

Infrared Investigation of Uranyl Chloride and Uranyl Fluoride

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In many uranyl compounds the most often literature found is for the fundamental vibrations of the uranyl ion while there is negligible literature on the anion vibrations which mostly fall in the far-IR region. The crystal structure studies of many uranyl compounds have shown the UO_2 bond as being almost linear. In the present study of UO_2Cl_2 and UO_2F_2 the UO_2 bond is assumed to be very nearly linear and belonging to the C_{2v} point group of symmetry. A normal coordinate analysis has confirmed the linear configuration of the UO_2 for the two molecules. A complete vibrational assignment of the anion vibrational modes in the IR spectra is well supported by high values of the potential energy distribution calculated from the force constants.

Key Words: Uranyl halides, Vibrational assignments, Force constant.

INTRODUCTION

The uranyl ion is the most extensively studied structure and never exists as a free triatomic ion. Zacharaisen¹ discusses the crystal structure of many uranyl compounds and in all cases the UO_2 bond is nearly linear. The crystal structure studies of anhydrous UO_2F_2 have shown that the trigonal layer of UO_2F_2 is a slightly puckered plane with the oxygen atoms in a dumbbell configuration perpendicular to this plane and the fluorine atoms situated $0.21 \pm 0.02 \text{ \AA}$ alternately above and below the median layer² formed by the UO_2 . The UO_2 is almost linear in uranyl chloride. As is the case where heavy atoms are involved the stretching and deformation fundamental vibrations of the anions lie below 600 cm^{-1} . In uranyl chloride and uranyl fluoride except the UO_2 stretching vibrations all other fundamentals appear in the far-IR spectrum of the compounds.

EXPERIMENTAL

The infrared spectrum of UO_2Cl_2 and UO_2F_2 recorded in the range $3800\text{-}400 \text{ cm}^{-1}$ and their far-infrared spectrum in the range $600\text{-}50 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

Assignment of fundamental frequencies of UO_2Cl_2 and UO_2F_2 : The uranyl ion has three vibrational frequencies, a symmetric stretching frequency ν_1 (860-880 cm^{-1}), an asymmetric stretching frequency ν_6 (930-960 cm^{-1}) and a bending frequency ν_3 (199-210 cm^{-1}). The symmetric O-U-O bending is split into two frequencies ν_{3a} in the plane of the ion and appears in the IR spectrum at about 200 cm^{-1} , ν_{3b} perpendicular to the plane of the ion, which does not appear in both IR and Raman but has been known to appear at about 275 cm^{-1} from fluorescence studies³. The symmetric stretching vibration of the uranyl ion is prohibited by selection rules but appears as a weak absorption in the infrared spectra has been discussed by Sutton⁴ for many halide complexes. In the IR spectra of UO_2Cl_2 and UO_2F_2 the assignment of the ν_1 and ν_6 fundamentals have been easily assigned. There has been conflicting views on the deformation fundamental of UO_2 . Ferraro and Walker⁵ assign absorption at 140 cm^{-1} while Topping⁶ have suggested a frequency near 210 cm^{-1} . Hart and Newbery⁷ have clearly shown that the vibration occurs at about 260 cm^{-1} in some halide complexes. Usually only one band is seen in the IR spectrum corresponding to this doubly degenerate mode, implying that UO_2 is linear in a variety of ligand environments. So the frequency at 250 cm^{-1} in UO_2Cl_2 and 260 cm^{-1} in UO_2F_2 has been assigned to the ν_3 mode of vibration. The stretching and bending fundamentals of the equatorial ligand occur in the far-infrared region. The symmetric stretching vibration of UX_2 is assigned to 320 cm^{-1} in UO_2Cl_2 and 390 cm^{-1} in UO_2F_2 while the asymmetric stretching vibration occurs at 450 cm^{-1} in UO_2F_2 and 400 cm^{-1} in UO_2Cl_2 . The four deformation fundamentals are spread over the entire class one in each species. The X-U-X deformation ν_4 mode is assigned to 122 cm^{-1} in UO_2Cl_2 and to 155 cm^{-1} in UO_2F_2 . The two other deformation fundamentals involving the oxygen and halide atom have been assigned to 152 cm^{-1} and 220 cm^{-1} in UO_2Cl_2 ; 180 and 230 cm^{-1} in UO_2F_2 , respectively. The only A_2 deformation fundamental is infrared inactive. The complete vibrational assignment of UO_2Cl_2 and UO_2F_2 , observed and calculated frequencies and P.E.D. is summarized in Table-1.

The uranyl fluoride has three bands due to O-H vibrations of the water molecule. The sharp absorption at 3600 cm^{-1} is due to interstitial water with weak hydrogen bonding. Two other bands of relatively less intensity have been observed at 3400 and 3175 cm^{-1} and assigned as asymmetric and symmetric O-H stretching vibrations, respectively. The nature of the bands suggest strong intermolecular hydrogen bonding. In uranyl chloride there is a strong broad absorption at about 3400 cm^{-1} due to strong and weak intermolecular hydrogen bonding. The in-plane bending vibration of water molecule is assigned to 1600 cm^{-1} in UO_2Cl_2 and 1620 cm^{-1} in UO_2F_2 while the band at 720 cm^{-1} is assigned to the out-of-plane deformation mode.

