

INTRA-MOLECULAR FORCE FIELDS AND IONIC CONSTANTS OF SOME OCTAHEDRAL XY_6 SYSTEMS

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The general valence force field has been applied to some hexahalide anions of germanium, arsenic, and antimony using molecular kinetic constants and Wilson's FG Matrix method. The compliance constants, vibrational mean amplitudes, shrinkage constants, Coriolis coupling constants and rotational distortion constants are reported here for these ions for the first time. The ionic character of the bonds is briefly discussed. It is also shown that kinetic constant method leads to acceptable sets of characteristic constants for these ions.

Keywords : Molecular Constants; Molecular Dynamics; Force Fields for XY_6 Systems; Vibrational Analysis

INTRODUCTION

THE general quadratic valence force field is applied in the present investigation to evaluate all the seven independent potential constants of germanium, arsenic and antimony hexahalide of anions using ionic kinetic constants. The kinetic constants are nothing but kinetic energy coefficients associated with molecular vibrations. The kinetic constants of molecules play an important role in the study of vibrational analysis of polyatomic molecules. They have been evaluated and utilised advantageously in different cases (Mohan, 1977 *a, b, c*, 1978, 1980) to obtain acceptable sets of potential constants in polyatomic molecules in a simple manner. In addition to potential constants, other ionic constants such as compliance constants (Decius, 1963), mean amplitudes of vibration and shrinkage effects at 298.16°K (Cyvin, 1968) coriolis coupling constants (Meal & Polo, 1956) and rotational distortion constants (Cyvin *et al.*, 1968) are evaluated in the present investigation and reported here for the first time. The knowledge of these constants is used to understand the structure and nature of these ions.

METHODS

The symmetry co-ordinates, F-Matrix, K-Matrix and the methods to solve the secular equations used in the present investigation are taken from our earlier paper (Mohan, 1977 *a, b, c*).

The mean square amplitude matrix elements may be obtained using the relation (Cyvin, 1968)

$$\Sigma = L \Delta L^1$$

and therefrom the mean amplitudes of vibration for both bonded and nonbonded distances may be calculated.

The Coriolis matrix elements C_{ij}^α ($\alpha = x, y, z$) may be obtained by the vector method of Meal and Polo (1956) and the Zeta matrix elements may be evaluated from the relation

$$\zeta^\alpha = L^{-1} C^\alpha (L^{-1})^1 \text{ where } L \text{ is the}$$

normal coordinate transformation matrix. Cyvin *et al.* (1968) have reformulated the theory of centrifugal distortion by introducing certain new elements $T_{\alpha\beta,s}$ instead of the partial derivatives of the inertia tensor components $J_{\alpha\beta,s}$ of Kivelson and Wilson (1952, 1953). The quantities $t_{\alpha\beta\gamma\delta}$ are easily obtained using Cyvin's method.

RESULTS AND DISCUSSION

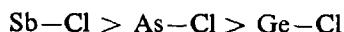
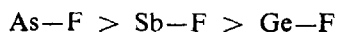
The structural parameters and the fundamental vibrational frequencies used in the present investigation are taken from Sutton (1958), Begun and Rutenberg (1967), Beattie (1968) and Qureshi (1971). The evaluated kinetic constants of these cases are reported in Table I. The stretch-stretch interaction kinetic constants k_{dd} is zero for octahedral XY_6 ions. The angle-angle interaction kinetic constants $k_{\alpha\alpha}$ and $k'_{\alpha\alpha}$ are

TABLE I
Kinetic constants ($10^{-23}g$)

