Bond and molecular parameters of some trigonal bipyramidal molecules

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Abstract : Force fields of some trigonal bipyramidal molecules of the type XY_5 (X- P, Sb, Nb; Y - F, Cl, Br) belonging to D_{3h} point group have been computed employing Redington's approach. The bond and molecular parameters viz., bond polarizability derivatives, mean molecular polarizability and mean amplitudes of vibration have also been obtained for understanding the intramolecular forces and the nature of the chemical bonds ocurring in these molecules. The trends of these parameters are discussed with their stretching force constants and some interesting conclusions are drawn.

Keywords : Force field, bond and molecular parameters.

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I. Introduction

Redington and Aljibury (1971) proposed a method of finding unique force field by the use of observed vibrational frequencies alone. It is of interest to attempt this method for the evaluation of the force field of some trigonal bipyramidal molecules of the type XY_5 possessing D_{3h} symmetry with eight normal modes of vibration under four species.

2. Theoretical considerations

The L matrix can be obtained by the relation

$$L = L_0 C \tag{1}$$

where L_0 is calculated from the inverse kinetic energy matrix G using the relation

$$L_0 = V \Gamma^{\frac{1}{2}} \tag{2}$$

V and Γ are the eigen vector and eigen value matrices of G respectively and C is the angle parameter matrix. To fix the C matrix Redington and Aljibury (1971) obtained the restoring forces for each coordinate as a function of angle parameter. The coordinate linked with the highest vibrational frequency is displaced and the other coordinates are allowed to relax to attain a restoring force balance and a minimum

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potential energy in order that the restoring force takes near maximum value. The parameterized *F* matrix is calculated through the relation

$$F_k = \frac{|F|}{D_{kk}}$$ (3)

where D_{kk} are cofactors of the diagonal force constants and $|F|$ is the determinant of the symmetrized force constant matrix *F*. Following Redington, it is found that

$$F_{steep} = \sum_{k}^{n} T_k D_{kk}^{-\frac{1}{2}}$$ (4)

and is used to arrive at a unique force field. Here T_k are the constants depending upon the geometry of the molecule and they can be obtained from the virial theorem.

The bond polarizability derivative (Lippincoat and Nagarajan 1965), mean molecular polarizability (Lippincoat and Stutman 1964) and mean amplitudes of vibration (Cyvin 1959) are evaluated by the usual procedures.

3. Results and discussion

The structural parameters and spectral data for the molecules under study are taken from Condrate and Nakamoto (1966) and Nour (1986). The symmetry coordinates are essentially the same as those reported by Nour (1986). The inverse kinetic energy matrix G is constructed by using Wilson's S_{kt} vectors (Wilson 1955).

The ϕ_{ij} parameters (ϕ_{12}, ϕ_{13}, ϕ_{23}), valence force constants and the bond polarizability derivative for all the molecules are presented in Table 1. The force constants listed have several interesting implications. The valence force constants of the molecules under the present study agree well with the values reported (Condrate and Nakamoto 1966, Nour 1986). In these pentahalides, the stretching force constant (symmetric and anti-symmetric) as well as bending force constants decrease with increase of mass of the end atom. Further, it is noticed that the variation of stretching force constant in the case of XF_5 and XCl_5 molecules under the present work for Sb and P are in the sequence X-F $>$ X-Cl, whereas for $NbCl_5$ and $NbBr_5$ the variation of stretching force constant is in the sequence X-Cl $>$ X-Br. The stretching force constants for the equatorial bond (f_r) are larger than those for the axial bond (f_a) in all the six molecules studied. The trend is consistent with the results of X-ray (Ohlberg 1954) and electron diffraction studies (Rouaut 1940, Brockway and Beach 1938) which indicate that the equatorial bonds are shorter than the axial bonds. Table 2 also indicates that the bending force constants of the bromides are larger than those of the correponding fluorides which in turn larger than their corresponding chlorides. The bending force constants of the phosphorous compounds are larger than those of the corresponding antimony compounds. All these changes which occur upon the replacement of

Table I. Angle parameters, valence force constants (md/Å) and bond polarizability derivative of some XY_5 type molecules.

