Force Field Study of Some Hexahalide Anions of Transition Metals

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(Z. Naturforsch. **26 a**, 1134—1136 [1971]; received 16 March 1971)

Using the L matrix approximation method of Müller the seven independent force constants for the hexahalide anions of zirconium and hafnium metals have been evaluated employing general valence force field (GVFF). The stretching force constant increases as the oxidation number of the metal increases. The mean amplitudes of vibration have been calculated using the L matrix approximation method. The trends of mean amplitudes of vibration have also been discussed.

Introduction

The force field of the octahedral molecules and anions has been widely studied in the recent years [1–4]. The complete and unique solution of the potential function is not possible when the secular equation is of second or higher degree, particularly in the absence of the additional experimental quantities such as coriolis coupling constants, rotational distortion constants and mean amplitudes of vibration constants. In the present investigation, we have made use of the widely used L matrix approximation method introduced by Müller [5], for the solution of the f_{1u} modes of vibration for both the symmetrized force constants (F) and the symmetrized mean amplitude matrix elements (Σ).

The vibrational spectra of hexachloride and hexabromide anions of Zr and Hf metals have been studied by Bridson et al. [6]. They have performed a normal coordinate analysis using MSVFF leading to only six force constants. In this work they have used two different arbitrary assumptions. The force constants thus evaluated by them show inconsistency when compared with similar anions. Under the circumstances, the force field was restudied, leading to all the seven independent force constants showing a definite trend. The mean amplitudes of vibration were also calculated with the help of the available vibrational data given in Table 1.

The anions under study are of XY_6 type belonging to the O_h symmetry point group and distribution of the fundamentals is given by

$$\Gamma_{\text{vib.}} = a_{1g} + e_g + 2\, f_{1u} + f_{2g} + f_{2u} \, .$$

Using the character table and the selection rules [7], it is found that the three gerade representations $a_{1g}(\nu_1)$, $e_g(\nu_2)$ and $f_{2g}(\nu_5)$ are Raman active and one ungerade representation f_{1u} (ν_3 and ν_4) is infrared active while the second ungerade representation $f_{2u}(\nu_6)$ is inactive in both Raman effect and infrared. The ν_1, ν_2 and ν_3 fundamentals are attributed to stretching vibrations while the remaining ν_4, ν_5 and ν_6 pertain to angle deformations.

Table 1. Fundamental frequencies in cm^{-1}.

Anions	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6†	Ref.
$HfCl_6^{-2}$	328	269	286	147	163	116	6
$HfBr_6^{-2}$	201	157	193	112	116	82	6
$ZrCl_6^{-2}$	323	275	297	146	159	112	6
$ZrBr_6^{-2}$	198	150	226	114	116	82	6

† Frequencies are calculated by Wilson's rule ($\nu_5 = \sqrt{2}\, \nu_6$) (see J. Gaunt, Trans. Faraday Soc. **49**, 1122 [1953]).

Force Constant Evaluation

Wilson's GF matrix method [8] has been used to carry out the normal coordinate analysis. The internal coordinates were taken as the changes in internuclear distances and in the interbond angles. The symmetry coordinates used are the same as those given by Pistorius [9]. The kinetic and potential en-

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ergy matrix elements were the same as reported earlier by the authors [1].

The well known secular equation $|FG - E\lambda| = 0$, on factorization led to one dimensional equation for a_{1g}, e_g, f_{2g} and f_{2u} mode of vibration and a two dimensional equation for f_{1u} mode of vibration. For the solution of the two dimensional secular equation some mathematical constraints have been suggested [10–13]. MÜLLER [14] has shown that the L matrix approximation method ($L_{12} = 0$ or F_{22} minimum) gives satisfactory results in the case of small mass coupling ($m_X > m_Y$). Other workers [12, 13] have also shown that F_{22} minimum leads to results which proved to be quite reasonable. This was used by the present authors for the solution of the secular equation for f_{1u} mode of vibration. The calculated symmetrized force constants for f_{1u} mode and valence force constants are given in Table 2.

Results and Discussions

The evaluated force constants show a definite and regular trend. On comparing the force constants of hexahalide anions of the same metal, the stretching force constant decreases from hexachloride to hexabromide anions. This can be explained in terms of internuclear distances involved and the electronegativity of the halogen ligands. Though the internuclear distances of the anions under study have not been experimentally observed it is sure that the internuclear distances for the chlorides are smaller than that of bromides of the same metal and the electronegativity decreases as we go from chlorine to bromine.

For the hexachloride and hexabromide anions of Zr and Hf metals, the stretching force constants are lower for Zr than that for the corresponding Hf hexahalide anions as expected.

A comparison of the stretching force constants (f_r) for hexahalides of Zr and Hf, as evaluated by BRISDON et al. [6] shows that $f_r(\text{Zr}-\text{Cl}) > f_r(\text{Hf}-\text{Cl})$ and $f_r(\text{Zr}-\text{Br}) < f_r(\text{Hf}-\text{Br})$. This, to the present authors' knowledge is difficult to explain on the basis of any of the known theories in the field.

