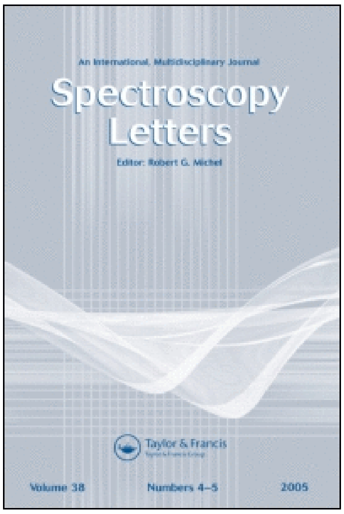

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IR-SPECTRA OF $M_2UO_2F_4 \cdot H_2O$ COMPLEXES

KEY WORDS: IR-spectra, uranyl fluoride complexes

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This work is devoted to the study of $Rb_2UO_2F_4 \cdot H_2O$ and $Cs_2UO_2F_4 \cdot H_2O$ IR-spectra with the aim of obtaining a set of vibration frequencies characterizing $M_2UO_2F_4 \cdot H_2O$ complexes; elucidating the role and nature of water bonds in the structures of the above-mentioned compounds; and receiving preliminary information on the structure of $M_2UO_2F_4 \cdot H_2O$. The investigated compounds were synthesized in accord with our previous paper[1]. $M_2UO_2F_4 \cdot D_2O$ and $M_2UO_2F_4 \cdot HDO$ were obtained by recrystallizing $M_2UO_2F_4 \cdot H_2O$ from D_2O and HDO respectively.

The IR-spectra were recorded with the aid of "UR-20" (Carl Zeiss Jena) and "IKS-12" spectrometers; the latter was supplied with a CsI prism. Both suspension in white mineral oil and moulding of discs with KBr were applied as methods for sample preparation. The frequency values found in the spectra and their respective assignings are cited in Table 1.

As is generally known, the UO_2^{2+} group asymmetric stretching vibration frequencies, found in the uranyl complex spectra, lie in the 830–1050 cm^{-1} range. The intensive 870–890 cm^{-1} bands in the $M_2UO_2F_4 \cdot H_2O$ spectra are assigned to the $\nu_{as}(UO_2^{2+})$ vibrations. Other intensive bands in the above-said $M_2UO_2F_4{\cdot}H_2O$ spectra range are not observed. It is noteworthy that the $\nu_{as}(UO_2^{2+})$ frequencies in the $M_2UO_2F_4{\cdot}H_2O$ spectra are considerably higher than the corresponding frequencies in the pentafluorouranylate spectra (855 and 847 cm^{-1} for $Rb_3UO_2F_5$ and $Cs_3UO_2F_5$ respectively)^2, which is indicative of the strengthening of the U–O bond at $M_3UO_2F_5$-to-$M_2UO_2F_4{\cdot}H_2O$ transfer.

TABLE 1

Frequencies (cm^{-1}) found in $Rb_2UO_2F_4{\cdot}H_2O$ and $Cs_2UO_2F_4{\cdot}H_2O$ IR-spectra and their assignments

$Rb_2UO_2F_4{\cdot}H_2O$	$Cs_2UO_2F_4{\cdot}H_2O$	Assignment
	192 vw	
	198 w	
203 vw		$\delta(FUF)$
219 w	216 w	$\delta(FUO)$
224 w	223 w	
232 vw		
288 s	281 s	$\delta(UO_2^{2+})$
322 w	320 w	
384 s	380 s	$\nu(UF)$
448 m	437 m	$\nu(UOH_2)$
548 w	557 w	$\gamma_{wag}(H_2O)$
727 w	720 w	$\gamma_{rock}(H_2O)$
814 w	814 w	$\nu_s(UO_2^{2+})$
890 s	889 s	$\nu_{as}(UO_2^{2+})$
	879 s	
1689 m	1682 m	$\delta(H_2O)$
3330 s	3290 s	$2\delta(H_2O)$
3400 s	3380 s	$\nu(H_2O)$
3530 s	3530 s	

s – strong; m – medium; w – weak; vw – very weak.

An interesting feature of the $M_2UO_2F_4 \cdot H_2O$ IR-spectra is the appearance therein of the UO_2^{2+} symmetric stretching vibration frequencies. These frequencies are presented in the $Rb_2UO_2F_4 \cdot H_2O$ and $Cs_2UO_2F_4 \cdot H_2O$ spectra by very narrow bands ($\Delta_{1/2} = 3 - 5$ cm^{-1}) at 814 cm^{-1}. The appearance of $\nu_s(UO_2^{2+})$ in the uranyl complex IR-spectrum may be caused by the symmetry violation of the uranyl group force field, this, as a rule, being due to the low symmetry either of the UO_2^{2+} equatorial surrounding or of the complex crystal lattice.