S No.	Ion	k_d	k'_{dd}	k_α	$-k_{\alpha\alpha}$	$k'_{\alpha\alpha}$	$k_{d\alpha}$
1	GeF_6^{2-}	2.8355	0.3192	0.8261	0.0792	0.1972	0.1598
2	$GeCl_6^{2-}$	5.0907	0.7151	1.4567	0.1786	0.3629	0.3578
3	AsF_6^{2-}	2.8374	0.3172	0.8272	0.0790	0.1972	0.1586
4	$AsCl_6^{2-}$	5.0932	0.7130	1.4581	0.1782	0.3629	0.3565
5	SbF_6^-	2.8991	0.2550	0.8581	0.0631	0.1972	0.1279
6	$SbCl_6^-$	5.1971	0.6141	1.5077	0.1536	0.3729	0.3070

negative in all these ions. For a given Y atom, the kinetic constants k_d and k_α increase in value while the interaction kinetic constants k'_{da} , $k_{d\alpha}$ and $|k_{\alpha\alpha}|$ decrease with the increase in mass of the central atom. The interaction kinetic constant $k'_{\alpha\alpha}$ is unchanged as it depends only on the mass of the Y atom.

The GQVFF has seven independent force constants. All the potential constants evaluated in the present work are listed in Table II. As expected, the angle-angle interaction potential constant $f'_{\alpha\alpha}$ is negative for all these ions studied here. The force constants are the convenient measure of the strength of a chemical bond and it is interesting to study the variations of the potential constants among the hexafluorides, and hexachlorides. It may be noticed that the strength of the chemical bond is in the order



in hexahalides of germanium, arsenic and antimony. Further, it may be noticed that decrease of electro-negativity of halogen atom decreases, the value of major potential constants, viz., stretching potential constant f_d and bending potential constant f_α . It is pleasing to note that the angle-angle interaction constant $k'_{\alpha\alpha}$ and the corresponding potential constant $f'_{\alpha\alpha}$ have the same sign. These observations clearly indicate that the ionic character of the bond is an important factor in determining the potential constants.

The compliance constant for the ions under consideration are given in Table III. These constants are invariant to the choice of co-ordinates defining the force field and they may be used as a measure of the bond strengths and interactions instead of force constants which are pointed out by Decius (1963) and Jones (1971). From Table III, it may be seen that the compliance constants exhibit trends opposite to that of the force constants.

TABLE II
Force constants (10^5 dynes/cm)

S. No.	Ion	f_d	f_{dd}	$-f'_{dd}$	$+f_\alpha$	$-f_{\alpha\alpha}$	$-f'_{\alpha\alpha}$	$f_{d\alpha}$
1	GeF_6^{2-}	2.9961	0.3121	0.1112	0.2645	0.0145	0.0781	0.0729
2	GeCl_6^{2-}	1.2541	0.1752	0.0126	0.1602	0.0042	0.0506	0.0578
3	AsF_6^{2-}	4.0681	0.2651	0.2281	0.3186	0.0112	0.0981	0.0822
4	AsCl_6^{2-}	1.6729	0.1035	0.2458	0.1687	0.0055	0.0528	0.0614
5	SbF_6^{2-}	3.9521	0.1511	0.0356	0.2367	0.0271	0.0605	0.0552
6	SbCl_6^{2-}	1.8133	0.0900	0.1110	0.1261	0.0046	0.0390	0.0353

TABLE III
Compliance constants (A/m dynes)

S. No.	Ion	c_d	$-c_{dd}$	$-c'_{dd}$	c_α	$-c_{\alpha\alpha}$	$c'_{\alpha\alpha}$	$c_{d\alpha}$
1	GeF_6^{2-}	0.3582	0.0289	0.0181	2.2160	0.0853	0.7962	0.0635
2	GeCl_6^{2-}	0.9391	0.0971	0.0433	3.7631	-0.0241	1.2381	0.2390
3	AsF_6^{2-}	0.2571	0.0131	0.0187	1.8152	0.0462	0.6355	0.0462
4	AsCl_6^{2-}	0.6885	0.0251	0.1581	3.5596	0.0022	1.1896	0.2042
5	SbF_6^-	0.2604	0.0149	0.0021	1.6475	0.2391	1.0336	0.0311
6	SbCl_6^-	0.5847	0.0144	0.0442	5.1307	0.1406	1.8047	0.1251

