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

A. K. Dublish^a; D. K. Sharma^b

^a Department of Physics, Meerut University, Meerut ^b Department of Physics, Meerut College, Meerut

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

by

A.K.Dublish, Department of Physics, Meerut University, Meerut.

and

D.K.Sharma, Department of Physics, Meerut College, Meerut.

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 Studies¹.

Method of Computation:

Wilson FG matrix method² has been used to calculate the force constants employing general quadratic potential function. The expressions for F and G matrices are taken from Literature³. Müller's method^(4,5,6) has been followed for the solution of 2×2 secular determinant of species f_{10} . These constants are, in turn, used to compute the coriolis coupling constants on the lines of Cyvin⁷. The results of these computations together with the fundamental frequencies are listed in table 1. in usual notations.

T A B L E I

VIBRATIONAL WAVE NUMBERS (IN cm^{-1}) FORCE CONSTANTS (mdyne/ \AA^0)
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	$\xi_3 = 0.3818$
ν_2	250	f_{rr}	0.0752	$\xi_4 = 0.1182$
ν_3	248	f_{rr}'	0.2723	
ν_4	184	$f_{rc} - f_{rc}''$	0.0765	
ν_5	186	$f_{rc} - f_{rc}'''$	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 method⁷ and L matrix approximation method (4, 5, 6) by Müller. The required expressions for these computations are taken from Cyvin's book⁷. 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 \AA) 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^{2-8} 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

TABLE 3

COMPARISON OF FORCE CONSTANT (in mdyne/ \AA) AND MEAN AMPLITUDES OF VIBRATION AT ROOM TEMPERATURE (in \AA) 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
$f_\infty - f_{\infty C''}$	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 $\text{In-Cl} < \text{Sn-Cl} < \text{Sb-Cl}$,
 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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