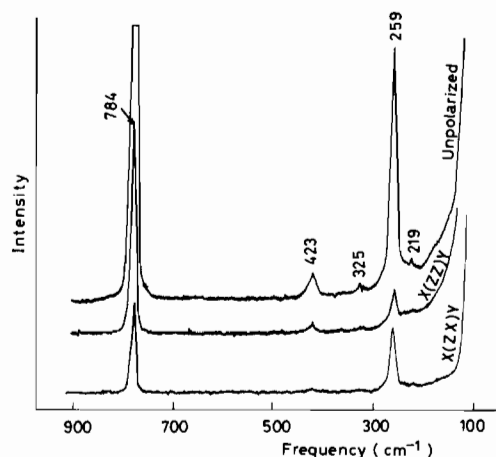

Fig. 18. Raman spectrum of $Cs_3UO_2F_5$.

to the polarisation ratio ρ_L (defined as I_{XY}/I_{XX}) > 1. The polarisation ratios ρ_L corresponding to vibration modes A_1' and E_2' are respectively 0 and $\frac{1}{2}$.

Figure 18 represents the non-polarised spectrum and the polarised spectra (ZZ) and (ZX) of $Cs_3UO_2F_5$. Due to the imperfection of the single crystal we could not obtain the theoretical polarisation ratios. However, the observed polarisation effect is sufficiently clear for an assignment of the fundamental bands of the $UO_2F_5^{3-}$ vibrations.

The two bands at 784 and 423 cm^{-1}, which appear more strongly on the X(ZZ)Y spectrum than on the X(ZX)Y spectrum, can only be assigned to the stretching vibrations of type A_1'. The band at 259 cm^{-1} which appears with weaker intensity for the (XX), (YY) and (ZZ) polarisations than on the (XY), (YZ) and (ZX) spectra is assigned to the double-degenerate frequency vibration E_1''. The two remaining, very weak bands at 325 cm^{-1} and 219 cm^{-1}, for which it is difficult to estimate the ρ_L ratios, are therefore assigned to the two frequencies of type E_2'.

For the rubidium and potassium compounds [17–19] we have studied the correlation diagram of the ion $UO_2F_5^{3-}$ on its site symmetry position in its unit cell (Table III). An examination of this diagram shows that for all non-degenerate vibration frequencies the site effect can only give rise to one frequency. For the double-degenerate band E_1'' which is active in Raman diffusion in the YZ and ZX polarisations of the ion, the site effect takes the form of a splitting into two bands. One of the bands is of A symmetry and active in Raman diffusion for the (XX), (YY), (ZZ) and (XY) directions, and the other of B symmetry is active in Raman diffusion in the (YZ) and (ZX) directions. The correlation effect causes splitting of the A-type band into four components A_g (XX + YY, ZZ), B_g (XX − YY, XY), A_u (T_Z) and B_u, and the B-type band is split into two components, of type E_g (YZ, ZX) and E_u (T_X, T_Y). On

TABLE III. Correlation Table of the $UO_2F_5^{3-}$ Ion in the Crystal Sites of the $K_3UO_2F_5$ and $Rb_3UO_2F_5$ Crystal Structures.

$UO_2F_5^{3-}$	Molecular Symmetry D_{5h}	Site Symmetry C_2	Crystal Symmetry C_{4h}	Vibration of $UO_2F_5^{3-}$ in the crystal
2	$A'_1(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$ $A'_2(R_z)$		$Ag(\alpha_{xx}+\alpha_{yy}, \alpha_{zz})$	9
3	$E'_1(T_x, T_y)$	$A(R_z); (T_z);$	$Bg(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$	9
2	$E'_2(\alpha_{xx}-\alpha_{yy}, \alpha_{xy})$ A''_1	$(\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy})$	$Eg(\alpha_{yz}, \alpha_{zx})$	9
2	$A''_2(T_z)$	$B(R_x, R_y); (T_x, T_y)$	$Au(T_z)$	9
1	$E''_1(R_x, R_y); (\alpha_{yz}, \alpha_{zx})$	$(\alpha_{yz}, \alpha_{zx})$	Bu	9
1	E''_2		$Eu(T_x, T_y)$	9

the Raman diffusion spectra of $K_3UO_2F_5$ and $Rb_3UO_2F_5$ a clear splitting effect can be observed at 271–258 (268–257) cm^{-1} of the E''_1 type band (Fig. 19 a, b) which is therefore due to the site effect.

