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Force constants and mean amplitudes of vibration of octahedral haloanions of IV B group elements

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General quadratic force constants for octahedral haloanions of O_h point group have been determined using IR and Raman spectral data The trends in the force constants and vibrational frequencies have been discussed and compared with those corresponding to MX_4 type molecules The mean-square amplitude quantities and mean amplitudes of vibration for the bonded as well as non-bonded atoms for chloro- and bromoanions have been evaluated at three temperatures, $T = 0°$, 298° and 500°K.

INTRODUCTION

Recently, the spectra of a large number of complexes of transition elements have been studied both theoretically and experimentally specially to understand the 'anomalous' intensity pattern of the fundamental frequencies (Woodward & Creighton 1961) consequences of different *d* orbital occupancies and Jahn- Teller effects. Adam & Newton (1968) studied the Raman and I. R. spectra of octahedral chloroanions of IVB group elements and calculated the force constants employing Urey-Bradley force field. Further Brisdon *et al* (1969) observed the Raman and I. R spectra of chloro- and bromo-anions of IVB group elements and reported valence force constants on the basis of their vibrational studies of chloro- and bromo-anions of IVB group elements Due to the increasing importance of the haloanions in the transition metal complexes, it was thought worthwhile to compute general quadratic force constants for the octahedral chloroanions ($TiCl_6^{2-}$, $ZrCl_6^{2-}$ and $HfCl_6^{2-}$) in order to study the nature of bonding in the octahedral chloroanions, and also to compare the vibrational frequencies and force constants with those of the corresponding tetrahedral molecules. Further, the generalized mean-square amplitude quantities and mean amplitudes of vibration for bonded as well as non-bonded distances have been evaluated.

METHOD

The ions of the type MX_6^{2-}(X = Cl, Br) possess O_h symmetry and the fundamental vibrations are distributed as, $(1a_{1g}+1e_g+2f_{1u}+1f_{2g}+1f_{2u})$, where a_{1g}, e_g+f_{2g} are Raman active and f_{1u} is infrared active, while f_{2u} is inactive in both.

The generalized quadratic potential field constant and the symmetrized mean-square amplitudes of vibrations were evaluated as in our earlier paper

(1969a, 1969b). The fundamental frequencies employed in the present computations were taken from literature (Adam & Newton 1968, Brisdon *et al* 1969) and are presented in table 1 along with computed bond distances. The $\nu_6(f_{2u})$ fundamental frequencies in case of bromoanions were evaluated by employing modified valence force constants reported by Brisdon *et al* (1969).

TABLE 1. Fundamental frequencies of octahedral haloanions (in cm^{-1})

Ion	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	M–X bond length (in Å)
$TiCl_6^{2-}$	331	284	330	193	194	142	2.31
$ZrCl_6^{2-}$	327	237	290	150	153	90	2.44
$HfCl_6^{2-}$	333	237	288	145	157	80	2.43
$TiBr_6^{2-}$	192	141	268	121	110	77.94	
$ZrBr_6^{2-}$	198	141.7	226	114	116	82.18	
$HfBr_6^{2-}$	201	157	193	112	116	82.18	

FORCE CONSTANTS

The force constants, computed here using the general quadratic potential function, are presented in table 2. The symbols have their usual meanings as explained in our earlier papers (1969a, 1969b). The reported constants reproduce the observed frequencies very well.

TABLE 2. Force constants (in *m* dynes/Å)

Force constant	$TiCl_6^{2-}$	$ZrCl_6^{2-}$	$HfCl_6^{2-}$
f_d	1.527	1.305	1.419
f_{dd}	0.100	0.177	0.190
$f_{d\alpha} - f_{d\alpha''}$	0.106	0.055	0.040
$f_\alpha - f_{\alpha\alpha'''}$	0.187	0.124	0.134
$f_{\alpha\alpha} - f_{\alpha\alpha''}$	−0.005	0.000	0.003
$f_{\alpha\alpha'} - f_{\alpha\alpha'''}$	−0.012	0.019	0.034
$f_{dd'}$	0.358	0.321	0.134

Neglecting the small difference in M—Cl stretching constant f_d for $TiCl_6^{2-}$, which is due to the use of ammonium instead of tetraethylammonium salt, it may be noted that f_d varies inversely with M—Cl bond length estimated from Pauling covalent radii (1960). This is anticipated for elements of a group when oxidation states are equal. Similar trend in UBFF stretching constant (K) has also been reported by Adam & Newton (1968). It is also apparent from the table that the stretching of the bond varies for different complexes. The bond-bond interaction constant f_{dd} increases with the increase of atomic weight of the central atom while the reverse trend is observed for the $f_{dd'}$ constant. The deformation constant, $f_{\alpha\alpha,}$, for Zr and Hf-chloroanions is approximately the same.

