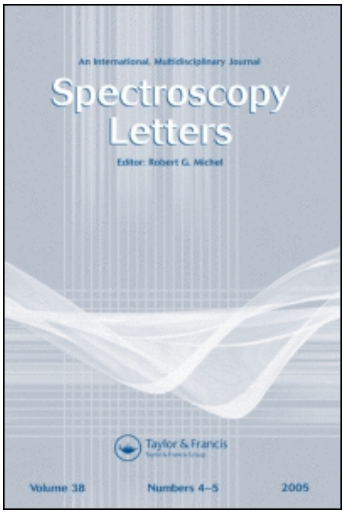

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Force Constants, Coriolis Coupling Constants, and Mean Amplitudes of Vibration of $InCl_6^{3-}$

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FORCE CONSTANTS, CORIOLIS COUPLING CONSTANTS AND MEAN AMPLITUDES OF VIBRATION OF $InCl_6^{3-}$

by

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ABSTRACT

The general quadratic force constants, coriolis coupling constants and mean amplitudes of vibration have been evaluated for $InCl_6^{3-}$ using recent vibrational data. The results are employed to study the trend of variation in the isoelectronic sequences e.g. $InCl_6^{3-}$, $SnCl_6^{2-}$ and $SbCl_6^{-}$.

In the present communication we report the force constants, coriolis coupling constants and mean amplitudes of vibration for $InCl_6^{3-}$ which have not been reported so far. The results are used to study the trend of variation of the molecular parameters in the isoelectronic sequence e.g. $InCl_6^{3-}$, $SnCl_6^{2-}$ and $SbCl_6^{-}$. The fundamental frequencies of $InCl_6^{3-}$, employed in this computation, have been reported on the basis of octahedral symmetry, from infrared and Raman Spectral Studies[1].

Method of Computation:

Wilson FG matrix method[2] has been used to calculate the force constants employing general quadratic potential function. The expressions for F and G matrices are taken from Literature[3]. Müller's method [4,5,6] has been followed for the solution of 2 x 2 secular determinant of species f_{1v}. These constants are, in turn, used to compute the coriolis coupling constants on the lines of Cyvin[7]. The results of these computations together with the fundamental frequencies are listed in table 1. in usual notations.

TABLE I

VIBRATIONAL WAVE NUMBERS (IN cm^{-1}) FORCE CONSTANTS(mdyne/Å) AND CORIOLIS COUPLING CONSTANTS OF $InCl_6^{3-}$

Symbol	$InCl_6^{3-}$	GQFF	$InCl_6^{3-}$	for $InCl_6^{3-}$
ν_1	290	f_r	1.1834	ζ_{13} =0.3818
ν_2	250	f_{rr}	0.0752	ζ_{34} =0.1182
ν_3	248	$f_{rr'}$	0.2723	
ν_4	184	$f_{r\alpha} - f_{r\alpha}''$	0.0765	
ν_5	185	$f_\alpha - f_{r\alpha}''$ '	0.1896	
ν_6	130.8	$f_{\alpha\alpha} - f_{\alpha\alpha}''$	0.00545	
		$f_{\alpha\alpha'} - f_{\alpha\alpha}''$ '	0.00543	

The mean amplitudes of vibration have been computed following Cyvin's method[7] and L matrix approximation method [4,5,6] by Müller. The required expressions for these computations are taken from Cyvin's book[7]. The mean amplitudes of vibration are calculated at temperatures ; T=0°K, T=298.16°K and T=500°K. These are summarized in table 2.

T A B L E 2

VIBRATIONAL MEAN AMPLITUDES (in Å) OF $InCl_6^{3-}$

Distance	Temperature	Mean Amplitude Quantities
In-Cl	T=0°K	0.0496
	T=298.16°K	0.0672
	T=500°K	0.0840
Cl..Cl Linear	T=0°K	0.0602
	T=298.16°K	0.0807
	T=500°K	0.1006
Cl..Cl Non-linear	T=0°K	0.0692
	T=298.16°K	0.1067
	T=500°K	0.1351

Results and Discussions

In order to discuss the trend of variation of force constants and mean amplitudes in the isoelectronic series $InCl_6^{3-}$, $SnCl_6^{2-}$ and $SbCl_6^{-}$, the important values are collected in table 3. It is seen from the table 3, that the stretching force constant, f_r, increases with the decrease of charge and increase of oxidation state. The bond-bond interaction constant, $f_{rr'}$, also follows the same pattern. From

T A B L E 3

COMPARISION OF FORCE CONSTANT (in mdyne/Å) AND MEAN AMPLITUDES OF VIBRATION AT ROOM TEMPERATURE (in Å) IN ISOELECTRONIC SEQUENCE

Symbols	$InCl_6^{3-}$	$SnCl_6^{2-}$	$SbCl_6^{-}$
f_r	1.1834	1.8173	2.2552
f_{rr}	0.0752	0.1895	0.1038
$f_{rr'}$	0.2724	0.4336	0.5142
$f_{\alpha} - f_{\alpha\alpha''}$	0.1896	0.1619	0.1929
$u(x-y)$	0.0672	0.0655	0.0539
$u(y..y)$ linear	0.0807	0.0855	0.0728
$u(y..y)$ Non-linear	0.1067	0.1249	0.1164

this type of variation, it is concluded that the strength of the chemical bond is in the order In-Cl< Sn-Cl<Sb-Cl, It is important to note that in this series $f_{rr'} > f_{rr}$ The force constants f_{rr} and f_{α} , in general show increasing tendency with the decrease of charge with slight discrepancy for $SnCl_6^{2-}$. This may be due to the fact that in case of $InCl_6^{3-}$ and $SbCl_6^{-}$, $f_{\alpha} > f_{rr}$, while for $InCl_6^{3-}$, $SnCl_6^{2-}$ it is opposite. On comparision of the mean amplitudes, for bonded distance, it is found that these decrease with the decrease of charge and increase of oxidation state. This behaviour is opposite to that of force constants. It is also noted that mean amplitude corresponding to non-linear distance is greater than the linear distance and it is approximately the same for this series of isoelectronic sequence.

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