Urey-Bradley force constants, bond-polarizability derivatives and molecular polarizabilities of the tetrahalides of group IVA elements

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The Urey-Bradley force field has been employed to calculate the force constants for the tetrahalides of group IV A elements The results are compared with the orbital valence force constants and it has been found that these are well comparable. The force constants have also been utilized to study the relative strength of the chemical bonds. Bond-polarizability derivatives are calculated following the methods of Lippincott and Nagarajan, and Long and Plane The delta-function potential model of chemical binding has been employed for the computation of molecular polarizabilities The calculated values are compared with the experimental values

1. INTRODUCTION

Bosworth *et al* (1974) have studied the vibrational spectra of the tetrahalides of group IVA elements with the aid of laser and far infrared devices On the basis of the spectral activity of the bands, they have assigned all the fundamental frequencies to their relevant species with more accuracy than previous results. Based on those assignments, Sanyal *et al.* (1974) have successfully applied orbital valency force field (OVFF) to the tetrahalides of group IVA elements In the present communication it is aimed (i) to apply Urey-Bradley force field to calculate force constants and compare these from those obtained by orbital valence force constants, (ii) to discuss the relative stability of chemical bonds in different molecules, (iii) to calculate bond polarizability derivatives and (iv) to compute the molecular polarizabilities for the tetrahalides of group IVA elements and to compare these with the experimental values

2 CALCULATION AND RESULTS

The tetrahalides of the type XY_4 belong to the point group T_d and the fundamental vibrations are distributed among different species as a_1+e+2f_2 The vibrations belonging to f_2 species are Raman and infrared active while the

vibrations of remaining species are only Raman active. Wilson's (1955) *FG* matrix method has been followed to compute *UBFF* constants The expressions for *F* and *G* matrices are taken from Müller & Krebs (1967). The fundamental frequencies used in the present computation are taken from Bosworth *et al* (1974).

The bond polarizability derivatives have been computed following the methods of Lippincott & Nagarajan (1965) and Long & Plane (1965). The delta-function potential model of chemical binding proposed by Lippincott & Stutman (1964) has been employed for the computation of bond and molecular polarizabilities

The four Urey-Bradley force constants . K, the bond stretching force constant, H, the angle bending constant F and F', the interaction constants between non-bonded atom pairs as well as the corresponding orbital valence force constants k_1, k_x', A and B/R reported by Sanyal *et al* (1974) are summarized in table 1 An inspection of these values shows that the evaluated UBFF constants K, H, F and F' are in good agreement with the values k_1 $k_x'/3$, $2A$ and $-B/R$ of a corresponding OVFF calculations

The force constants are a convenient measure of the strength of a chemical bond and, therefore, it is interesting to study the trend of the force constants among the tetrahalides under present study. The only force constant sufficiently large to warrant discussion is the bond stretching force constant K. A comparison of the stretching force constant K from table 1, shows that it decreases in the order $MF > MCl > MBr > MI$ ($M = C$, Si, Ge or Sn) This is consistent with the decrease in electronegativity from F to Cl, Cl to Br and then from Br to I. In this series it is found that the value of the non-bonded repulsion is in decreasing order.

The UBFF bond stretching force constants of hexahalide anions—$SiF_6{}^{2-}$, $GeCl_6{}^{2-}$, $SnCl_6{}^{2-}$, $SnBr_6{}^{2-}$ with those of tetrahalides—SiF_4, $GeCl_4$, $SnCl_4$, and $SnBr_4$ are compared in table 2. From this comparison it is inferred that the chemical bond in tetrahedral species is stronger than in the octahedral species. A similar variation has also been reported in case of OVFF bond stretching force constants of the tetrachlorides and tetrabromides with hexachloride and hexabromide anions of Ti, Zr and Hf in our earlier work Pandey *et al* (1972).

