BOND PROPERTIES OF ANIONIC MIXED HALOGENO-COMPLEXES $InX_{3}Y^{-}$ (X \neq Y = Cl, Br, I)

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The normal coordinate analysis has been performed for the anionic mixed halogeno-complexes InX_3Y^- ($X \neq Y = Cl$, Br, I). The trends among the force constants are discussed and the assignments of the observed fundamental frequencies are examined thoroughly. It has been found that the present analysis provides reliable data to introduce a light into the bond properties of InX_3Y^- ions. In addition to this the mean amplitudes of vibrations, bond order and bond polarizability derivatives have been studied for the systems under investigation and a comparison of bond parameters among the halides of indium are made.

Drake and coworkers¹ investigated the chemical properties of anionic mixed halogeno-complexes InX_3Y^- (X \neq Y = Cl, Br, I) obtained through the oxidation of indium (II) complexes $In_2X_6^{2-}$ (X = Cl, Br, I) with halogen (Y₂; Y = Cl, Br, I). Further they have also studied the far-infrared and Raman spectra of the anionic complexes and supported vibrational assignments on the bases of force constant calculations employing modified valence force field model assuming C_{3y} point group for the $InX_{\lambda}Y^{-}$ species. In normal coordinate analysis they have utilized a least squares fitting technique to evaluate the force constants, therefore, their vibrational assignments need further checking. Besides the above procedure another way to evaluate the reliable set of force constants for the complex systems with the help of the observed fundamentals alone is to rely on the approximation methods, which are popular in recent years. In view of the above discussion it is the purpose of the present investigation to study the trend among the force constants, relative strength of the chemical bonds in the anionic mixed halogeno-complexes InX_3Y^- and related species and confirmation of the vibrational assignments by performing the fresh normal coordinate analysis in the framework of reasonable approximation. Further, it is intended to compute the vibrational amplitudes, bond order and bond polarizability derivative of the InX_3Y^- species which constitute some of the important bond parameters. Such study helps us in understanding the bond properties in complexes under current investigation and provides data for the relative comparison to be made with other complexes.

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Method of Computation

The anion of the type InX_3Y^- possessing C_{3v} point group gives rise to six fundamental frequencies which are distributed as

$$\Gamma_{\rm vib} = 3(A_1) + 3(E)$$

The three A_1 species contain two stretching and one deformation modes while the three *E* species involve one stretching and two deformation modes. The normal coordinate analysis has been performed in Wilson's **FG** matrix framework² using general valence force field (*GVFF*) model. The three-dimensional secular equation occurring in each species has been solved by the extended L-F approximation method³.

For computing the vibrational amplitudes Cyvín's secular determinant⁴ $|\Sigma \mathbf{G}^{-1} - \Delta E| = 0$, where the symbols have their usual meanings⁴, has been used. It has been solved by the method of Müller and coworkers⁵.

The bond polarizability derivative has been computed following Lippincott and Nagarajan⁶ using the relation

$$ar{lpha}'=rac{1}{3}inom{n}{2}rac{\sigma}{a_0}A_{12}R^3$$
 ,

where the entering quantities n/2, σ , a_0 , A_{12} and R are: bond order, Pauling's covalent character⁷, Bohr's radius, geometrical mean of the delta potential strengths⁸ and interatomic distance, respectively.

In the above relation the required bond order has been computed following Verma and Pandey⁹.

RESULTS AND DISCUSSION

The vibrational wavenumbers for InX_3Y^- species, required in the present study are collected in Table I. The structural parameters for the pyramidal anionic system used here are¹⁰: In-Cl = 240 pm, In-Br = 260 pm, In-I = 280 pm and $X-In-X = X-In-Y = 109.5^{\circ}$.

The GVFF model for InX_3Y^- species includes the bond stretching force constants

 $f_r(\text{In-X})$ and $f_R(\text{In-Y})$, deformation force constants $f_{\alpha}(X-\text{In-X})$ and $f_{\beta}(X-\text{In-Y})$ and the following interaction force constants: f_{rr} and f_{Rr} representing the stretch interaction, $f_{\alpha\alpha}$ and $f_{\beta\beta}$ representing angle bending interactions and $f_{R\alpha}$, $f_{R\beta}$, $f_{r\beta}$ and $f_{r'\beta}$ involving interactions between an angle and one of the bonds. The force

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constants computed under *GVFF* model are collected in Table II. Among a set of force constants, the stretching force constants deserve special attention on account of their dependence on bond properties such as bond strength, bond length, oxidation number, bond order, polarity, covalency, ligancy, dissociation energy and effective nuclear charges of the atoms involved in bonding.