The polarised Raman spectra showed that the E''_1 type frequency situated at 271 (268) cm^{-1} appears more strongly on the (YZ) and (ZX) spectra. It corresponds to the vibration modes B(YZ, ZX) of the site group. In contrast, the band at 258 (257) cm^{-1} which appears with greater intensity for the (XX), (YY), (ZZ) and (XY) polarisations than for the (YZ) and (ZX) spectra seems to correspond to the vibration mode A(XX, YY, ZZ, XY) of the site group. If the correlation effect had been sufficiently great, the E''_1 type band would have split into three components Ag, Bg, Eg. Such a splitting is not observed.
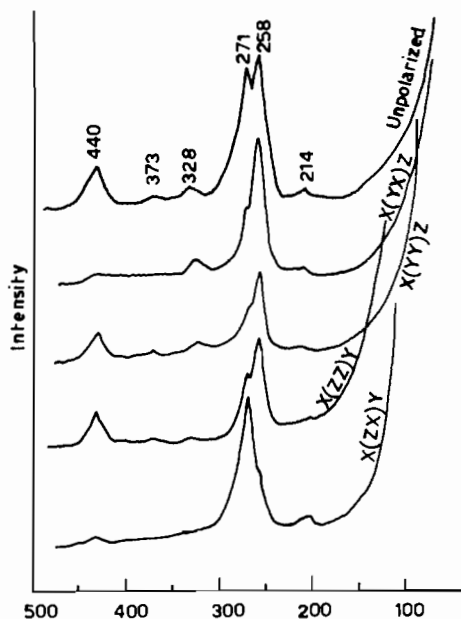

Fig. 19a. Polarised Raman spectra of $K_3UO_2F_5$.
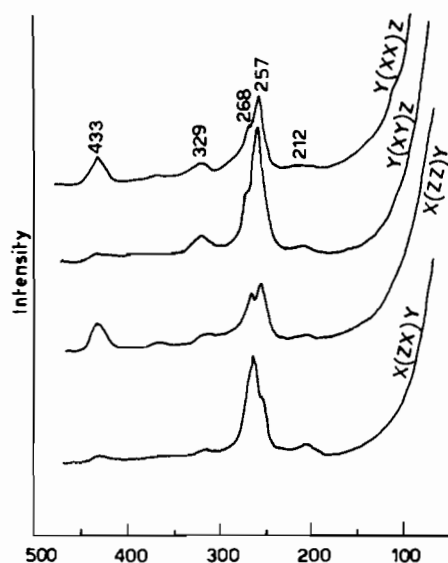

Fig. 19b. Polarised Raman spectra of $Rb_3UO_2F_5$.

It must then be the site effect which is essentially at the origin of the splitting of the E''_1 band into 2 distinct components A and B.

Similarly Table III shows that the site effect causes splitting of each of the two E'_2 type bands into 2 components A(XX, YY, ZZ, XY) and B(YZ, ZX) which then went on to split by the correlation effect. The first splits into four components Ag (XX + YY, ZZ), Bg (XX −YY, XY), Au (T_z) and Bu and the second splits into two components Eg (YZ, ZX) and Eu (T_X, T_Y). However, for the two E'_2 bands which appear at 329 (328) and 214 (212) cm^{-1} respectively, it was not possible to observe the effect of splitting of the bands due to the crystal effect, because their intensity is too weak.

