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NOTES

Force Constants and Other Related Constants of XY_5Z Ions

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Force constants and other related constants of XY_5Z ions are calculated in the present work.

A normal coordinate analysis of XY_5Z type complex ions ($X = Re, Tc$; $Y = O$; $Z = Cl, Br$) is performed using the kinematic method suggested by Herranz and Castano[1]. These complex ions have vibrations of the type $4A_1 + 2B_1 + B_2 + 4E$ in the point group C_{4v}. General valence force field has been used to calculate the force constants. The other molecular constants like mean amplitudes of vibration, Coriolis coupling constants and centrifugal distortion constants are also evaluated for these ions. Among the possible internal symmetry coordinates sets, the characteristic set can be defined as that for which the trace value of the L matrix is maximum. The L-matrix which is symmetric takes the most diagonal form in this method. Consequently, the characteristic set is particularly important because it provides the most physically significant set of valence (symmetry) coordinates for use in assigning all the fundamental bands of the spectra. For this set of coordinates the L-matrix is given by $L = V\Gamma^{(1/2)}\tilde{V}$ where V is an orthogonal matrix which diagonalises the G-matrix and $\Gamma^{(1/2)}$ is the diagonal matrix whose elements are the positive square roots of the eigen values of G ($VGV^{-1} = \Gamma$). The potential energy constants were obtained using the relation $F = \tilde{L}^{-1}\Lambda L^{-1}$ where is Λ a diagonal matrix whose diagonal elements are given by $\lambda_k = 4\pi^2C^2\nu_k^2$ in which ν_k are the vibrational frequencies expressed in cm^{-1}.

Mean amplitudes of vibration are obtained from the L-matrix by using Cyvin's theory of mean amplitudes[2]. The Coriolis coupling constants are obtained from the relation given by Meal and Polo[3]. The C^α matrices are obtained from B matrix and the Coriolis coupling constants ζ^α are then calculated by using the relation $\zeta^\alpha = (L^{-1})C^\alpha(\tilde{L}^{-1})$. Centrifugal distortion constants are determined using Kivelson and Wilson's[4] formalism linking them with the force constants.

The oxo-ligands are strong Π donors and the mono-oxy group influences the properties and reactivities of the metal ions in complex chemical process. Vibrational data on IR and Raman spectra of rhenium (V) and technetium (V) mono-oxy complexes were given by Hanuza *et al*[5]. Force constant calculations were carried out for both modified valence and Urey-Bradley force fields. In this paper the force constants obtained using GVFF are presented in Table 1 alongwith those of earlier authors.

TABLE 1

VALENCE FORCE CONSTANTS (mydn/Å)

f_{ij}	$TcCl_5O^{2-}$		$TcBr_5O^{2-}$		$ReCl_5O^{2-}$		$ReBr_5O^{2-}$	
	P.W.	Ref (5)	P.W.	Ref (5)	P.W.	Ref (5)	P.W.	Ref (5)
f_D	2.117	1.537	1.700	1.344	2.354	1.763	1.774	1.118
f_R	8.536	7.355	8.189	7.998	8.732	8.473	8.358	7.495
f_d	1.633	1.567	1.379	1.411	1.679	1.799	1.559	1.251
f_α	0.181	0.280	0.175	0.221	0.187	0.250	0.169	0.232
f	0.433	0.267	0.384	0.209	0.450	0.227	0.343	0.203
f_ϕ	0.162	0.141	0.129	0.120	0.140	0.141	0.116	0.116
f_{dd}	−0.148	0.224	0.136	0.183	0.145	0.209	0.108	0.259
f_{DR}	0.635	0.033	0.671	0.024	0.466	0.036	0.523	0.029
$f_{d\alpha}$	0.098	0.209	0.131	0.176	0.071	0.135	0.133	0.163
$f_{\alpha\phi}$	−0.008	−0.001	−0.004	−0.006	−0.006	−0.007	−0.003	−0.001

P.W.—Present work

From the values of these constants it is seen that equatorial (Re-Cl) and (Tc-Cl) stretching force constants f_d are generally less than the axial stretching force constants f_D (Re-Cl and Tc-Cl) and f_R (Re-O and Tc-O). The bending force constant f_ϕ ($\mathrm{Cl'\widehat{Re}O}$ and $\mathrm{Cl'\widehat{Tc}O}$) is less than the constants f_α ($\mathrm{Cl\widehat{Re}Cl}$ and $\mathrm{Cl\widehat{Tc}Cl}$) and f_r ($\mathrm{Cl\widehat{Re}Cl'}$ and $\mathrm{Cl\widehat{Tc}Cl'}$) in all cases studied here. In general the stretching force constants f_d, f_D and f_R and the bending force constants f_α, f_r and f_ϕ decrease with the increase in the mass of the halogens for the same central atom. The force constants f_{dD}, f_{dR}, $f_{D\alpha}$ and f_{dr} assume zero values for all the molecules indicating no interaction at all between them. The results obtained here suggest some general patterns for XY_5Z type systems involving some influence of halogens. Hiraishi *et al.*[6] calculated the ratio of stretching force constants f(M-Br)/f(M-Cl) and found it to be 0.79 for a large number of molecules. Clark and Williams[7] report that the ratio of (M-Br)/(M-Cl) is 0.74–0.77 for terminal metal-halogen stretching frequencies. For the XY_5Z type complex ions studied here, the ratio is 0.85 for f(Re-Br)/f(Re-Cl). The $\nu_2(A_1)$ vibrational frequencies and corresponding force constants f_R are greater for bromide compounds than for the chlorides. This effect is opposite to that observed in modes involving metal-halogen bonds. Stronger coupling exists in the XY_5 group for the chloride complex (the force constants are stronger) and hence the metal-oxygen bonds are weaker.

