Normal Coordinate Analysis of Some Hexahalide Anions of IV Group Elements

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The normal coordinate analysis has been applied to the hexachloride and hexabromide of tin, titanium, zirconium and hafnium, using the Urey-Bradley force field (UBFF) and orbital valence force field (OVFF). It is observed that the stretching force constant increases as the oxidation number of the metal increases within isoelectronic series.

Introduction

The orbital valence force field (OVFF) has been rarely applied to XY_6 type of molecules [1, 2]. Recently, KIM et al. [2] have shown the suitability of OVFF for hexafluoride molecules but none has applied this potential model to hexahalides with the exception of hexafluorides. In the present investigation, we have applied OVFF to some hexachloride and hexabromide anions of IV group elements and have made a comparative study of the results with those obtained by using Urey-Bradley force field (UBFF).

The vibrational spectra and frequency assignments of the hexahalide anions under study were investigated by CLARK et al. [3] for Sn and Ti and by BRISDON et al. [4] for Zr and Hf. Using these vibrational data, the normal coordinate analysis of the hexahalide anions has been carried out.

Using the character table and the selection rules [5] the vibrational representation of XY_6 type of molecules or ions of O_h symmetry is

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

Among these, one nondegenerate a_{1g} vibration (ν_1), one doubly degenerate e_g vibration (ν_2) and one triply degenerate f_{2g} vibration (ν_5) are Raman active and two triply degenerate f_{1u} vibration (ν_3 and ν_4) are infrared active, while one triply degenerate f_{2u} vibration (ν_6) is inactive. The vibrations ν_1, ν_2 and ν_3 involve stretching of metal-halogen bond, while the remaining vibrations ν_4, ν_5 and ν_6 are essentially deformation vibrations.

The Urey-Bradley force field involves basically a combination of general valence force field and central forces between nonbonded atoms and is given by [2],

$$2\,V = K \sum_{i}^{6} (\Delta r_i)^2 + H\,r_0^2 \sum_{i,j}^{6} (\Delta \alpha_{ij})^2 + F \sum_{j}^{12} (\Delta q_{ij})^2 + 2\,q_0\,F' \sum_{i,j}^{12} \Delta q_{ij} + 2\,r_0\,f' \sum_{i}^{6} \Delta r_i\,. \qquad (1)$$

Here K is the bond stretching constant, H is the bending constant and (F and F') are Urey-Bradley constants whereas r_0 and q_0 are equilibrium metal-halogen and nonbonded halogen-halogen distances respectively.

HEATH and LINNETT [2] improved the UB potential model by introducing a new idea — the angular force constant can not have a simple meaning even for molecules consisting of more than three atoms because one angle cannot change without bringing about a change in the other angles. This model includes stretching constant, K, Urey-Bradley forces (F and F') and an angular deformation force constant D, expressed in terms of the angle between actual positions of ligand atoms and preferred position where the orbital overlap is maximum and is given by [2]

$$2\,V = K \sum_{i}^{6} (\Delta \gamma_i)^2 + D\,r_0^2 \sum_{i}^{6} (\Delta \beta_i)^2 + F \sum_{i,j}^{12} (\Delta q_{ij})^2 + 2\,q_0\,F' \sum_{i,j} (\Delta q_{ij}) + 2\,r_0\,f' \sum_{i} \Delta r_i \qquad (2)$$

where $\Delta\beta_i$ is the angle between the line from the central metal atom to the i-th halogen ligand and the axis of the i-th orbital.

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Table 1. Kinetic energy and potential energy matrix elements.

Species	Kinetic energy	Potential energy	
		OVFF	UBFF
a_{1g}	$G_{11} = \mu_y$	$F_{11} = K + 4F$	$K + 4F$
e_g	$G_{22} = \mu_y$	$F_{22} = K + F + 3F'$	$K + F + 3F'$
f_{1u}	$G_{33} = 2\mu_x + \mu_y$	$F_{33} = K + 2F + 2F'$	$K + 2F + 2F'$
	$G_{34} = -4\,4_x$	$F_{34} = F + F'$	$F + F'$
	$G_{44} = 8\mu_x + 2\mu_y$	$F_{44} = \frac{1}{2}(D + F - 3F')$	$H + \frac{1}{2}(F - 3F')$
f_{2g}	$G_{55} = 4\mu_y$	$F_{55} = \frac{1}{4}(D + 2F - 2F')$	$H + \frac{1}{2}(F - F')$
f_{2u}	$G_{66} = 2\mu_y$	$F_{66} = \frac{1}{2}(D + F + F')$	$H + \frac{1}{2}(F + F')$

Using the similarity transformations after expanding the potential energy expressions (1) and (2), the symmetrized F-matrix for both the potential models are obtained and are given in Table 1.

Force Constant Evaluation

Wilson's GF matrix method[6] has been used to carry out the normal coordinate analysis. The symmetry coordinates are the same as that of PISTORIUS[7] and the kinetic energy matrix elements are taken from our previous work[8].

