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Spectroscopic Investigation and Molecular Dynamics of $UO_2(Cl_4)^{2-}$ and $UO_2(F_5)^{3-}$ Ions

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Force field studies of $UO_2(Cl_4)^{2-}$ $[XY_2Z_4]$ and $UO_2(F_5)^{3-}$ $[XY_2Z_5]$ of bipyramidal type molecules and ligands have been carried out using the kinetic constant method. The structural parameters and vibrational frequencies for the ions under study are presented. The method of kinetic constants is employed to evaluate the molecular constants *viz.*, force constants, compliance constants, mean square amplitudes and mean amplitudes for the ions $UO_2(Cl_4)^{2-}$ and $UO_2(F_5)^{3-}$ have been evaluated. The kinetic constants are presented, it is oberved that the angle-angle interaction kinetic constants $K_{\beta\beta}$, $K'_{\beta\beta}$ and $K_{\alpha\beta}$ are uniquely negative for $UO_2(F_5)^{3-}$ and $K_{\beta\beta}$ is negative in $UO_2(Cl_4)^{2-}$ and it is observed that all the constants are expected to be in the characteristic values. A fresh set of force constants evaluated in the present study, it is noticed that the structuring force constant for the U—O bond (f_d) is much stronger than that of the U—Cl and U—F bonds (f_r). This means that the U—O bond is much stronger than the U—Cl and U—F bonds in these ions. Further it is seen that the value of f_d agrees quite well with the value reported in the literature.

INTRODUCTION

The infrared absorption spectra of $UO_2(Cl_4)^{2-}$ and $UO_2(F_5)^{3-}$ have been reported by Semmer *et al.*[1] The small relative scattermg power of the oxygen atoms makes it very difficult to determine the U—O bond length in uranyl complexes. It would be quite convenient if one could use infrared absorption spectra to measure the U—O bond length. As pointed out by the author in a previous publication[2], provided a relation such as Badger's rule[3] is applicable, a small change in U—O bond distance leads to a large change in the U—O bond force constant.

In reference[1] it was pointed out that fairly accurate force constants can be calculated for the uranyl U—O bond (F_{UO}) and for the bond-bond interaction ($F_{UO,\,OU}$). The bare uranyl ion UO_2^{2+} is in itself a strong complex of U(VI) with O(II). Infrared and Raman spectra have been reported[4–12] on many of these uranyl

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compounds. Also, extensive studies have been made of the fluorescence spectra and visible absorption spectra of many uranyl compounds. These are reported and discussed by Dieke and Duncan and by Rabinowitch[14]. Zacharisen[13] discusses the crystal structures of many uranyl compounds and points out that in all cases known the uranyl group in collinear[15].

The present investigation is aimed towards a complete vibrational analysis for XY_2Z_4 and XY_2Z_5 type ions, *viz.*, $UO_2(Cl_4)^{2-}$ and $UO_2(F_5)^{3-}$ using F.G. matrix technique along with the method of kinetic constants.