Bond polarizability derivatives calculated following Lippincott & Nagarajan, and Long & Plane for the tetrahalide molecules and hexahalide anions of group IVA elements are presented in table 3 This Table also includes the experimental results reported by Bosworth *et al* (1974) for some hexahalide anions of group IVA elements It is noted from table 3, that the bond polarizability derivatives increase in the order

$$ \left(\frac{\partial \alpha}{\partial R} \right)_{MF} < \left(\frac{\partial \alpha}{\partial R} \right)_{MCl} < \left(\frac{\partial \alpha}{\partial R} \right)_{MBr} < \left(\frac{\partial \alpha}{\partial R} \right)_{MI} $$

Table 1 UBFF constants (in mdyn/Å) for the Group IV A a tetrahalides
(The values in parentheses indicate OVFF constants, l_1, $k'/3$, $2A$ & $- B/R$)

Molecules	K (l_1)	H ($k'/3$)	F ($2A$)	F' ($-B/R$)
CF_4	5 2813 (5.288)	0 3619 (0.418)	0 9887 (0.990)	-0 0376 (0 110)
SiF_4	5.7871 (5.807)	0.0972 (0 115)	0 3475 (0.342)	-0.1420 -(0.094)
CCl_4	1 8423 (1.900)	0 0094 (0.089)	0 6443 (0.628)	-0.1057 -(0.062)
$SiCl_4$	2.6449 (2.654)	0.0337 (0 039)	0.2735 (0.270)	-0.0655 -(0.050)
$GeCl_4$	2.5165 (2.513)	0 0297 (0 033)	0 1901 (0 192)	-0.0469 -(0 034)
$SnCl_4$	2 3324 (2.465)	-0 0268 (0.031)	0.2361 (0.098)	-0 0338 -(0 022)
$SiBr_4$	2.0575 (2.194)	0 0295 (0.050)	0.2019 (0.168)	-0 0480 -(0.020)
$GeBr_4$	1.9395 (2 318)	0 0192 (0.091)	0 1689 (0.074)	-0.059 +(0 086)
$SnBr_4$	1.9136 (2 003)	0 0129 (0.037)	0.1021 (0.080)	-0 0257 +(0.024)
SiI_4	1.4917 (1.593)	0 0247 (0.045)	0.1439 (0.118)	-0.0297 -(0.006)
GeI_4	1.4964 (1.507)	0.0310 (0.037)	0.0807 (0 078)	-0.0252 -(0.010)
SnI_4	1.2830 (1.279)	0.0097 (0 010)	0.0809 (0.088)	-0 0183 -(0.014)

Table 2 Comparison of the bond stretching force constants (in mdyn/Å) of
the tetrahalides with the hexahalide anions of IV A Group elements

Tetrahalide Molecules	K (UBFF)	Hexahalide Anions	K (UBFF)
SiF_4	5 79	SiF_6^{2-}	2.06*
$GeCl_4$	2.52	$GeCl_6^{2-}$	0.73*
$SnCl_4$	2.33	$SnCl_6^{2-}$	1.00*
$SnBr_4$	1.91	$SnBr_6^{2-}$	0 77*

Labonville *et al* (1972)

This is in agreement with all reported results of this kind This result is expected
to arise on account of the increased polarizability of the heavier halogen atoms
and of the increase in the degree of covalent character as well as interatomic

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distance of the MX bond in the order $MF < MCl < MBr < MI$. The bond polarizability derivative values calculated for hexahalide anions and tetrahalide molecules are in good agreement with the available experimental data   This shows the basic soundness of these calculations   It is also noted that bond polarizability derivatives calculated following Lippincott & Nagarajan, and Long & Plane for tetrahalides and hexahalides (table 3) are well comparable

Table 3   Bond polarizability derivatives (in Å^2) for the tetrahalide molecules and octahedral ions of group IVA