Molecule	ϕ_{ij} parameters in (deg)			f_r	f_d	f_{rr}	f_{dd}	$f_\alpha - f_{\alpha\alpha}$	$f_\beta - f_{\beta\beta}$	$\partial\alpha/\partial R$
	ϕ_{12}	ϕ_{13}	ϕ_{23}							
PF_5	−30	3	5	6.624 (5.971)*	3.674 (3.85)	0.223 (0.15)	0.909 (−)	0.579 (0.37)	1.548 (1.342)	8.107
PCl_5	16	1	−2	2.186 (2.10)	1.246 (1.00)	0.505 (0-404)	0.189 (0.213)	0.103 (0.107)	0.435 (0.528)	30.096
SbF_5	18	−9	13	5.44 (5.30)	4.52 (4.60)	0.160 (0.07)	0.531 (−)	0.083 (0.095)	0.672 (0.12)	12.161
$SbCl_5$	10	−7	7	2.485 (2.20)	1.925 (1.83)	0.062 (0.08)	0.075 (−)	0.042 (0.06)	0.231 (0.085)	35.071
$NbCl_5$	13	−7	12	2.707** (2.61)	1.915 (1.94)	−0.05 (0)	0.154 (0.11)	0.475 (0.59)	0.460 (0.57)	21.472
$NbBr_5$	9	10	−6	2.152 (2.17)	1.314 (1.42)	0.190 (0.15)	0.061 (0.05)	0.791 (0.92)	0.762 (0.94)	44.538

*Condrate and Nakamoto (1966).
**Nour (1986).

Table 2. Mean molecular polarizabilities and mean vibrational amplitude (Å) for some XY$_5$ type molecules.

Molecule	$\Sigma\sigma_i a_{ibi}$	$\Sigma f_{ij} a_j$	$\Sigma_j \sigma_\perp$	$\dfrac{aM}{(10^{-16}\,cm^3)}$	$[\sigma_{X-Y}]_{eq}$	$[\sigma_{X-Y}]_{ax}$	$\sigma_{Y_{eq}\cdots eq}$	$\sigma_{Y_{ax}\cdots eq}$
PF$_5$	47.882	45.179	84.334	59.133	0.0087	0.0156	0.0151	−0.0508
PCl$_5$	230.613	282.034	263 231	258.626	0.0235	0.0397	0.0377	0.0994
SbF$_5$	91.523	76.373	142.563	103.486	0.0096	0.0145	0.0531	0.0801
SnCl$_5$	304.275	370.398	345.705	340.126	0.0248	0.0452	0.0602	0.2071
NbCl$_5$	108.514	280.151	261.475	240.713	0.0257	0.0485	0.1155	0.2283
NbBr$_5$	274.187	1331.956	497.263	701.135	0.0498	0.1191	0.2173	0.5249

either the central or the halogen atom can be explained satisfactorily in terms of electron pair repulsion theory developed by Gilliespie (1963). His theory also predicts that the bending force constants for the axial bond angle (f_β) should be larger than that for the equatorial bond angle (f_α). Further it is observed from Table 1 that the bond polarizability derivative α' increases with the increase of mass of the halogen atoms. The trend is in the order α'P(orSb)-F $<$ α'P(orSb)-Cl and α'Nb-Cl $<$ α'Nb-Br.

The mean molecular polarizability α_M and mean vibrational amplitudes are tabulated in Table 2. It is interesting to note that both the values increase with the increase of mass of the halogen atom of the molecules. This shows that with the increase of mass of halogen atoms, the rigidity of the molecule decreases. It is also evident that σ_{x-y} for the axial bond is greater than that of equatorial bond in all molecules. Thus the influence of halogen atom plays a significant role for X-Y [X=P, Sb, Nb ; Y= F, Cl, Br] bond parameters in these molecules.

Since the Redington's method leads to a consistant force field and all the molecular parameters are found to agree well with those reported earlier, it may be pointed out that the present method of calculating the force constant is better than other methods.

Acknowledgment

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