THEEORETICAL CONSIDERATIONS

Molecular Configuration and Normal Modes of Vibration of XY_2Z_4 Type Molecules

The structure of the molecules of XY_2Z_4 type (Fig. 1) belong to D_4h point

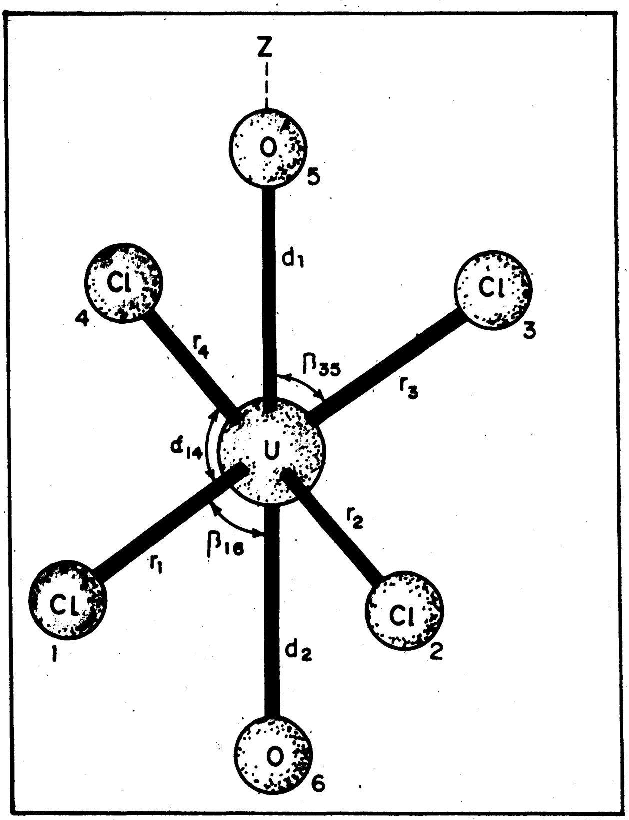

Fig. 1 The internal coordinates, the numbering of atoms and the orientation of the cartesian coordinates axes of $UO_2(Cl_4)^{2-}$ ion.

group, with all the normal vibrational modes distributed according to the irreducible representations.

$$\tau = 2A_{1g} + 2A_{2u} + 1B_{1g} + 1B_{2g} + 1B_{2u} + 1E_g + 3E_u$$

Symmetric Coordinates

The orthonormalized set of symmetry coordinates has been used to describe the normal modes of vibration.

A_{1g} Species

$$S_1 = (1/\sqrt{2})(d_1 + d_2)$$

$$S_2 = (1/2)(r_1 + r_2 + r_3 + r_4)$$

A_{2u} Species

$$S_3 = (1/\sqrt{2})(d_1 - d_2)$$

$$S_4 = (\sqrt{RD}/\sqrt{8})(\beta_{51} + \beta_{52} + \beta_{53} + \beta_{54} - \beta_{61} - \beta_{62} - \beta_{63} - \beta_{64})$$

B_{1g} Species

$$S_5 = (1/2)(r_1 - r_2 + r_3 - r_4)$$

B_{2g} Species

$$S_6 = (R/2)(\alpha_{12} - \alpha_{23} + \alpha_{34} - \alpha_{41})$$

B_{2u} Species

$$S_7 = (\sqrt{RD}/\sqrt{8})(\beta_{51} - \beta_{52} + \beta_{53} - \beta_{54} - \beta_{61} + \beta_{62} - \beta_{63} + \beta_{64})$$

E_g Species

$$S_{8a} = (\sqrt{RD}/\sqrt{8})(\beta_{51} + \beta_{52} - \beta_{53} - \beta_{54} - \beta_{61} - \beta_{62} + \beta_{63} + \beta_{64})$$

E_u Species

$$S_{9a} = \tfrac{1}{2}(r_1 + r_2 - r_3 - r_4)$$

$$S_{10a} = (R/2)(\alpha_{12} + \alpha_{23} - \alpha_{34} - \alpha_{41})$$

$$S_{11a} = (\sqrt{RD}/\sqrt{8})(\beta_{51} + \beta_{52} - \beta_{53} - \beta_{54} + \beta_{61} + \beta_{62} - \beta_{63} - \beta_{64})$$

G-matrix

The inverse kinetic energy matrix G can be constructed from the relation $G = B\mu B'$; the elements of G matrix are obtained. Here μ_U and μ_{Cl} represent the reciprocal masses of the atoms of uranium and chlorine.

