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Estimation of some Vibrational Spectroscopic Constants of Group V Trihalides

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ABSTRACT From the available experimental reports on structural and vibrational spectroscopic data of group V trihalids, it was observed that the bond distances bear a linear relationship with their respective vapour phase vibrational frequencies and bond angles. A least squares fit was made between bond distances and bond angles on one hand and bond distances and vibrational frequencies on the other hand. Using this method, some unknown structural data and vapour phase vibrational frequencies of some molecules of group V trihalides for which the data is not so far available were estimated. From the experimental and estimated data, the molecular constants like force constants, coriolis coupling constants, centrifugal distortion constants and mean amplitudes of vibration have been evaluated.

(Molecular force field, Normal coordinate analysis, least squares fit, group V trihalides)

INTRODUCTION

Fifth group elements nitrogen (N), phosphorous (P), arsenic (As), antimony (Sb) and bismuth (Bi) form pyramidal molecules of the type XY_3 where X is one of the fifth group atoms and Y can be any one of the halogen atoms or hydrogen. The pyramidal XY_3 structure belongs to the C_{3v} point group and gives rise to two non-degenerate vibrations of $A_{1\ type}$ and two doubly-degenerate vibrations of E type. In group V trihalides, the lone pair of electrons of the Y atom occupies one of the tetrahedral sites of the coordination polyhedron of the group V (X) element. As the mass of group V atom increases, the vibrational frequencies decrease. Mass effects may be employed as confirmatory evidence for assignment of vibrational frequencies by the use of isotopes. In continuation of research on evaluating spectroscopic constants and force constants of some unstable group V trihalides [1], the present work deals with all such molecules.

Table 1 provides the experimental vibrational spectroscopic and structural data available for various group V trihalides with the thirty literature references as mentioned in the squared brackets. The structural and vibrational spectroscopic data have been collected from the reports of electron diffraction experiments, millimeter and micro-wave spectra, infrared spectra and Raman spectra of the respective group V trihalide molecules. From Table 1, it may be noticed that the data on the molecules is not complete in several cases. For some molecules reliable bond angles are not reported because of the difficulty in measurement. For BiF_3, the value of bond distance is not available in literature because it is a very unstable compound. To make such vibrational spectroscopic data of group V trihalides complete, it has been attempted to calculate the missing data of some molecules using different approximation methods.

Table 1. Reported vibrational spectroscopic and structural data of group V trihalides

Molecule	Vapour phase vibrational frequencies (cm^{-1})				Bond parameters Bond distance	Bond angle	Coriolis coupling constant,	Centrifugal distortion constant,
	ν_1	ν_2	ν_3	ν_4	d.A	∝°	ζ_{44}	D_J
NF_3	1031.9	647.3	908.4	492.6 [2]	1.365	102.367[3]	-0.895 [4]	14.63 [4]
PF_3	893.2	486.5	858.4	345.6 [5]	1.57	97.8 [6]	-0.6297[7]	7.845 [8]
AsF_3	738.5	336.8	698.8	262 [5]	1.706	95.97 [9]	-0.435[10]	4.631 [11]
SbF_3	654	259	624	- [12]*	-	-	-	-
NCl_3	540.5	349	643	257.5[13]@	1.7593	107.367[14]	-	1.863 [14]
PCl_3	515	258.3	504	186 [5]	2.0426	100.1 [15]	-0.738[11]	1.17 [8]
$AsCl_3$	423.5	194.2	398	152.7 [16]	2.162	98.63 [9]	-0.57 [16]	0.7746 [17]
$SbCl_3$	380.7	150.8	358.9	121.8 [5]	2.3217	97.19 [18]	-	0.5489 [18]
$BiCl_3$	342	123	322	107 [19]	2.48	100±6 [20]	-	-
PBr_3	390	159.9	384.4	112.8 [5]	2.216	101 [21]	-	0.22 [21]
$AsBr_3$	289.7	125.4	284	92.5 [5]	2.3236	99.94 [22]		0.172 [23]
$SbBr_3$	256	101.2	248.9	76.2 [5]	2.49	98.2 [24]	-	-
$BiBr_3$	220	77	214	63 [25]	2.63	100±6 [20]	-	-
NI_3	-	-	-	-	2.15	- [26]	-	-
PI_3	303	111	325	79 [27]	2.43	102 [28]	-	-
AsI_3	212	89.6	201	63.9 [5]	2.557	100.2 [29]	-	-
SbI_3	186.5	74	147	54.3 [5]	2.719	99.1 [30]	-	-
BiI_3	145	90	115	71 [31]	-	-	-	-