Each A'_1 type band which is Raman active in the (XX), (YY) and (ZZ) polarisation of the ion gives rise to an A type band in the site group and the correlation effect should cause a splitting of each A band into 4 components Ag, Bg, Au and Bu. However, on

the Raman spectra of $K_3UO_2F_5$ and $Rb_3UO_2F_5$ only one very intense band at 804 (797) cm^{-1} can be observed. We can thus deduce from this that the correlation effect on the vibration frequency of the ion $UO_2F_5^{3-}$ in the compounds $K_3UO_2F_5$ and $Rb_3UO_2F_5$ is very weak.

Furthermore, we note that the selection rules relative to IR and Raman activity are no longer respected when the site group symmetry of the ion is taken into consideration. The bands which are active in Raman diffusion are equally active in IR absorption, and vice versa. In fact, this has been observed for other intense bands. In the non-polarised spectra of $K_3UO_2F_5$ and $Rb_3UO_2F_5$ (Fig. 19 a, b) and the polarised spectra (XX), (YY), (ZZ) a band of very weak intensity at 373 (366) cm^{-1} can be observed, which should correspond to the stretching vibrations U−F $[\nu_5(E')]$ which is active in IR absorption and in principal forbidden in Raman diffusion. In fact the IR spectra of $K_3UO_2F_5$ and $Rb_3UO_2F_5$ show a band of very weak intensity at 380 (375) cm^{-1}, which has been assigned to the double-degenerate stretching vibration frequency U−F $[\nu_5(E')]$.

As for the ammonium compound in the pseudo-orthorhombic cell the crystal effect takes the form of a lifting of the degeneracy of the double-degenerate frequency, while in the real monoclinic unit cell this effect shows as a sextuplet for each of the vibrations of the ion $UO_2F_5^{3-}$.

On the Raman spectrum of $(NH_4)_3UO_2F_5$ recorded at low temperature (-180 °C) (Fig. 20), splitting of the bands were observed for the frequencies $\nu_1(A'_1)$ and $\nu_9(E'_2)$ and $\nu_{10}(E''_1)$. Furthermore, the Raman spectrum of this compound also shows the vibration frequencies in IR absorption. The defor-
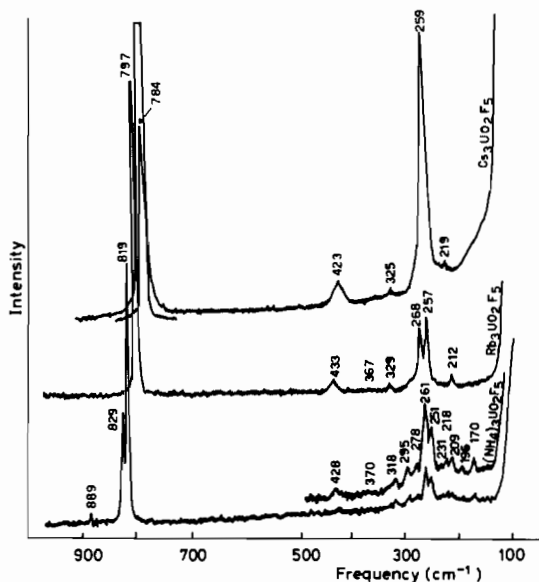
mation of the $UO_2F_5^{3-}$ ion of the ideal D_{5h} symmetry observed in the crystal structure of the compound [4] is probably due to the existence of hydrogen bonds in this compound.

These are some of the spectroscopic results obtained for the mononuclear compounds. As for IR spectroscopy, the results are less evident due to the fact that on the one hand we were not able to examine the polarisation effect and on the other hand the numerous combination bands made the interpretation of the spectra more difficult. However a close examination of the IR spectra of all the compounds shows that the results are quite equivalent.