A_{1g} Species

$$G_{11} = \mu_O$$

$$G_{12} = 0$$

$$G_{22} = \mu_{Cl}$$

A_{2u} Species

$$G_{33} = 2\mu_U + \mu_O$$

$$G_{34} = -4p\mu_U$$

$$G_{44} = 2p^2(\mu_{Cl} + 4\mu_U)$$

B_{1g} Species

$$G_{55} = \mu_{Cl}$$

B_{2g} Species

$$G_{66} = 4\mu_{Cl}$$

E_u Species

$G_{99} = \mu_{Cl} + 2\mu_U$

$G_{9,10} = -2\mu_U$

$G_{9,11} = -\sqrt{8}\, q\mu_U$

$G_{10,10} = 4\mu_U + 2\mu_{Cl}$

$G_{10,11} = \sqrt{8}\, q\mu_U$

$G_{11,11} = 2q^2(2\mu_U + \mu_O)$

B_{2u} Species

$G_{77} = 2p^2\mu_{Cl}$

E_g Species

$G_{88} = 2(p^2\mu_{Cl} + q^2\mu_O)$

where $p = \sqrt{D}/\sqrt{r}$ and $q = 1/p$

Molecular Configuration and Normal Modes Of Vibration of XY_2Z_5 Type Molecules

The structure of the molecules of XY_2Y_5 type (Fig. 2) belongs to D_5h point

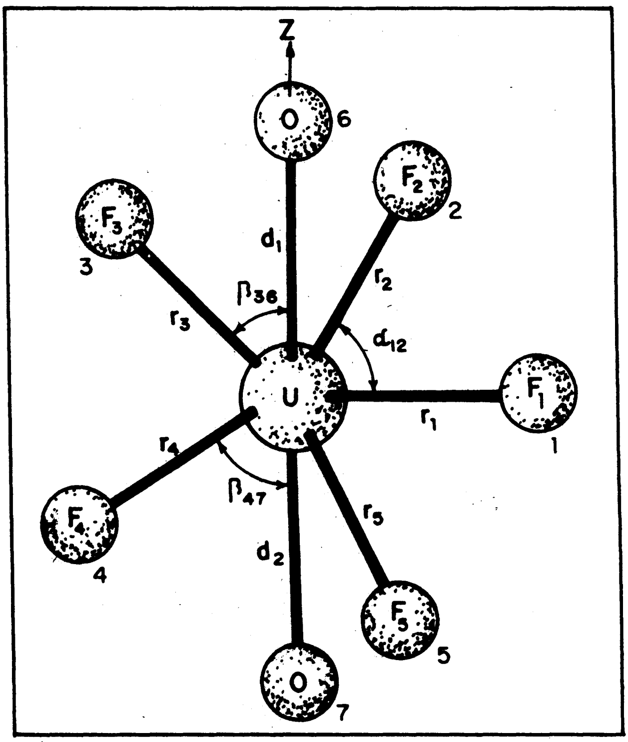

Fig. 2 The internal coordinates, the numbering of atoms and the orientation of the cartesian coordinates axes of $UO_2(F_5)^{3-}$ ion.

group, with all the normal modes distributed according to the irreducible representations.

$$\tau = 2A'_1 + 2A'_2 + 3E'_1 + 1E''_1 + 2E'_2 + 1E''_2$$

A'_1, E''_1 and E'_2 are Raman active and A''_2 and E'_1 are IR active. E''_2 is inactive in both.

Symmetric Coordinates

The orthonormalized set of symmetry coordinates has been used to describe the normal modes of vibration.

A'_1 Species

$$S_1 = (1/\sqrt{5})(r_1 + r_2 + r_3 + r_4 + r_5)$$
$$S_2 = (1/\sqrt{2})(d_1 + d_2)$$

A''_2 Species

$$S_3 = (1/\sqrt{2})(d_1 - d_2)$$
$$S_4 = (\sqrt{RD}/10)(\beta_{16} + \beta_{26} + \beta_{36} + \beta_{46} + \beta_{56} - \beta_{17} - \beta_{27} - \beta_{37} - \beta_{47} - \beta_{57})$$

E'_1 Species

$$S_{5a} = (\sqrt{2}/\sqrt{5})(r_1 + (r_2 + r_5)\cos\alpha + (r_3 + r_4)\cos 2\alpha)$$
$$S_{6a} = (\sqrt{2}/\sqrt{5})(\alpha_{34} + (\alpha_{45} + \alpha_{23})\cos\alpha + (\alpha_{15} + \alpha_{12})\cos 2\alpha)$$
$$S_{7a} = (\sqrt{RD}/\sqrt{5})((\beta_{16} + \beta_{17}) + (\beta_{26} + \beta_{27} + \beta_{56} + \beta_{57})\cos\alpha + (\beta_{36} + \beta_{37} + \beta_{46} + \beta_{47})\cos 2\alpha)$$