[ ] : Reference; * : Solid state; @ : Liquid phase

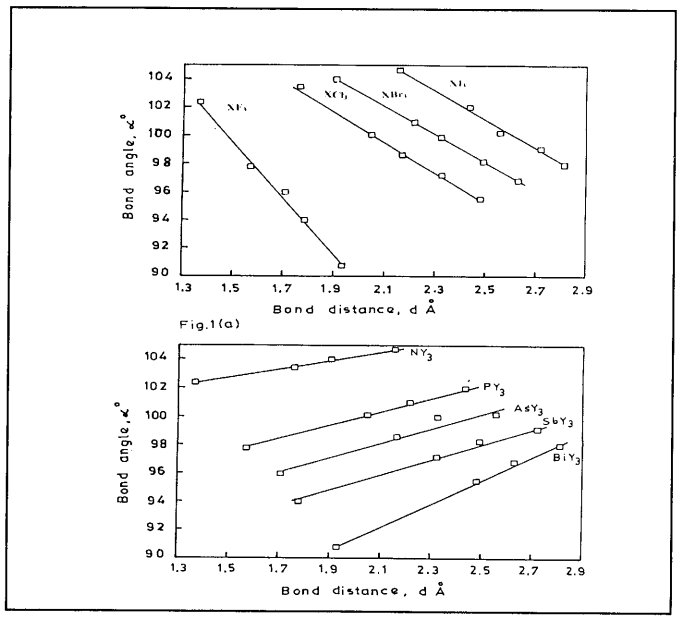

Figure 1. Relationship between bond distance (d) and bond angle (α) of group V trihalides

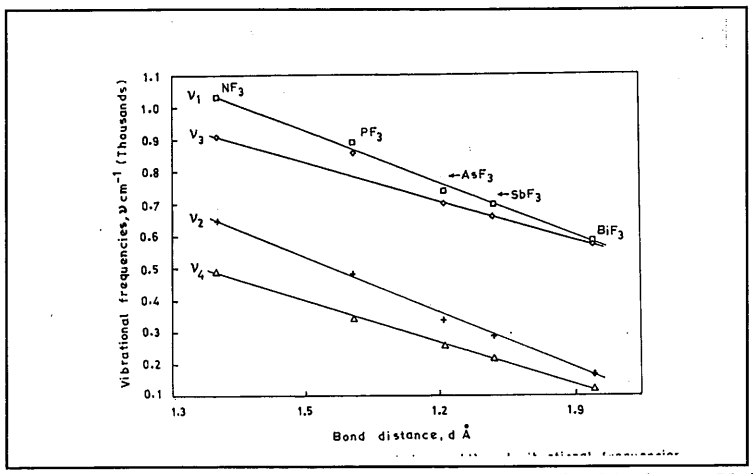

Figure 2. Relationship between bond distances (d) and vibrational frequencies (ν) of group Vtrifluorides