Molecule	Lippincott & Nagarajan Method	Long & Plane Method	Expt.
CF_4	0.7016	0.7146	—
CCl_4	1.3606	1 3808	2.04**
SiF_4	0 5268	0.4984	—
$SiCl_4$	2 3048	2 1632	1.90**
$SiBr_4$	2.9540	2.9454	2.98**
SiI_4	4.6697	4 6331	4.11**
$GeCl_4$	2.4075	2.3971	2.65**
$GeBr_4$	[3.4057	3.6027	3.65**
GeI_4	4.7931	5.0451	5.22**
$SnCl_4$	' 3.1432	3.2411	3.06**
$SnBr_4$	[3 8758	4.2436	4 34**
SnI_4	[5.4503	5.9411	6.86**
$PbCl_4$	[3 1645	3.8223	—
$PbBr_4$	[3 7324	4.7805	—
PbI_4	[5.3746	6.8626	—
SnF_6^{2-}	[1.03	0.83	0.81*
$SnCl_6^{2-}$	[3.71	2 90	2.3*
$SnBr_6^{2-}$	[4 91	' 3.75	3.9*
SnI_6^{2-}	5.76	' 4 07	5.0*
$PbCl_6^{2-}$	3.40	[2 88	2.0*

* Bosworth *et al* (1974)   ** Clark *et al* (1971).

The individual values of the bond parallel and bond perpendicular components of the polarizability and contribution from non-bonded electrons are collected in table 4   The last column in Table 4 includes the mean molecular polarizability of the molecules   The bond perpendicular component is independent of internuclear distance and hence it may be transferred from one molecular system to another for the same pair of atoms   The computed values of bond perpendicular components depend on electronegativity, atomic polarizability and residual atomic polarizability degrees of freedom.   The parallel component of a particular bond is not readily transferable from one molecular system to another because it depends on the fourth power of the nuclear distance   However, in cases where the distances are identical in different molecules, they are transferable.   The bond parallel components for M–X bonds (M = C, Si, Ge or Sn, X = F, Cl, Br or I) in tetrahalides show expected trend.   Similar trend

Table 4. Bond and molecular polarizabilities in 10^{-25} cm³ for the group IV A tetrahalides

Molecule	$\Sigma 2\alpha_\perp$	$\Sigma\alpha_{11b}$	$\Sigma\alpha_{11n}$	α_M	Expt
CF_4	52.3361	(28 9657)	23 5542	(34.9520)	28.57
SiF_4	55.8512	(25.2934)	23.5542	(34 8996)	33.01
CCl_4	111.1691	(130.3468)	55.7485	(99.0881)	102.56
$SiCl_4$	121.6921	(141.9095)	55.7485	(106 4500)	111.72
$GeCl_4$	129.1422	(153.1093)	55.7485	(112,6667)	121.23
$SnCl_4$	134.8007	(220.1397)	55.7485	(136.8963)	137.08
$PbCl_4$	183.0795	(234.5822)	55.7485	(157.8034)	—
$SiBr_4$	184.0991	(194 9514)	88.9028	(155 9845)	156.14
$GeBr_4$	192.5484	(239 7183)	88 9028	(173.7232)	—
$SnBr_4$	198.9657	(287.5401)	88.9028	(191.8029)	189.07
$PbBr_4$	253.7189	(288.8499)	88.9028	(210.4905)	—
SiI_4	208 1684	(345.0646)	101.8971	(218.3767)	—
GeI_4	218.5206	(364.0009)	101.8971	(228 1395)	—
SnI_4	226.3831	(436 3267)	101.8971	(254.8690)	277.81
PbI_4	293.4674	(452 1202)	101 8971	(282.4949)	—

* Lippincott & Stutman (1964)

has also been noticed in our earlier work (Sharma *et al* 1974) The evaluated values of mean molecular polarizability of the present systems in some cases have been compared with the available experimental values, and are found in good agreement The results will be helpful for the interpretation of Raman intensities and allied experimental data

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