The ion $(UO_2)_2F_9^{5-}$ can be considered as being the condensation of two $UO_2F_5^{3-}$ ions sharing one common fluorine atom.
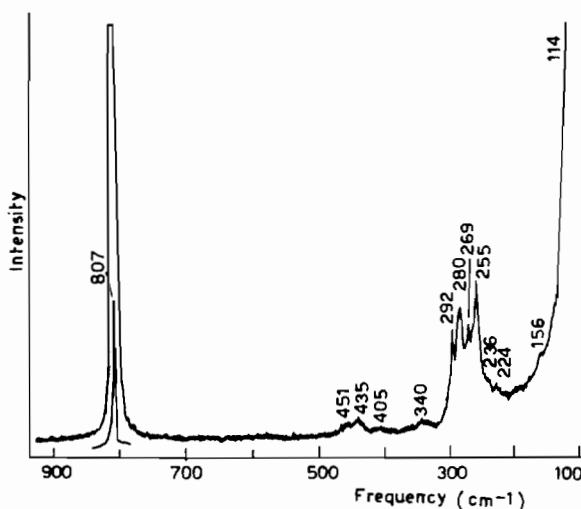

Fig. 21. Raman spectrum of $K_5(UO_2)_2F_9$.

Figure 21 shows the spectrum of the compound $K_5(UO_2)_2F_9$ [20]: the condensation of the two $UO_2F_5^{3-}$ groups by a fluorine bridge giving the binuclear ion $(UO_2)_2F_9^{5-}$ leaves the vibrational spectrum of the mononuclear ion $UO_2F_5^{3-}$ practically unchanged. However the fundamental bands observed for this ion are split, due to the interaction between two $UO_2F_5^{3-}$ ions through one common fluorine atom.

The frequency of the U−F bridge has been assigned to the band situated at 405 cm^{-1}.

We now consider the case of the quadruplet situated at 292, 280, 269, 255 cm^{-1} that we assigned to the 4 fundamental deformation frequencies OUF δ_{10}^1, δ_{10}^2, δ_{10}^3, δ_{10}^4 corresponding to the fundamental frequency δ_{10} [(OUF)] (E''_1) of the isolated ion $UO_2F_5^{3-}$. When the ion $UO_2F_5^{3-}$ associates with another $UO_2F_5^{3-}$ to give the ion $(UO_2)_2F_9^{5-}$ its symmetry is lowered from D_{5h} to C_{2v}. In these conditions the double degenerate frequency $\delta_{10}(E''_1)$ splits

Fig. 20. Raman spectrum of $M_3UO_2F_5$.

into 2 components of A_2 and B_2 type active in Raman diffusion. The effect of the condensation of the two $UO_2F_5{}^{3-}$ ions is then to split the last two frequencies giving a quadruplet. If for the compounds $M_3UO_2F_5$ (M = K, Rb, NH$_4$) the splitting of certain bands is due to the lowering of the site symmetry with lifting of the degeneracy, for the compound $K_5(UO_2)_2F_9$ this phenomenon is a result of both the lowering of the molecular symmetry and the interaction of the two units of the binuclear ion.

Figures 22 a, b show the polarised Raman spectrum of the compound $M_2(UO_2)_2F_8-2H_2O$: the spectrum is different from that of the mononuclear ion $UO_2F_5{}^{3-}$. The assignment of the bands is possible because of the polarisation effect and the normal coordinate analysis. These calculations showed that there are many couplings between various vibrational modes [21].