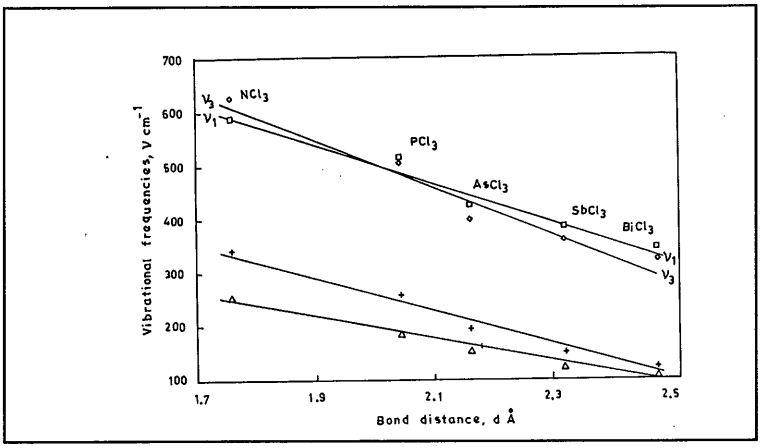

Figure 3. Relationship between bond distances (d) and vibrational frequencies (ν) of group *V* trichlorides

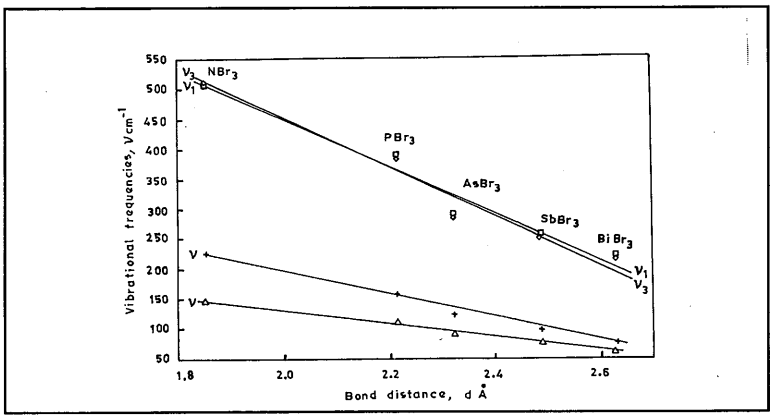

Figure 4. Relationship between bond distances (d) and vibrational frequencies (ν) of group *V* tribromides

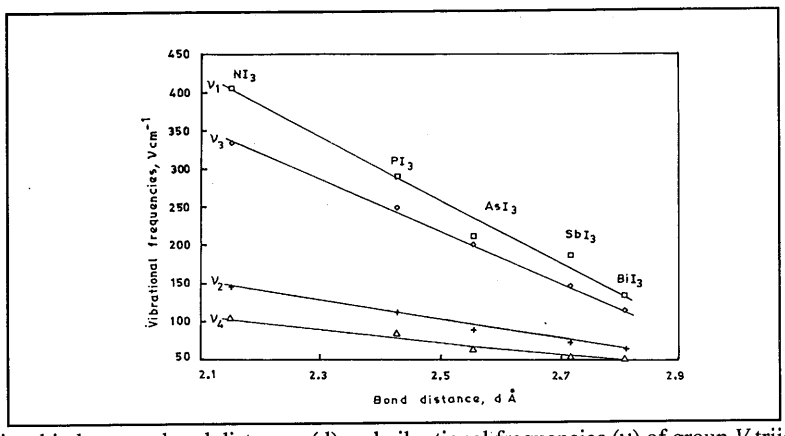

Figure 5. Relationship between bond distances (d) and vibrational frequencies (ν) of group *V* triiodides

METHODOLOGY

Normal coordinate analysis

Along with the least squares fit method, the present work made use of Wilson's GF matrix method and different approximation methods to estimate the molecular force field of each and every group V trihalide.