Table 3. Stretching force constants (f_r) for some hexahalide anions and molecules of O_h symmetry. [a] Present work.

Molecule or anion	f_r	Ref.	Molecule or anion	f_r	Ref.
$HfCl_6^{-2}$	1.51	a	$ZrCl_6^{-2}$	1.31	a
$TaCl_6^-$	1.96	16	$NbCl_6^-$	1.83	16
WCl_6	2.30	2			
$HfBr_6^{-2}$	1.23	a	$ZrBr_6^{-2}$	1.21	a
$TaBr_6^-$	1.54	16	$NbBr_6^-$	1.48	16

In order to study the variation of stretching force constants with the change in the number of electrons of the central metal atom, we have included the results of our previous work in Table 3. It shows that the stretching force constants have the trend

(i) $f_r(\text{Zr}-\text{X}) < f_r(\text{Nb}-\text{X})$,

(ii) $f_r(\text{Hf}-\text{X}) < f_r(\text{Ta}-\text{X}) < f_r(\text{W}-\text{X})$.

This trend indicates that these stretching force constants increase with the decrease in the negative charge i. e. with the increase in the oxidation number.

The above discussion definitely shows that the force consants evaluated by the present authors are reasonably correct.

Table 2. Symmetrized force constants for f_{1u} mode and valence force constants in mdyne $Å^{-1}$.

Anions	symmetrized force constants for mode				Valence force constants				
		f_{1u}	f_r	f'_{rr}	f_{rr}	$(f_{r\alpha} - f''_{r\alpha})$	$(f_\alpha - f'''_{\alpha\alpha})$	$(f_{\alpha\alpha} - f''_{\alpha\alpha})$	$(f'_{\alpha\alpha} - f'''_{\alpha\alpha})$
$HfCl_6^{-2}$	1.27	0.04 0.14	1.51	0.24	0.12	0.04	0.14	0.00	0.00
$HfBr_6^{-2}$	1.06	0.07 0.15	1.23	0.17	0.12	0.07	0.16	0.00	0.00
$ZrCl_6^{-2}$	1.127	0.05 0.12	1.31	0.26	0.13	0.05	0.13	0.00	0.00
$ZrBr_6^{-2}$	1.09	0.09 0.13	1.21	0.11	0.13	0.09	0.15	0.00	0.00

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Table 4. Mean amplitudes of vibration in Å.

Anions	$T = 0\,^\circ$K X−Y	 Y...Y short	 Y...Y long	$T = 298\,^\circ$K X−Y	 Y...Y short	 Y...Y long
$HfCl_6^{-2}$	0.0141	0.0227	0.0182	0.0578	0.1170	0.0748
$HfBr_6^{-2}$	0.0129	0.0182	0.0158	0.0200	0.1102	0.0807
$ZrCl_6^{-2}$	0.0151	0.0231	0.0185	0.0616	0.1210	0.0771
$ZrBr_6^{-2}$	0.0139	0.0833	0.0161	0.0659	0.1111	0.0837

Mean Amplitudes of Vibration

The mean amplitudes of vibration of the anions under investigation have been evaluated by solving the CYVIN's secular equation[15] $|G^{-1}\Sigma - \Delta E| = 0$, at 0 °K and 298 °K using the vibrational data only. The temperature dependent quantity Δ_k is related to the normal mode of vibration ν_k by the expression

$$\Delta_k = \frac{h}{8\,\pi^2\,\nu_k\,c}\coth\frac{h\,\nu_k\,c}{2\,K\,T}\,.$$

Here T is absolute temperature and K is Boltzmann constant.

The above secular equation for mean amplitudes of vibration can also be factorised into four one dimensional and a two dimensional secular equation. Though the vibrational parameters are less than the symmetrized mean square amplitude matrix elements for f_{1u} modes of vibration, the L matrix approximation method[5] can be used to calculate all the three symmetrized mean square amplitude matrix elements with only two observed fundamentals. Mean amplitudes of vibration for bonded or non-bonded atom pairs are related to symmetrized mean amplitude matrix elements through linear expressions[15]. The calculated mean amplitudes of vibration for X−Y, Y...Y short and Y...Y long distances are given in Table 4.

The evaluated mean amplitudes of vibration show a definite trend for these anions at both temperatures. They are higher for the hexachloride than that for hexabromide anions of the same metal and are lower for hafnium hexahalides than the corresponding zirconium hexahalides. These mean amplitudes of vibrations have a trend-$u(\mathrm{X-Y}) < u(\mathrm{Y\ldots Y})$ long $< u(\mathrm{Y\ldots Y})$ short and increase with the temperature. Similar conclusions were drawn by the present authors for a number of XY_6 type of molecules and anions[1, 2, 16].

Acknowledgements

The authors wish to thank Prof. A. MÜLLER, University of Dortmund, Germany, for consultation. One of us (M. L. M.) is also grateful to U. G. C. (India) for the grant of a Post-graduate research scholarship.

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