TABLE-1
VIBRATIONAL ASSIGNMENT, CALCULATED FREQUENCIES OF THE
FUNDAMENTALS AND POTENTIAL ENERGY DISTRIBUTION FOR
URANYL CHLORIDE AND URANYL FLUORIDE

Frequency (cm^{-1})		Assignment	P.E.D. (%)
UO_2Cl_2	UO_2F_2		
122 (124)	155 (156)	ν_4 X-U-X bending	93
152 (152)	180 (180)	ν_9 O-U-X deformation	100
220 (220)	230 (230)	ν_7 O-U-X deformation	100
250 (247)	260 (259)	ν_3 O-U-O symmetric bending	99
320 (317)	390 (390)	ν_2 X-U-X symmetric stretching	100
400 (400)	450 (450)	ν_8 X-U-X asymmetric stretching	100
–	640	$\nu_3 + \nu_8$ or $\nu_2 + \nu_7$	–
720	720	O-H bending o.p.	–
780	–	$2\nu_2$	–
870 (870)	865 (865)	ν_1 O-U-O symmetric stretching	100
950 (950)	935 (935)	ν_6 O-U-O asymmetric stretching	100
–	960	$2\nu_2 + \nu_9$	–
–	1010	$\nu_1 + \nu_3$	–
1160	1160	$\nu_3 + \nu_6$	–
1340	1340	$\nu_6 + \nu_8$	–
1600	1620	O-H bending i.p.	–
–	2340	$2\nu_6 + \nu_8$	–
–	3175	O-H stretching	–
3400	3410	O-H stretching (bonded)	–
–	3600	O-H stretching (interstitial)	–

X is Cl or F; i.p.- in-plane; o.p.- out-of-plane

Frequency within brackets is the calculated value using the force constant

Force constants: The uranyl chloride and uranyl fluoride belong to C_{2v} symmetry the same as that of the uranyl ion. The nine fundamental vibrational distributed among the species as $4A_1 + A_2 + 2B_1 + 2B_2$. In the structural configuration of the molecule the YZ plane contains the UO_2 while the XZ plane contains UX_2 . The U-O bond distance in most uranyl salts varies from 1.71 to 1.76 Å. The U-O bond distance in UO_2F_2 is 1.74 ± 0.02 Å and the U-F bond distance is 2.429 ± 0.002 Å from crystal structure studies. In UO_2Cl_2 the U-O bond distance is 1.732 Å and U-Cl bond distance is 2.41 Å. The bond angle of UO_2 has been assumed to be $179^\circ 30'$ while $\alpha = \beta = 109^\circ 28'$ as it is for most molecules of the XY_2Z_2 type. The normal coordinate analysis was carried out by the kinetic constant method. The major potential constants of stretching, bending and interaction for the two molecules is given in Table-2. The U-O force constant in UO_2F_2 is $7.166 \text{ m dyn}/\text{Å}$ while it is $7.324 \text{ m dyn}/\text{Å}$ in UO_2Cl_2 compares well with the average U-O force constant of $7.324 \text{ m dyn}/\text{Å}$ calculated for the free uranyl ion. The U-O bond distance calculated using the Badger formula $R_{\text{UO}} = \beta F_{\text{UO}}^{-1/3} + d_{\text{UO}}$ where F_{UO} is the U-O force constant and $d_{\text{UO}} = 1.17$ yields

1.726 Å for UO_2F_2 and 1.73 for UO_2Cl_2 which is the average U-O bond distance in many uranyl complexes. The U-O bond distance decreases with increase in magnitude of the symmetric stretching frequency was observed by Ohwada⁸. The U-F force constant is 1.83 mdyn/Å and U-Cl force constant is 1.56 mdyn/Å from normal coordinate analysis compare well with similar values in other uranyl halide complexes. The ratio of f_D/f_d gives a value of 0.21 for UO_2Cl_2 and 0.25 for UO_2F_2 which shows that the increase in the mass of the ligand atoms is associated with increasing covalency. It is generally observed that the force constant decreases with increase in the mass of the halogen substituent atom as it is observed $f_{\text{U-Cl}} < f_{\text{U-F}}$ in the present case.

TABLE-2
MAJOR POTENTIAL CONSTANTS (mdyn Å⁻¹, mdyn Å rad⁻², mdyn rad⁻¹)
OF UO_2Cl_2 AND UO_2F_2

Potential constant	UO_2Cl_2	UO_2F_2	Potential constant	UO_2Cl_2	UO_2F_2
f_d	7.32480	7.16630	$f_{\alpha\beta}$	- 0.07582	- 0.05890
f_{dd}	-0.18520	- 0.10580	$f_{\gamma\gamma}$	0.08330	0.06822
f_D	1.56900	1.83420	$f_{d\alpha}$	- 0.00059	- 0.00063
f_{DD}	0.31640	- 0.21700	$f_{D\alpha}$	- 0.04103	- 0.01864
f_α	0.16155	0.15915	$f_{d\beta}$	0.00137	0.00148
f_β	0.12147	0.12256	$f_{D\beta}$	0.04694	0.02096
f_γ	0.19930	0.19543			

Conclusion

In molecules involving heavier atoms the fundamental usually lie in the far-infrared region and rather difficult to assign without a normal coordinate analysis. A complete vibrational assignment has been made for uranyl chloride and uranyl fluoride assuming C_{2v} point group of symmetry. The UO_2 configuration being linear has now been confirmed by normal coordinate analysis. The good values of force constants and P.E.D. confirm the assignment of fundamental frequencies and hence the molecular structure for the two uranyl halides investigated.

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