The valence vibration frequencies of the double bridge are found at 445 and 324 cm^{-1}: the same vibration range of the frequency of the single bridge UFU. Figure 23 shows the Raman spectra of the compound $Cs_4(UO_2)_2F_8-2H_2O$ compared with that of the compound $Cs_2(UO_2)_2F_6-2H_2O$ and the compound $K_3(UO_2)_2F_7-2H_2O$. We see that there is a similarity between the $(UO_2)_2F_8{}^{4-}$ ion and the
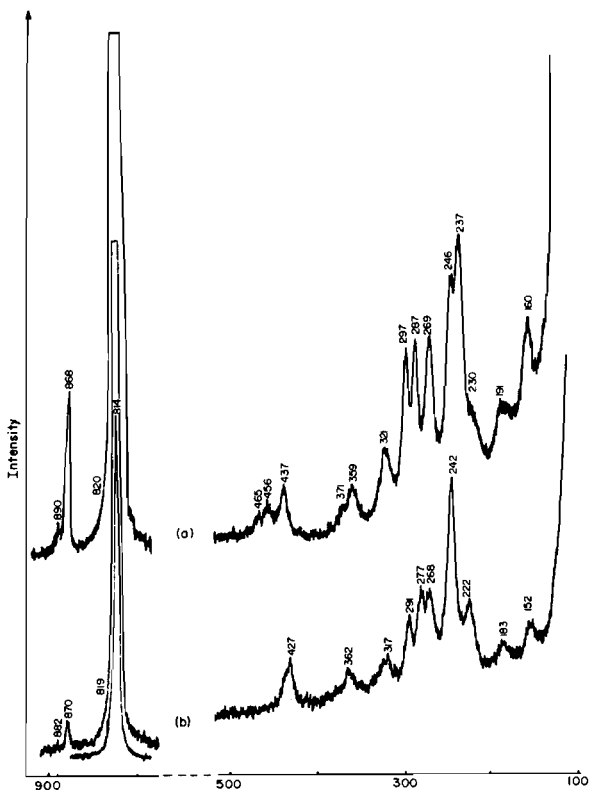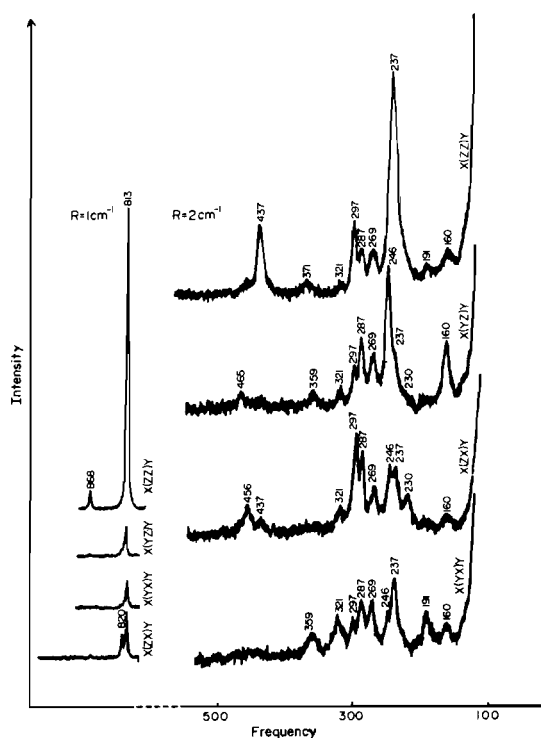

Fig. 22b. The polarised spectra of $Rb_4(UO_2)_2F_8-2H_2O$.

$[(UO_2)_2F_6-2H_2O]^{2-}$ ion, *i.e.* when 2 fluorine atoms are replaced by 2 water molecules.

In the case where the ion $[(UO_2)_2F_6-F_{2/2}]^{3-}$ forms a chain through the intermediary of a single fluorine bridge, which is what happens for the compound $K_3(UO_2)_2F_7-2H_2O$ [22–23], very clear splittings of the Raman bands can be seen. The same is also true for the IR spectra. While for the compounds $Cs_2(UO_2)_2F_8-2H_2O$ and $Cs_2(UO_2)_2F_8-2H_2O$ the spectra are quite comparable, in the case of the polynuclear chain very clear splittings can be observed.

This phenomenon is the same as the one we observed earlier on with the ion $(UO_2)_2F_9{}^{5-}$ *i.e.* condensation by a single fluorine bridge.

Conclusion

The uranyl ion has an invariable geometry. In all the structures studied the average value of the U–O bond is 1.78 Å. The O–U–O angle is 180°.