The far IR-spectra ($<$ 400 cm^{-1}) of $Rb_2UO_2F_4 \cdot H_2O$ and $Cs_2UO_2F_4 \cdot H_2O$ contain intensive bands at 384, 288 and 380, 281 cm^{-1} respectively. By analogy with our previous work[2], the 384, 380 cm^{-1} bands are assigned to the stretching vibrations of the U-F bonds, while those at 288, 281 cm^{-1} to the bending vibrations of the UO_2^{2+} groups in the said compounds. It should be noted that the ν (UF) frequencies in the $M_2UO_2F_4 \cdot H_2O$ spectra are located in a higher frequency range compared to ν (UF) found in $M_3UO_2F_5$ spectra, and this indicates a certain strengthening of U-F bonds in $M_2UO_2F_4H_2O$.

Knowing the values of ν_s and ν_{as} in UO_2^{2+}, one can evaluate (by Jones's[3] method) the force constant F_{uo}, which, in turn, allows to obtain several other characteristics for the uranyl group and U-F bonds. To calculate the U-O bond order (n_{uo}) and its length (R_{uo}), the formulae $F_{uo}=3.33n - 0.73$ and $R_{uo}= R_1 - \log n$ were used.[4] The results are shown in Table 2, which, with comparison in view, also cites the results obtained for rubidium pentafluorouranylate. The $\nu_s(UO_2^{2+})$ value for $Rb_3UO_2F_5$, according to the luminescence data, is 795 cm^{-1}.

TABLE 2

Force constants, U-O bond lengths and bond orders for U-O and U-F in certain uranyl fluorides.

Compound	F_{uo}(mdyn/Å)	R_{uo}(Å)	n_{uo}	n_{UF}
$Rb_2UO_2F_4\cdot H_2O$	6.40	1.739	2.14	0.430
$Rb_3UO_2F_5$	6.01	1.764	2.02	0.392

Comparison of the calculated F_{uo}, R_{uo} and n_{uo} values for $Rb_2UO_2F_4\cdot H_2O$ and $Rb_3UO_2F_5$ allows us to infer considerable strengthening of the uranyl group bonds with less fluorine atoms involved in the complex ion. On the other hand, it is apparent from Table 2 that the U-F bond order changes insignificantly. The 180-250 cm^{-1} range of the $M_2UO_2F_4\cdot H_2O$ spectra show several low-intensity bands. However, their assignment is extremely difficult.

Three bands of approximately equal intensity are observed in the $M_2UO_2F_4\cdot H_2O$ spectra in the water stretching vibration range. At deuteration the said bands show a low-frequency shift (ν_H/ν_D= 1.34 - 1.36). Their small half-width and relatively high $\nu(H_2O)$ values indicate the absence of strong H-bond in $M_2UO_2F_4\cdot H_2O$. H-bond energy assessment for these compounds with Sokolov's method[5] gives 2.5 - 4.0 kcal/mol.

To elucidate the nature of the water bond in the investigated complexes, IR-spectra for $M_2UO_2F_4\cdot D_2O$ and $M_2UO_2F_4\cdot HDO$ were obtained. The frequencies found in the

$Rb_2UO_2F_4 \cdot D_2O$ and $Rb_2UO_2F_4 \cdot HDO$* spectra in the stretching vibration range for the OH and OD bonds are cited in Table 3.

TABLE 3

Stretching vibration frequencies in H_2O, D_2O and HDO found in deuterated rubidium tetrafluorouranylate spectra.

ν (OH)		ν (OD)	
$Rb_2UO_2F_4 \cdot H_2O$	$Rb_2UO_2F_4 \cdot HDO$	$Rb_2UO_2F_4 \cdot D_2O$	$Rb_2UO_2F_4 \cdot HDO$
3530 3400 3330	3520 3380	2610 2500 2445	2620 2520