E'_2 Species

$$S_{8a} = (\sqrt{2}/\sqrt{5})(r_1 + (r_2 + r_5)\cos 2\alpha + (r_3 + r_4)\cos\alpha)$$
$$S_{9a} = (\sqrt{2}/\sqrt{5}R)(\alpha_{34} + (\alpha_{45} + \alpha_{23})\cos 2\alpha + (\alpha_{15} + \alpha_{12})\cos\alpha)$$

E''_1 Species

$$S_{10a} = \sqrt{RD}/\sqrt{5}[\beta_{16} - \beta_{17}) + (\beta_{26} - \beta_{27}) + (\beta_{56} - \beta_{57})\cos\alpha + (\beta_{36} - \beta_{37} - \beta_{46} - \beta_{47})\cos 2\alpha]$$

E''_2 Species

$$S_{11a} = (\sqrt{RD}/\sqrt{5})[(\beta_{16} - \beta_{17}) + (\beta_{26} - \beta_{27} + \beta_{56} - \beta_{57})\cos 2\alpha + (\beta_{36} - \beta_{37} + \beta_{46} - \beta_{47})\cos\alpha]$$

where r_i and d_i represent the changes in U—X and U—O bond lengths respectively. α_{ij} and β_{ij} indicate the changes in the corresponding interbond angles. R and D are equilibrium bond lengths of U—X and U—O bonds respectively (X = F).

G-Matrix

The inverse kinetic energy matrix G can be constructed from the relation $G = B\mu B'$ the elements of G matrix are obtained. Here μ_O and μ_F represent the reciprocal masses of the atoms of uranium and fluorine.

A_1' Species

$G_{11} = \mu_F$

$G_{12} = 0$

$G_{22} = \mu_O$

A_2' Species

$G_{33} = 2\mu_U + \mu_O$

$G_{34} = -2\sqrt{5}\mu_U$

$G_{44} = 10\mu_U + 2\mu_F$

E_1' Species

$G_{55} = (5/2)\mu_U + \mu_F$

$G_{56} = 5\sqrt{5}\mu_U/4 \sin\alpha$

$G_{57} = -5/\sqrt{2}\mu_U$

E_1' Species

$G_{66} = \mu_U + 4\mu_F \sin^2 2\alpha$

$G_{67} = -5\sqrt{10}\mu_U/4 \sin\alpha$

$G_{77} = 5\mu_U + (5/2)\mu_O$

E_2' Species

$G_{88} = \mu_F$

$G_{89} = 0$

$G_{99} = 4\mu_F \sin^2\alpha$

For E_1'' Species

$G_{10,10} = 2\mu_F + (5/2)\mu_O$

For E_2'' Species

$G_{11,11} = 2\mu_F$

where $a = \sqrt{D}/r$ and $b = 1/a$; μ_U, μ_F denote the reciprocal masses of uranium and fluorine atoms respectively.

Method of Kinetic Constants

The secular equations involving symmetric force constants have been solved using the method of kinetic constants. The study of kinetic constants provides the required number of additional data through the symmetric kinetic constants and the corresponding force constants that is

$$\frac{F_{ij}}{F_{jj}} = \frac{K_{ij}}{K_{jj}} \quad (i < j,\ ij = 1, 2, 3, 4)$$

where K's are the linear combinations of the relevant kinetic constants. This method has been used to solve the 3 × 3 problems.

Vibrational Mean Amplitudes

Utilizing Cyvin's equation[16] $\Sigma = L\Delta L^{\sim}$ the symmetrized mean square amplitudes and hence the valence mean square amplitudes for both bonded and non-bonded distance can be evaluated at 298.16 K, using the present set of force constants. On the basis of these values, the mean amplitudes of vibration of these ions are evaluated.

RESULTS AND DISCUSSION

The structural parameters and vibrational frequencies for the ions under study are presented in Table-1. The method of kinetic constants is employed to evaluate the molecular constants, *viz.*, potential constants, compliance constants and mean squre amplitudes of vibrations for the ions $UO_2(Cl_4)^{2-}$ and $UO_2(F_5)^{3-}$.