The coordination number 5 has been observed in all the structures studied. It is moreover systematically observed for the ligands whose size is analogous to that of the fluorine ions such as the hydroxo, aquo, oxo groups. The U–F distance is approximately 2.23 Å when the fluorine ion is submitted to a homogenous electrostatic field due to the cations. When it is attracted moreover by a hydrogen bond its distance is longer, varying from 2.27 to 2.36 Å.
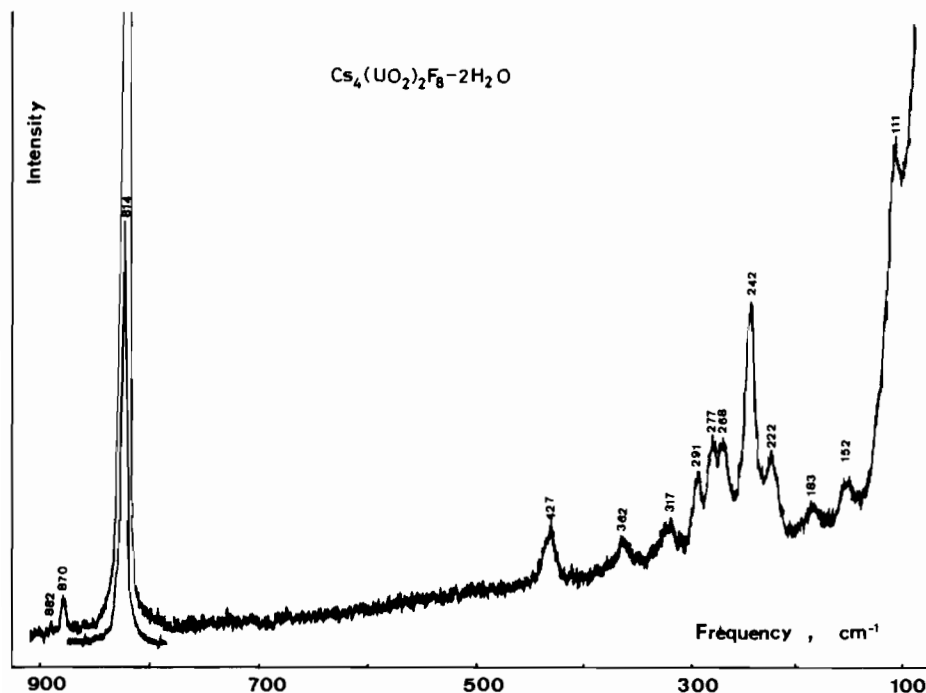