A comparison of the force constants of MCl_6^{2-} ions with those of the corresponding MCl_4 molecules (Muller & Krebs 1967 and Nagarajan, 1964) in table 3

TABLE 3. Comparison of force constants and frequencies of MX_4 molecules and MX_6^{2-} ions.

Species	Force constants (*m* dynes/Å)			Frequencies (cm^{-1})	
	f_d	f_{dd}	$f_\alpha - f_{\alpha\alpha}'''$	ν_1	ν_5
$TiCl_4$	2.59	0.19	0 11	389	140
$TiCl_6^{2-}$	1 53	0.10	0 19	331	194
$ZrCl_4$	2.56	0.17	0.09	383	120
$ZiCl_6^{2-}$	1.31	0.18	0.12	327	153
$HfCl_4$	2.42	0 03	0.07	347	94
$HfCl_6^{2-}$	1.42	0.19	0.13	333	157

shows that the stretching constants for the octahedral chloroanions are less than those for tetrahedral molecules, indicating a loosening of the bonds in MCl_6^{2-} ions. An opposite trend is noticed for f_{dd} and the bending constants except for $TiCl_6^{2-}$ due to different salt used in spectral studies. Further, a greater force is required to open the $Cl—\hat{M}—Cl$ angle in MCl_6^{2-} ion as compared with the MCl_4 molecules.

TREND IN FREQUENCIES

The stretching frequency $\nu_1(a_{1g})$ for the ions under investigation is nearly the same. In the case of Zr and Hf, all the frequencies are approximately the same. A comparison of the frequencies of the MCl_6^{2-} ions with MCl_4 molecules in table 3 indicates that the symmetrical stretching frequencies of the ions are less than those of the molecules while for bending frequencies the behaviour is opposite.

MEAN AMPLITUDES OF VIBRATION

The generalized mean-square amplitude quantities, viz. mean-square parallel amplitude $<\Delta z^2>$ and mean-square perpendicular amplitudes $<\Delta x^2>$ and

$\langle \Delta y^2 \rangle$ at three temperatures $T = 0°$, $T = 298°$ and 500°K are given in table 4 The mean amplitude of vibration for bonded as well as nonbonded atom pairs at temperatures $T = 0°$, 298° and 500°K are given in table 5. The mean amplitude of vibration for bonded atom pairs increases with the increase of mass of the central atom for chloro- and bromo-anions while the corresponding force constants show a reverse trend (1969). The mean amplitude quantities for non-bonded distances in general also increase. On the other hand, as one moves from chloro- to bromospecies for the same element, the mean

TABLE 4. Generalized mean-square amplitude quantities in 10^{-4}Å^2 for octahedral haloanions.

Ion	Distance	Symbol	Mean-square amplitude quantities		
			$T = 0°$K	$T = 298°$K	$T = 500°$K
$TiCl_6^{2-}$	Ti–Cl	$\langle \Delta z^2 \rangle$	25.834	39.957	60.211
		$\langle \Delta x^2 \rangle$	34.361	80.046	128.310
		$\langle \Delta y^2 \rangle$	34.361	80.046	128.310
	Cl–Cl (linear)	$\langle \Delta z^2 \rangle$	31.887	51.921	79.218
		$\langle \Delta x^2 \rangle$	24.501	56.088	90.052
		$\langle \Delta y^2 \rangle$	24.501	56.088	90.052
	Cl–Cl (non-linear)	$\langle \Delta z^2 \rangle$	87.246	165.142	257.249
		$\langle \Delta x^2 \rangle$	75.788	139.263	215.828
		$\langle \Delta y^2 \rangle$	45.722	129.481	211.136
$ZrCl_6^{2-}$	Zr–Cl	$\langle \Delta z^2 \rangle$	23.672	40.711	62.786
		$\langle \Delta x^2 \rangle$	38.606	131.082	215.315
		$\langle \Delta y^2 \rangle$	38.606	131.082	215.315
	Cl–Cl (linear)	$\langle \Delta z^2 \rangle$	36.431	66.458	103.528
		$\langle \Delta x^2 \rangle$	31.065	87.886	143.411
		$\langle \Delta y^2 \rangle$	31.065	87.886	143.411
	Cl–Cl (non-linear)	$\langle \Delta z^2 \rangle$	81.864	212.056	341.579
		$\langle \Delta x^2 \rangle$	68.171	173.683	279.185
		$\langle \Delta y^2 \rangle$	68.344	290.792	481.795
$HfCl_6^{2-}$	Hf–Cl	$\langle \Delta z^2 \rangle$	20.593	35.676	55.095
		$\langle \Delta x^2 \rangle$	36.209	138.557	228.581
		$\langle \Delta y^2 \rangle$	36.209	138.557	228.581
	Cl–Cl (linear)	$\langle \Delta z^2 \rangle$	36.255	66.014	102.791
		$\langle \Delta x^2 \rangle$	30.275	83.669	136.290
		$\langle \Delta y^2 \rangle$	30.275	83.669	136.290
	(Cl · · · Cl) (non-linear)	$\langle \Delta z^2 \rangle$	69.962	192.254	329.625
		$\langle \Delta x^2 \rangle$	56.754	167.113	271.159
		$\langle \Delta y^2 \rangle$	74.550	353.330	586.607

TABLE 4 (contd.)