It is evident from Table II that the stretching force constant in InX_3Y^- species varies in order $f_{In-Cl} > f_{In-Br} > f_{In-l}$. This result is consistent with the trend in the

Ions	$v_1(A_1)$	$v_2(A_1)$	$v_3(A_1)$	$v_4(E)$	$v_5(E)$	$v_6(E)$
InCl ₃ Br ⁻	320	228	103	330	113	80
	(320)	(228)	(100)	(330)	(114)	(78)
InCl ₃ I ⁻	315	170	100	330	100	65
	(315)	(171)	(97)	(330)	(100)	(64)
InBr ₃ Cl [−]	197	325	85	225	70	104
	(192)	(326)	(87)	(226)	(77)	(100)
InBr ₃ I ⁻	191	168	60	226	76	50
	(195)	(163)	(62)	(226)	(74)	(51)
InI ₃ Cl ⁻	147	312	65	186	45	65
	(143)	(315)	(69)	(187)	(45)	(65)
Inf ₃ Br ⁻	139	214	61	183	45	64
	(139)	(212)	(61)	(184)	(45)	(65)

^a Computed wavenumbers are in parentheses.

TABLE II

Force constants (in 10	2 Nm ⁻¹)	of InX ₃ Y ⁻	anions
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Ions	$f_{\mathbf{r}}$	f _{rr}	f _R	f _{Rr}	f_{α}	f _β	$f_{R\alpha} - f_{R\beta}$	$f_{r\beta} - f_{r\beta}$	$f_{\alpha\alpha} \approx f_{\beta\beta}$
InCl ₃ Br ⁻	1.747	0.124	1.527	0.092	0.086	0.0614	0.044	-0.032	0.008
InCl ₃ I ⁻	1.746	0.094	1.158	0.077	0.077	0.020	-0.048	-0.024	0.009
InBr ₃ Cl	1.371	0.105	1.727	0.088	0.083	0.091	-0.028	-0.047	0.001
InBr ₃ I ⁻	1.349	0.076	1.104	0.115	0.069	0.038	-0.032	-0.047	0.006
InI ₃ Cl ⁻	1.158	0.083	1.614	0.110	0.062	0.057	-0.033	-0.032	0.019
InI ₃ Br ⁻	1.100	0.021	1.351	0.111	0.054	0.067	-0.034	-0.031	0.002

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corresponding bond lengths. Therefore, the relative strength of the chemical bond is following also the same trend. The interaction force constant f_{rr} in general shows the decreasing tendency with growing mass of the halogen atoms X or with decreasing electronegativity of these atoms. The force constant f_{α} also exhibits the above trend which further lends support to our finding about the relative stability of the chemical bond. It is noted that in general the interaction force constant f_{R} is approximately equal for the same In-X and In-Y pair of bonds occurring in different species. The angle bending force constant f_{β} in general decreases with the increase of mass of the Y halogen atom. An inspection of the magnitude of the remaining interaction force constants reveals that the force constant $(f_{R\alpha} - f_{R\beta})$ in general increases slightly with the increase of the mass of the Y atom keeping the atom X same in the InX₃Y⁻ species, while the force constant $(f_{r\beta} - f_{r'\beta})$ shows slightly decreasing tendency. The contribution of bend-bend interaction is negligible.

TABLE III Potential energy distribution (*PED*) in A_1 species of InX_3Y^- anions

Anions	v _i	$f_{\mathbf{r}}$	$f_{\rm rr}$	$f_{\mathbf{R}}$	f _{Rr}	f_{α}	f_{β}	$f_{\mathbf{R}\alpha} - f_{\mathbf{R}\beta}$
InCl ₂ Br ⁻	V ₁	0.883	0.125	0.015	-0.046			
5	V 2			1.014		0.027	0.019	-0.069
	v_3^2			0.011		0.570	0.400	0.019
InCl ₃ I	v ₁	0.908	0.098	0.018	0.025			
·	v_2			1.070		0.073	0.047	-0.154
	v_3			0.022		0.571	0.371	-0.036
InBr ₃ Cl ⁻	٧ ₁	0.896	0.136	0.065	-0.013			
,	v_2			0.979		0.007	0.002	0.000
	<i>v</i> ₃			0.030		0.721	0.230	0.018
InBr ₃ I	V ₁	0.989	0.111	0.002	-0.024			
5	V2			0.977		0.038	0.021	-0.088
	v_3^2			0.051		0.582	0.320	0.045
InI ₃ Cl ⁻	V 1	0.946	0.125	0.000	- 0.006			
5	$\tilde{\nu}_{2}$			0.969		0.003	0.003	0.009
	v_3^2			0-040		0.495	0.447	0.012
InI ₃ Br ⁻	V ₁	0.856	0.122	0.023	-0.047			
-	v_2			0.919		0.012	0.008	0.044
	v ₃			0.045		0.610	0.312	0.033