Fig. 22a. The polarised Raman spectra of $Cs_4(UO_2)_2F_8-2H_2O$.
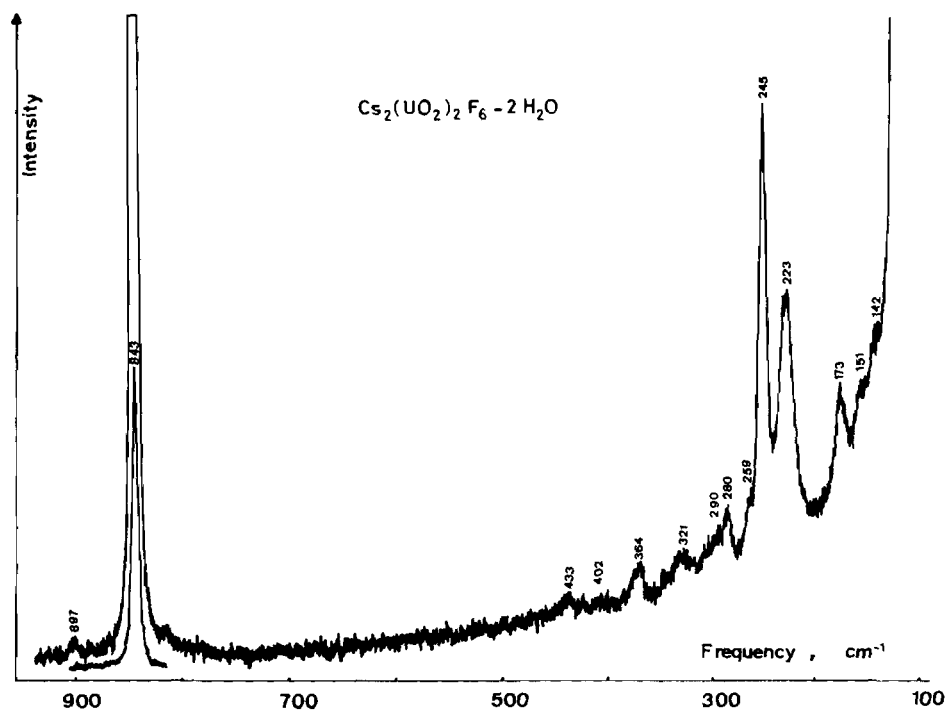
(a)
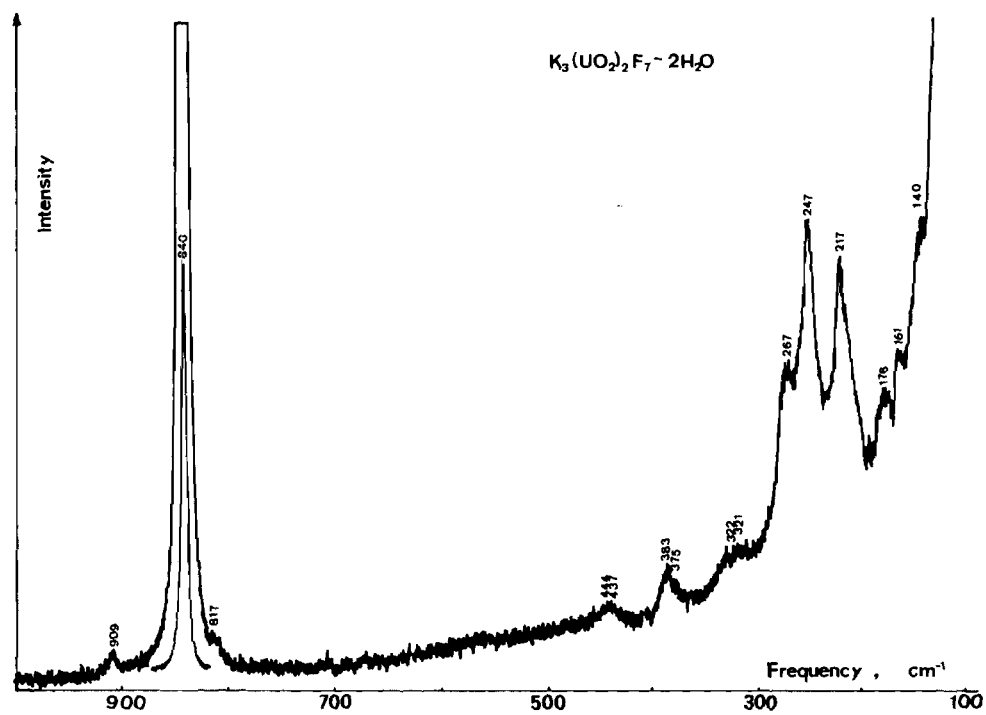
(b)

Fig. 23a, b. *(For legend see facing page)*

$Cs_4(UO_2)_2F_8-2H_2O$

(c)

Fig. 23. Raman spectra of $Cs_4(UO_2)_2F_8-2H_2O$, $Cs_2(UO_2)_2F_6-2H_2O$ and $K_3(UO_2)_2F_7-2H_2O$.

TABLE IV. Characteristic Interatomic Distances and Valence Angles of $UO_2F_5^{3-}$, $[UO_2F_4-H_2O]^{2-}$ and Polynuclear Ions.