The vibrational mean amplitudes for both the bonded and the non-bonded distances and shrinkage effects at 298.16 K are reported in Table IV. The vibrational mean amplitudes evaluated in the present investigation are in the expected range. It may be noticed from Table IV that the value of $l_{Y\dots Y}$ short is greater than that of $l_{(Y\dots Y)}$ long, which in turn is greater than the bonded X—Y distance in all the cases studied here. In a similar manner δ_d is found to be greater than δ_p in all these ions. Further the variation in mean amplitudes of vibration for bonded distances is opposite to that of the corresponding stretching force constants. These results are useful in the interpretation of electron diffraction data of these ions.

TABLE IV
Mean amplitudes and shrinkage constants (10^{-2}A) at 298.16 K

S. No.	Ion	$l(x-y)$	$l_{(Y\dots Y)}$ short	$l_{(Y\dots Y)}$ long	δ_p	δ_d
1	GeF_6^{2-}	4.7725	8.2057	6.4309	0.0696	0.3888
2	GeCl_6^{2-}	6.6492	10.0042	9.0202	0.0959	0.4739
3	AsF_6^{2-}	4.2811	8.2151	5.6769	0.07032	0.2897
4	AsCl_6^{2-}	5.8132	9.5546	7.1493	data not	available
5	SbF_6^-	4.2320	8.6392	5.8209	0.0569	0.3951
6	SbCl_6^-	5.3426	10.7432	7.1386	0.1067	0.5221

The first order Coriolis coupling constants ζ_{44} , ζ_{55} , ζ_{45} and the second order constants ζ_{46} , and ζ_{56} of these molecules are presented in Table V. The zeta values may be seen to obey the following sum rules (McDowell, 1964,1965) :

$$\zeta_{44} + \zeta_{55} = 1/2$$

$$\zeta_{44} \cdot \zeta_{55} - \zeta_{45}^2 = -1/2$$

$$\zeta_{46} + \zeta_{66} = 3/4$$

The second order constant ζ_{56} is negative in all the ions.

TABLE V
Coriolis coupling constants

S. No.	Ion	First order			Second order	
		ζ_{44}	ζ_{55}	ζ_{45}	ζ_{46}	ζ_{66}
1	GeF_6^{2-}	0.3395	0.1605	0.7446	0.5747	0.6479
2	GeCl_6^{2-}	0.4862	0.0139	0.7119	0.5069	0.7022
3	AsF_6^{2-}	0.3365	0.1635	0.7450	0.5760	0.6467
4	AsCl_6^{2-}	0.4828	0.0172	0.7130	0.5085	0.7010
5	SbF_6^-	0.2391	0.2609	0.7499	0.6168	0.6079
6	SbCl_6^-	0.3665	0.1335	0.7409	0.5628	0.6582

The rotational distortion constants are reported in Table VI, and they are in the expected range. It is interesting to note that the rotational distortion constants for this type of molecules are independent of the mass of the Y-atom, the inter-nuclear distance and the three vibrational frequencies of the A_{1g} , E_g and F_{2g} species.

TABLE VI
Rotational distortion constants (Hz)

S. No.	Ion	D_J	$-D_K$	D_{JK}	R_6
1	GeF_6^{2-}	160.2621	163.9625	140.5471	11.7115
2	GeCl_6^{2-}	18.5092	3.3231	2.8482	0.2378
3	AsF_6^{2-}	140.4561	130.4121	111.7812	9.3152
4	AsCl_6^{2-}	data not available			
5	SbF_6^-	108.0302	218.8821	187.6102	15.6346
6	SbCl_6^-	11.6494	17.1669	14.7148	1.2261

All the characteristic ionic constants have been evaluated for the hexahalides of germanium, arsenic and antimony anions by kinetic constants method. There

are, to the authors' knowledge, no experimental data available for these ions for the comparison of the values of mean amplitudes, Coriolis coupling constants and centrifugal distortion constants of the present study. It may be added that a systematic sets of ionic constants relating to these ions are available for the first time.

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