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The evaluated set of force constants reproduce the observed wave numbers within reasonable limit as shown in Table II. In order to examine the vibrational assignments the potential energy distribution coefficients have been determined following the standard procedure¹¹ and are listed in Tables III and IV. It is evident from the values of *PED* that v_1 , v_2 and v_4 are pure stretching modes since these vibrations involve very negligible contribution from other force constants. In contrast to this Drake and coworkers¹ have shown considerable mixing between v_1 and v_2 vibrations in case of InBr₃I⁻ and InI₃Br⁻ on the basis of their normal coordinate analysis using least square technique. Regarding the deformation modes v_3 , v_5 and v_6 which represent symmetric bending, scissoring and wagging vibrations respectively, our results favour the deformation characteristics of these vibrations and show considerable contribution of wagging mode in symmetric bending vibration v_3 .

Anions	v _i	f _r	f _{rr}	f _a	f_{β}	$f_{\mathbf{r}\boldsymbol{\beta}} - f_{\mathbf{r}'\boldsymbol{\beta}}$	faa	f _{ββ}
InCl ₃ Br ⁻	V _A	1.086	-0.077			0.0164		
5	V 5			0.989	0.010		-0.009	0.000
	v ₆			0.110	0.889		-0.09	-0.004
InCl ₃ I ⁻	V _A	1.061	0.057			-0.012		
5	v 5			0.994	0.006		-0.012	-0.003
	v ₆			0.155	0.985		-0.091	-0.087
InBr ₂ Cl ⁻	V.	1.107	0.086			-0.053		
	24 V 5			1.009	0.001		0.011	0.000
	v_6			0.119	0.889		0.000	-0.008
InBr ₂ I ⁻	V.	1.058	0.061			-0.052		
.,	4 V 5			1.080	0.017		-0.099	-0.002
	v ₆			0.090	1.027		-0.008	-0.170
InL ₁ C ¹	¥.a	1.106	0.079			-0.052		
5	4 V 5			1.180	0.009		-0.430	-0.005
	v ₆			0.087	1.340		0.032	-0.402
InL Br	¥ a	0.981	-0.050			-0.048		
3	+ 1'5			1.138	0.089		-0.148	0.000
	v ₆			0.068	1.050			-0.110

TABLE IV

Potential energy distribution in E species of InX_3Y^- anions

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TABLE V

Bonds	InX ₃	$InX_{3}Y^{-}$	InX_4	$\ln X_5^2$	InX_6^3
f In-Cl	2.491	1.710	1.770	1.317	1.183
f In-Br	1.945	1.370	1.440		
f In-I	1.105	1.110	1.060		
u In–Cl	0.046	0.054	0.053	0.061	0.067
u In-Br	0.020	0.029	0.056		
u In–I	0.103	0.071	0.063		
n In–Cl		0.624			
n In-Br		0.695			
n In–I		0.669			
ā′ In−Cl		2.113			
α′ In−Br		3.045			
α̃' In–I		4.033			

Force constants $f(10^2 \text{ Nm}^{-1})$, vibrational amplitudes $u(10^{-10} \text{ m})$, bond order n and bond polarizability derivatives $\overline{\alpha}'(10^{-22} \text{ m}^2)$ of halides of indium

It is interesting to investigate the trend in the stretching force constants and corresponding vibrational amplitudes among the halides of indium(III). For this purpose the computed results along with the reported values are summarized in Table V. A survey of the results shows that there is a decreasing tendency of the stretching force constants as one moves from neutral to ionic species. The corresponding vibrational amplitudes show consistent trend and are in line with our expectation. The bond order and the bond polarizability derivative calculated for individual bond, are also included in this table. As the value of the bond order in halide complexes is generally less than one, therefore the values presented here are reasonable. The bond polarizability derivatives will be helpful in interpreting the Raman intensity data whenever available.

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