Simple Ions:

$UO_2 = 1.76$ Å		$O-U-O = 180°$
$U-F_5 = 2.23$ Å	$U-F... = 2.67$ Å	$F-U-F = 72°$
$U-H_2O_1 = 2.26$ Å	$U-H_2O... = 2.35$ Å	

Condensed Ions:

Single bridge:

$U-F_s = 2.30-2.36$ Å	$U-F_s-U = 135°$
$U-U = 4.34-4.63$ Å	$U-F_s-U = 180°$

Double bridge:

$U-F_d = 2.37$ Å	$F_d-U-F_d = 64°$
$U-U = 3.93-4.15$ Å	$U-F_d-U = 166°$

Triple bridge:

$U-F_T = 2.30-2.36$ Å	$U-F_t-U = 137°$
$U-U = 4.38-4.58$ Å	$U-F_T-U = 153°$

The fluorine atom can be replaced by water molecules to complete when necessary the coordination number 5.

Condensation occurs in several different ways (Table IV):

a) When it occurs with a simple bridge, the bridge angle is variable and depends on the surrounding atoms of the anion. The simple bridge angles U—F—U were found to be 137° and 180°.

b) When it occurs with a double bridge, the bonds which are formed seem to be more stable. The double ion is the same and its geometry does not change from one structure to another. This is why we have considered the binuclear ion $(UO_2)_2F_8^{4-}$ as a new

TABLE V. Structural Relationship of Different Uranyl-Fluorine Complex Ions.
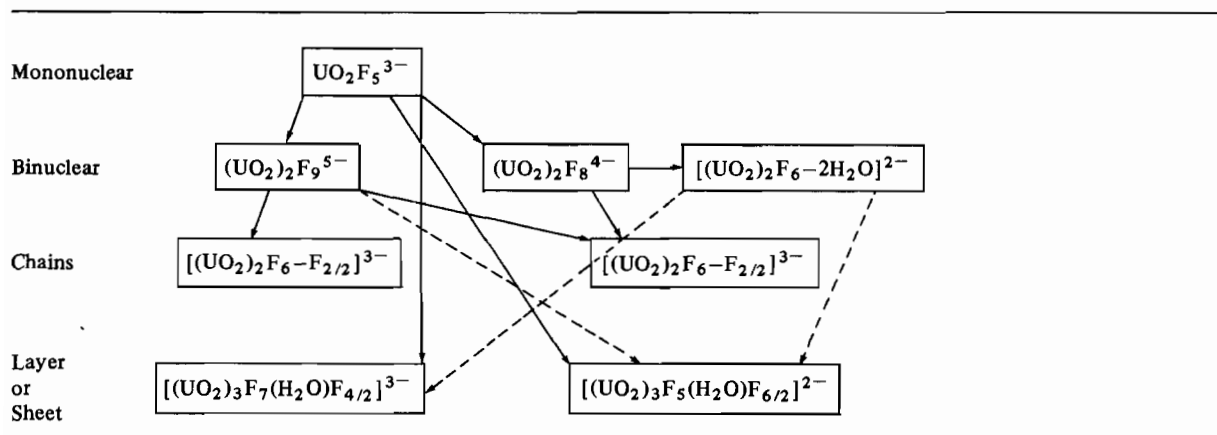
anion unit different from the $UO_2F_5^{3-}$ ion and have then considered it as a unit of the different chains observed. The results obtained from absorption and Raman spectroscopic studies confirm this feature.

c) Although the trinuclear motif has an original geometry, its condensation mode has characteristics which are very close to those of the simple bridge. In fact there is a superposition of three simple fluorine bridges forming a double chain or a layer.

Table V shows the structural relationship of the different ions demonstrated in our laboratory and the absence of framework structures. An examination of structures already described in the literature shows that it is true there also. This is understandable since the only atoms capable of polymerisation are those atoms situated in the equatorial plane of the UO_2^{2+} ion. In these conditions they can only form polynuclear ions along the direction of the ligand plane.

These structures cannot therefore be tri-dimensional. It is our opinion that interesting applications in the field of chemical synthesis can be foreseen thanks to the directional properties of the secondary bonds.

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