TABLE-1
MOLECULAR PARAMETERS AND THE VIBRATIONAL FREQUENCIES OF $UO_2(Cl_4)^{2-}$ AND $UO_2(F_5)^{3-}$ IONS

	Bond distances		Frequencies				
Ions	Å	Å	$\nu_1(A_{1g})$ $\nu_2(A_{1g})$	$\nu_3(A_{2u})$ $\nu_4(A_{2u})$	$\nu_5(B_{1g})$ $\nu_6(B_{2g})$	$\nu_7(B_{2u})$ $\nu_8(E_g)$	$\nu_9(E_u)$ $\nu_{10}(E_u)$ $\nu_{11}(E_u)$
$UO_2(Cl_4)^{2-}$	1.76	2.14	837 264	905 140	202 113	113 85	245 265 110
			$\nu_1(A'_1)$ $\nu_2(A'_1)$	$\nu_3(A''_2)$ $\nu_4(A''_2)$	$\nu_3(E'_1)$ $\nu_6(E'_1)$ $\nu_7(E'_1)$	$\nu_8(E''_1)$ $\nu_9(E'_2)$	$\nu_{10}(E'_2)$ $\nu_{11}(E''_2)$
$UO_2(F_5)^{3-}$	1.76	2.24	819 428	885 184	350 270 235	318 218	261 159

TABLE-2
KINETIC CONSTANTS ($\times 10^{-26}$ kg) OF $UO_2(Cl_4)^{2-}$ AND $UO_2(F_5)^{3-}$ IONS

$UO_2(Cl_4)^{2-}$		$UO_2(F_5)^{3-}$	
k	Values	k	Values
k_d	2.5440	k_d	2.7436
k_{dd}	0.1117	k_{dd}	−0.0878
k_r	5.2573	k_r	2.8475
k_{rr}	0	k_{rr}	−0.1897
k'_{rr}	0.5477	k'_{rr}	0.3432
k_α	2.3229	k_α	1.8829
$k_{\alpha\alpha}$	0.8713	$k_{\alpha\alpha}$	0.6248
k_β	3.0996	k_β	1.1329
$k_{\beta\beta}$	0.0531	$k_{\beta\beta}$	−0.2746
$k'_{\beta\beta}$	1.5982	$k'_{\beta\beta}$	−0.0987
$k_{\alpha\beta}$	−0.0933	$k_{\alpha\beta}$	−0.0870

The kinetic constants are presented in Table 2. From the table it is observed that the angle-angle interaction kinetic constants $k_{\beta\beta}$, $k'_{\beta\beta}$ and $k_{\alpha\beta}$ are uniquely negative for $UO_2(F_5)^{3-}$ and $k_{\alpha\beta}$ is negative in $UO_2(Cl_4)^{2-}$ and it is observed that all the constants are expected to be in the characteristic values. A fresh set of force constants evaluated in the present study are given in Table 3. From Table 3 it is noticed that the stretching force constant for the U—O bond (f_d) is much stronger than that of the U—Cl and U—F bonds (f_r). This means that the U—O bond is much stronger than the U—Cl and U—F bonds in these ions. Further it is seen that the value of f_d agrees quite well with the value reported in the literature. The compliance constants for these ions are given in Table 4. It may be noticed that the compliance constants exhibit trends opposite to that of force constants as expected.

TABLE-3
VALENCE FORCE CONSTANTS (× 10^2 N/m) OF $UO_2(Cl_4)^{2-}$ AND $UO_2(F_5)^{3-}$ IONS

$UO_2(Cl_4)^{2-}$		$UO_2(F_5)^{3-}$	
f	Values	f	Values
f_d	6.6882	f_d	4.6230
f_{dd}	–0.0866	f_{dd}	-2.8969
f_r	0.3602	f_r	0.9682
f_{rr}	0.1487	f_{rr}	–0.1011
f'_{rr}	0.7779	f'_{rr}	3.3708
f_α	1.2397	f_α	0.6312
$f_{\alpha\alpha}$	1.1739	$f_{\alpha\alpha}$	0.2993
f_β	0.1673	f_β	0.1756
$f_{\beta\beta}$	0.0090	$f_{\beta\beta}$	0.0211
$f'_{\beta\beta}$	0.0800	$f'_{\beta\beta}$	–0.0109
$f_{\alpha\beta}$	–4.0090	$f_{\alpha\beta}$	-1.7048