The number of force constants to be evaluated is less than the observed fundamentals in either of the force fields. Therefore, the study of the unique potential function of the anions under investigation has been restricted in view of the lack of the useful additional experimental data like coriolis coupling constants or mean amplitudes of vibration for the best fit of the force constants. However, a weighted least square method introduced by MANN et al.[9] was used for fitting the force constants. The initial set of force constants are calculated from one dimensional vibrational species for both the force fields. The elements of the Jacobian matrix were constructed by giving an infinitesimal increment ∂f_m (0.01 mdyne $Å^{-1}$) in one of the force constants at a time from the relation[10]

$$J_{n,m} = -\partial \nu_n / \partial f_m \tag{3}$$

where $\partial \nu_n$ is the corresponding difference between the calculated and observed frequencies. The error vector V, can be constructed from the difference in the observed and the calculated fundamentals. Following MANN et al.[9] the refinement in the force constant Δf_m is given by

$$\Delta f_m = (J' W J)^{-1} J' W V \tag{4}$$

and is added to the corresponding initial set of force constants, to give the result

$$f_m = \Delta f_m + f_{m,\,\text{initial}}\,. \tag{5}$$

These improved set of force constants were used to construct the new Jacobian for the next iteration. This procedure is repeated till all the force constants converge to a definite value i. e. the next contribution to the force constants is negligible to effect a change in the calculated frequencies. In Eq. (4), W is the diagonal weight matrix whose elements are the reciprocals of the square of the observed fundamentals. The calculations were carried out on a computer IBM 1620. The observed fundamentals and the calculated force constants and fundamental frequencies using both the force fields are given in Table 2.

Results and Discussions

Using both force fields it is found that the calculated vibrational frequencies are very close to those observed for Sn, Zr and Hf hexahalide anions under investigation but the fitting is not as good for those of $TiCl_6^{-2}$.

The evaluated force constants using both the force fields, show a definite trend. The stretching force constants (K) are higher for hexachloride anions as compared to the corresponding hexabromide

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[10] The Jacobian is taken negative to make the final expression (4) for the refinement in the force constants positive. Unfortunately MANN et al. have some how omitted a minus sign.

Table 2. Observed and calculated frequencies in cm^{-1} and force constants in mdyne $Å^{-1}$.

Ions		ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	K	H or D	F	F'	Ref.
$SnCl_6^{-2}$	Obs.	309	232	291	163	159	112†					3
	UBFF	302	231	298	159	166	109	0.93	0.01	0.24	− 0.02	
	OVFF	300	231	298	162	162	112	0.94	0.04	0.23	− 0.02	
$SnBr_6^{-2}$	Obs.	182	135	203	111	102	71†					3
	UBFF	181	136	202	110	103	70	0.69	− 0.02	0.21	− 0.01	
	OVFF	181	136	202	111	101	71	0.69	0.03	0.21	− 0.01	
$TiCl_6^{-2}$	Obs.	320	271	316	183	173	123†					3
	UBFF	324	236	346	178	177	122	0.85	− 0.01	0.33	− 0.01	
	OVFF	336	246	332	183	166	124	0.68	− 0.16	0.42	0.06	
$TiBr_6^{-2}$	Obs.	192	141	244	119	115	82†					3/4
	UBFF	192	141	244	119	115	84	0.61	0.02	0.28	0.01	
	OVFF	192	143	241	120	114	93	0.60	0.09	0.29	0.03	
$ZrCl_6^{-2}$	Obs.	323	275	297	146	159	112†					4
	UBFF	318	248	325	144	161	112	1.02	0.00	0.27	0.00	
	OVFF	316	248	325	144	160	113	1.03	0.00	0.26	0.00	
$ZrBr_6^{-2}$	Obs.	198	150	226	114	116	82†					4
	UBFF	199	150	226	114	115	83	0.76	0.02	0.27	0.01	
	OVFF	203	149	224	114	114	82	0.74	0.02	0.30	0.00	
$HfCl_6^{-2}$	Obs.	328	264	286	147	163	116†					4
	UBFF	316	254	309	145	167	114	1.14	0.02	0.24	− 0.01	
	OVFF	318	253	308	146	164	115	1.12	0.04	0.25	− 0.01	
$HfBr_6^{-2}$	Obs.	201	157	193	112	116	82†					4
	UBFF	200	150	202	111	117	83	0.80	0.03	0.27	− 0.00	
	O⊿FF	202	149	201	112	115	82	0.78	0.04	0.29	− 0.01	

† Frequencies are calculated using the Wilson's rule ($\nu_5 = \sqrt{2}\, \nu_6$).

anions of the same metal. This is expected because of the lower internuclear distance of hexachloride, than the hexabromide anions of the same metal and higher electronegativity for chlorine than bromine.

The anions under investigation can also be studied according to the electronic configuration of the central metal atom (see also [11]). The calculated stretching force constants for hexahalide of Nb, Mo, Ta and W metals are included in Table 3. On comparing the stretching force constants of Zr, Nb and Mo hexahalides on one hand and of Hf, Ta and W hexahalides on the other, it is concluded that tive charge decreases. This trend is observed by tion number of the metal increases, i. e. as the negative charge decreases. This trend is also observed by other workers [12–14] also. A similar trend has been found by the present authors using the general valence force field for these hexahalide anions [15].

Table 3. The stretching force constants K, of some hexahalide anions and molecules of O_h symmetry. [a] This work; [b] authors' unpublished work.

Molecules or anions	UBFF	OVFF	Ref.	Molecules or anions	UBFF	OVFF	Ref.
$ZrCl_6^{-2}$	1.02	1.03	a	$HfCl_6^{-2}$	1.14	1.12	a
$NbCl_6^-$	1.28	1.31	b	$TaCl_6^-$	1.44	1.45	b
$MoCl_6$	1.43	—	12	WCl_6	1.45	1.63	b
$ZrBr_6^{-2}$	0.76	0.74	a	$HfBr_6^{-2}$	0.80	0.78	a
$NbBr_6^-$	0.98	0.97	b	$TaBr_6^-$	1.03	1.05	b

In view of the small differences in the magnitudes of the nonbonded repulsion force constants F, for the anions studied, nothing definite can be said about them.

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