The mean amplitudes of the non-bonded atom pairs are greater than those of the bonded atom pairs in all molecules. It is seen that the mean amplitude values of the $Y_{eq} \ldots Z$ atom pair are greater than the values corresponding to all the other atom pairs. The present values of the mean amplitudes of vibration as 298 K are given in Table 2. The Coriolis coupling constants all all the ions studied here are listed in Table 3. In

TABLE 2

MEAN AMPLITUDE OF VIBRATION AT 298 K (Å)

Atom pairs	$TcCl_5O^{2-}$	$TcBR_5O^{2-}$	$ReCl_5O^{2-}$	$ReBr_5O^{2-}$
$X\text{-}Y_{eq}$	0.061	0.075	0.056	0.063
$X\text{-}Y_{ax}$	0.063	0.072	0.050	0.059
X-Z	0.040	0.048	0.037	0.039
$Y_{eq} \ldots Y_{eq}$ (short)	0.092	0.092	0.096	0.090
$Y_{eq} \ldots Y_{eq}$ (long)	0.078	0.085	0.076	0.092
$Y_{eq} \ldots Y_{ax}$	0.089	0.099	0.075	0.092
$Y_{eq} \ldots Z$	0.100	0.116	0.106	0.116
$Y_{ax} \ldots Z$	0.057	0.061	0.056	0.059

TABLE 3

CORIOLIS COUPLING CONSTANTS

Type	ζ_{ij}	$TcCl_5O^{2-}$	$TcBr_5O^{2-}$	$ReCl_5O^{2-}$	$ReBr_5O^{2-}$
$A_1 \times E$	$\zeta_{1,10}$	0.592	0.594	0.587	0.588
	$\zeta_{2,9}$	−0.674	−0.692	−0.676	−0.693
	$\zeta_{3,10}$	−0.268	−0.272	−0.274	−0.274
	$\zeta_{4,8}$	−0.485	−0.471	−0.489	−0.480
	$\zeta_{4,11}$	0.515	0.523	0.510	0.515
$B_1 \times B_2$	$\zeta_{5,7}$	−1.000	−1.000	−1.000	−1.000
$B_1 \times E$	$\zeta_{5,10}$	−0.268	−0.272	−0.274	−0.274
	$\zeta_{6,8}$	−0.513	−0.524	−0.511	−0.518
	$\zeta_{6,11}$	−0.483	−0.474	−0.489	−0.481
$B_2 \times E$	$\zeta_{7,10}$	0.268	0.272	0.274	0.274
$E \times E$	$\zeta_{8,8}$	0.054	0.104	0.044	0.076
	$\zeta_{8,9}$	−0.025	−0.031	−0.016	−0.003
	$\zeta_{8,10}$	−0.007	−0.019	−0.003	−0.003
	$\zeta_{8,11}$	0.997	0.990	0.999	0.995
	$\xi_{9,9}$	−0.914	−0.961	−0.918	−0.962
	$\zeta_{9,10}$	−0.156	−0.108	−0.156	−0.107
	$\zeta_{9,11}$	−0.008	−0.005	−0.005	−0.002
	$\zeta_{10,10}$	−0.712	−0.710	−0.699	−0.698
	$\zeta_{10,11}$	−0.003	−0.062	−0.024	−0.045
	$\zeta_{11,11}$	−0.064	−0.099	−0.043	−0.073

the first order (E × E) case, all Coriolis constants are given. In the second order coupling involving $A_1 \times E$, $B_1 \times B_2$, $B_1 \times E$ and $B_2 \times E$ types constants with significant values only are included in the table. The values of these constants are a measure of the coupling between the concerned modes. Hence large values in some cases indicate strong coupling between the corresponding modes.

The centrifugal distortion constants for all molecules studied here are presented in Table 4. From the values it is seen that the constant D_K is negative in all cases. The value of D_J increases with the incrcase in the mass of X atom and decreases with the increase in the mass of the Y atom. The values of D_K and D_{JK} are large compared to D_J. The constants R_5 and δ_J assume zero values in all the ions studied here.

TABLE 4

CENTRIFUGAL DISTORTION CONSTANTS OF XY_5Z IONS

Ions	D_J(Hz)	D_K(kHz)	D_{JK}(kHz)	R_6(kHz)
$TcCl_5O^{2-}$	22.4	−70.3	70.3	2.0
$TcBr_5O^{2-}$	5.9	−79.6	79.5	0.1
$ReCl_5O^{2-}$	26.5	−67.0	67.0	2.6
$ReBr_5O^{2-}$	6.0	−85.0	85.6	1.1

The values of the force constants and other molecular constants like mean amplitudes of vibration, Coriolis coupling constants and centrifugal distortion constants obtained for XY_5Z (X = Tc, Re, Y = Cl, Br) ions by Herranz and Castano's method obtained here are reasonable. Here in this type of ions two fourth order vibrational problems have been tested and it may be concluded that the method may be extended for higher order cases also.

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