TABLE-4
COMPLIANCE CONSTANTS (× 10^{-2} M/N) OF $UO_2(Cl_4)^{2-}$ AND $UO_2(F_5)^{3-}$ IONS

$UO_2(Cl_4)^{2-}$		$UO_2(F_5)^{3-}$	
n	Values	n	Values
n_d	0.1496	n_d	0.3557
n_{dd}	0.0018	n_{dd}	0.2235
n_r	–0.7089	n_r	1.0674
n_{rr}	–0.1232	n_{rr}	0.1136
n'_{rr}	1.6520	n'_{rr}	–0.5807
n_α	0.8646	n_α	2.7934
$n_{\alpha\alpha}$	-14.3421	$n_{\alpha\alpha}$	-2.4773
n_β	6.0125	n_β	5.7878
$n_{\beta\beta}$	-12.0152	$n_{\beta\beta}$	–0.7912
$n'_{\beta\beta}$	-22.2617	$n'_{\beta\beta}$	0.3947
$n_{\alpha\beta}$	0.1033	$n_{\alpha\beta}$	0.0125

The valence mean square amplitudes and hence the mean amplitudes of vibration for the bonded distances at 298.16K have been evaluated and are given in Tables 5 and 6 respectively. These values are found to be in the expected range.[17–21]

TABLE-5
MEAN SQUARE AMPLITUDES OF VIBRATION (× 10^{-3} $Å^2$) AT 298.16K OF $UO_2(Cl_4)^{2-}$ AND $UO_2(F_5)^{3-}$ IONS

$UO_2(Cl_4)^{2-}$		$UO_2(F_5)^{3-}$	
σ	Values	σ	Values
σ_d	1.3293	σ_d	2.1860
σ_{dd}	–0.0251	σ_{dd}	0.9905
σ_r	4.5261	σ_r	3.6500
σ_{rr}	–0.5080	σ_{rr}	–0.4147
σ'_{rr}	–0.2676	σ'_{rr}	–0.8474
σ_α	8.5328	σ_α	14.4061
$\sigma_{\alpha\alpha}$	-55.5495	$\sigma_{\alpha\alpha}$	-9.9533
σ_β	25.5201	σ_β	26.2072
$\sigma_{\beta\beta}$	–48.7678	$\sigma_{\beta\beta}$	-2.6427
$\sigma'_{\beta\beta}$	-92.6488	$\sigma'_{\beta\beta}$	1.7580
$\sigma_{\alpha\beta}$	1.3404	$\sigma_{\alpha\beta}$	-0.4411

TABLE-6
MEAN AMPLITUDES OF VIBRATION (× 10^{-2} Å) at 298.16K OF $UO_2(Cl_4)^{2-}$ AND $UO_2(F_5)^{3-}$ IONS

$UO_2(Cl_4)^{2-}$		$UO_2(F_5)^{3-}$	
l	Values	l	Values
l_d	3.64595	l_d	4.67551
l_r	6.50084	l_r	6.04153

The mean amplitude of U—O stretch is found to be smaller than those relating to equatorial U—Cl and U—F stretch, since f_d value is higher compared with f_r and f_{rr}. This is in accordance with the theory that the smaller the force constants higher will be the mean amplitudes of vibration. These mean amplitude calcualtions are useful in the interpretation of electron diffraction studies in the molecular structure determination.

Conclusion

Thus a satisfactory set of molecular constants *viz.*, potential constants, compliance constants, mean square amplitudes and mean amplitudes of vibration have been evaluated afresh for $UO_2(Cl_4)^{2-}$ and $UO_2(F_5)^{3-}$ ions by the method of kinetic constants.

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