Ion	Distance	Symbol	Mean-square; amplitude quantities		
			$T = 0°K$	$T = 298°K$	$T = 500°K$
$TiBr_6^{2-}$	Ti–Br	$\langle \Delta z^2 \rangle$	23.876	49.384	78.115
		$\langle \Delta x^2 \rangle$	32.716	111.492	182.759
		$\langle \Delta y^2 \rangle$	32.716	111.492	182.759
	Br–Br (linear)	$\langle \Delta z^2 \rangle$	27.263	77.740	126.797
		$\langle \Delta x^2 \rangle$	19.170	73.867	122.112
		$\langle \Delta y^2 \rangle$	19.170	73.867	122.112
	Br–Br (non-linear)	$\langle \Delta z^2 \rangle$	86.976	222.053	357.165
		$\langle \Delta x^2 \rangle$	78.715	191.870	307.430
		$\langle \Delta y^2 \rangle$	36.634	182.348	303.354
$ZrBr_6^{2-}$	Zr–Br	$\langle \Delta z^2 \rangle$	19.575	44.877	71.928
		$\langle \Delta x^2 \rangle$	26.739	99.036	163.245
		$\langle \Delta y^2 \rangle$	26.739	99.036	163.245
	Br..Br (linear)	$\langle \Delta z^2 \rangle$	26.943	76.216	124.252
		$\langle \Delta x^2 \rangle$	18.179	66.614	109.933
		$\langle \Delta y^2 \rangle$	18.179	66.614	109.933
	Br..Br (non-linear)	$\langle \Delta z^2 \rangle$	66.440	189.907	308.753
		$\langle \Delta x^2 \rangle$	58.760	163.678	265.656
		$\langle \Delta y^2 \rangle$	34.750	164.335	273.068
$HfBr_6^{2-}$	Hf–Br	$\langle \Delta z^2 \rangle$	16.580	40.065	64.609
		$\langle \Delta x^2 \rangle$	22.424	89.396	153.667
		$\langle \Delta y^2 \rangle$	22.424	89.396	153.667
	Br..Br (linear)	$\langle \Delta z^2 \rangle$	24.902	65.021	105.473
		$\langle \Delta x^2 \rangle$	18.179	66.614	109.933
		$\langle \Delta y^2 \rangle$	18.179	66.614	109.933
	Br..Br (non-linear)	$\langle \Delta z^2 \rangle$	52.842	166.206	278.025
		$\langle \Delta x^2 \rangle$	122.482	137.608	230.786
		$\langle \Delta y^2 \rangle$	34.750	164.335	273.068

amplitudes of vibration for bonded as well as non-bonded linear distances in general increases. The quantities corresponding to non-linear non-bonded distances show an opposite behaviour. In the case of octahedral titanium chloro- and bromo-anions such variation has not been observed due to reasons stated earlier. The mean amplitude quantities increase with temperature as expected.

TABLE 5. Mean amplitude quantities in 10^{-2} XÅ for octahedral chloroanions and bromoanions.

Ion	Distance	Mean amplitude quantities		
		$T = 0°K$	$T = 298°K$	$T = 500°K$
$TiCl_6^{2-}$	Ti–Cl	5.083	6.321	7.760
	Cl..Cl (linear)	5.647	7.206	8.900
	Cl..Cl (non-linear)	9.341	12.852	16.039
$ZrCl_6^{2-}$	Zr–Cl	4.865	6.381	7.924
	Cl..Cl (linear)	6.036	8.132	10.175
	(non-linear)	9.048	14.562	18.482
$HfCl_6^{2-}$	Hf–Cl	4.538	5.973	7.423
	Cl..Cl (linear)	6.021	8.125	10.139
	Cl..Cl (non-linear)	8.364	13.866	18.156
$TiBr_6^{2-}$	Ti–Br	4.886	7.027	8.838
	Br..Br (linear)	5.221	8.817	11.260
	Br..Br (non-linear)	9.326	14.902	18.899
$ZrBr_6^{2-}$	Zr–Br	4.242	6.699	8.841
	Br..Br (linear)	5.191	8.730	11.146
	Br..Br (non-linear)	8.151	13.781	17.571
$HfBr_6^{2-}$	Hf–Br	4.072	6.330	8.038
	Br..Br (linear)	4.990	8.064	10.270
	Br..Br (non-linear)	7.269	12.896	16.674

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