The number of bands in the OH (OD) range of the stretching vibrations in the half-deuterated hydrate spectrum, as is generally known, determines the number of various hydroxyl groups in the compound. The study of the half-deuterated hydrate absorption spectrum allows, likewise, to divide the fundamental vibration bands and their overtones. Since two bands are observed in the $M_2UO_2F_4 \cdot HDO$ spectra stretching vibration OH (OD) range, it was inferred that the compounds studied contain two different types of OH groups (or two kinds of water molecules) to which the 3530 and 3400 cm^{-1} bands correspond in the $Rb_2UO_2F_4 \cdot H_2O$ spectra, and the 3530 and 3380 cm^{-1} bands — in the $Cs_2UO_2F_4 \cdot H_2O$ spectra respectively. The 3330 and 3290 cm^{-1} bands found in the spectra of these compounds belong to the overtone of the bending vibrations, its intensity being strengthened as a result of the Fermi resonance. Bending vibrations, discovered in the $M_2UO_2F_4 \cdot H_2O$ IR-spectra, possess unusually

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* $Cs_2UO_2F_4 \cdot D_2O$ (HDO) IR-spectra are identical.

(for crystal hydrates) high frequencies: 1689 and 1682 cm^{-1}.

The appearance in the $M_2UO_2F_4 \cdot HDO$ IR-spectra of two OH-bond stretching vibration bands may be explained in two ways. On the one hand, these bands may correspond to the vibrations of two different kinds of water molecules, differing, for example, in H-bond energies, or situated differently in the crystal lattice. On the other hand, these bands may correspond to the symmetric and asymmetric stretching vibrations of H_2O in $M_2UO_2F_4 \cdot H_2O$. The second explanation, however, seems less probable. It is generally known[6] that if the H_2O molecule forms asymmetric H-bonds, then this leads to a very strong increase of the $\Delta = (\nu_{as} - \nu_s)$. In the case of $M_2UO_2F_4 \cdot H_2O$, the distance between the spectrum components is 120-150 cm^{-1} (theoretical $\Delta =$ 110-115 cm^{-1}), from which follows that, if the 3530 (3530) and 3400 (3380) cm^{-1} bands in the $M_2UO_2F_4 \cdot H_2O$ spectrum correspond to the symmetric and asymmetric stretching vibrations of the water molecules, its OH-bond load is practically the same and, consequently, one OH stretching vibration band should be observed in the half-deuterated hydrate spectrum.

Thus, the appearance of OH (OD) stretching vibration bands in the $M_2UO_2F_4 \cdot HDO$ spectra is in all probability connected with the presence of two kinds of water molecules in the $M_2UO_2F_4 \cdot H_2O$ compounds.

Besides absorption bands, belonging to the stretching and bending vibrations of water, low-intensity bands, part of which are displaced ($\nu H/\nu_D$=1.36 - 1.38) at deuteration, were discovered in the 400 - 800 cm^{-1} range of the $M_2UO_2F_4 \cdot H_2O$

spectra. These bands obviously correspond to the torsion vibrations of water. The appearance of these vibrations in the crystal hydrate spectra is possible[7] only in the case of "rigid" fixation of the H_2O molecules in their structure either by means of strong H-bonds, or coordination of the water molecules to the metal ion. Strict assignment of γ (H_2O) frequencies is hampered. According to Nakagawa et al.[7], the high-frequency band in the $M_2UO_2F_4 \cdot H_2O$ spectra is ascribed to rocking vibrations, and the low-frequency band to the wagging vibrations of the water molecules (see Table 1).

The study of $M_2UO_2F_4 \cdot H_2O$ IR-spectra allows stating certain considerations on the structure of complex anions involved in the composition of these substances.

The presence in the $M_2UO_2F_4 \cdot H_2O$ spectra of bands caused by libration vibrations of water molecules may serve as evidence of the coordination of H_2O molecules to UO_2^{2+}. The possibility of these vibrations appearing on account of strong H-bonds in $M_2UO_2F_4 \cdot H_2O$ falls away due to high (H_2O) values. If the water molecule in $M_2UO_2F_4 \cdot H_2O$ is considered coordinated, one may assign the 448 (437) cm^{-1} band, which practically does not displace at deuteration, to the stretching vibrations of $U\text{-}OH_2$. The high value of this frequency proves the strong fixation of H_2O in the coordination sphere of uranyl.

Thus, the obtained data allow assuming that in the $M_2UO_2F_4 \cdot H_2O$ structure the coordination polyhedron is a distorted pentagonal bipyramid, whose equatorial plane consists of four fluorine atoms and one water molecule.

The proposed structure for the complex anion in $M_2UO_2F_4 \cdot H_2O$ explains both the rise of the $\nu_s(UO_2^{2+})$ values and the appearance of the $\nu_s(UO_2^{2+})$ frequency in the spectra.

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