Wilson's GF matrix method – Application to XY_3 pyramidal type molecules

Wilson [33] developed a fundamental and theoretical method for the determination of frequencies and normal modes of vibration in terms of the atomic masses and force constants and the method is known as Wilson's GF matrix method. Using internal coordinates R_i the potential (V) and kinetic (T) energies are written as

$$2V = R'fR \quad (1)$$
$$2T = \dot{R}'g^{-1}\dot{R} \quad (2)$$

where R is the column matrix of internal coordinates, R' is the transpose of R and $\dot{R}$ is the corresponding time derivative matrix, f is the symmetric matrix whose elements are the force constants f_{ij} and g^{-1} is known as the kinetic matrix and the set g_{ij} define the kinetic potentials of the system. The g matrix may be formulated in the matrix form as $g = BM^{-1}B'$, where M is the matrix involving masses. The symmetry coordinates can be generated as a linear combination of the internal coordinates satisfying some conditions stipulated by group theory. This results in the division of various symmetry coordinates and vibrational frequencies into different groups. By taking linear combination of these symmetry coordinates the normal coordinates can be generated using the relation, S = LQ, where Q is the column matrix of normal coordinates. Here, L is the normal coordinate transformation matrix.

The f and g matrices, expressed in terms of internal coordinates can be transformed into symmetrised F and G matrices by the relations

$$F = UfU' \text{ and } G = UgU' \quad (3)$$

Where U matrix is formed from the coefficients in the symmetry coordinates. From the above, the following equations can be obtained:

$$L'FL = \lambda \quad (4)$$
$$L'G^{-1}L = E \quad (5)$$
$$LL' = G \quad (6)$$

Pre-multiplying both sides of equation (4) with L results

$$GFL = L\lambda \quad (7)$$

Which is the famous equation in the theory of molecular vibrations.

The characteristic values of FG and GF are the same and always real. Application of Wilson's method gives the relation

$$|FG - \lambda E| \quad (8)$$

As the problem is expressed in terms of normal coordinates, the equation (8) is called the secular equation, which will split into several blocks, each one corresponding to a given representation of the molecular point group. In general, for a vibrational species with n modes, the frequencies will be n and the number of relations obtained from secular equation will also be n. The secular equation generates n equations in n(n-1)/2

unknowns and hence this system of equations has an infinite set of solutions for F_{ij}.

The secular equation is quadratic in λ and the roots of the equation can be generally represented as

$$G_{ii} F_{ii}^2 - (\lambda_i + \lambda_j - 2 G_{ij} F_{ij}) F_{ii} + G_{jj} (\lambda_i \lambda_j / |G| + F_{ij}^2) = 0 \quad (9)$$

$$F_{jj} = (\lambda_i + \lambda_j - 2 G_{ij} F_{ij}) / G_{jj} - G_{ii} F_{ii} / G_{jj} \quad (10)$$

In order to realize the unique set of force constants, several methods are developed, all of which use one or more sets of molecular constants which themselves can be obtained experimentally.

Apart from force constants, other related molecular constants include Coriolis coupling constants (ζ), Centrifugal distortion constants (D), and Mean square amplitudes (l). Coriolis coupling constants are dimension less quantities – $1 \leq \zeta \leq 1$ which pertain to the Coriolis coupling of vibration-rotation. These constants are given in terms of L through the relation, $L^{-1} C (L^{-1}) = \zeta$, C being the matrix given by the masses and the relative equilibrium positions of the atoms.

Nuclei in a polyatomic molecule are held together by finite restoring forces and therefore the molecular framework cannot be regarded as rigid. Thus bond distances and angles will vary because of the centrifugal forces produced by rotation, which gives rise to a centrifugal distortion. These effects are large for light molecules because of their small amount of inertia. The Centrifugal distortion constant of a diatomic molecule can be simply correlated with the stretching force constant. The distortion constants of a polyatomic molecule are correlated with the F matrix and give information about the diagonal and off-diagonal force constants. Since these constants are affected least from anharmonicity of vibration and are obtainable from experimental observations with extremely high accuracy, they should form a much preferable set of additional experimental data for ascertaining the correct set of force constants.

Another set of parameters, values of which can be obtained experimentally, are the mean square amplitudes of vibration of the molecule. If R_{ij} is the instantaneous inter-nuclear distance between a pair of atoms i and j during vibrations and R_{ij}^e is the equilibrium value of R, l is the root mean square amplitude for the variation of R and is given by

$$l_{ij} = \langle (R_{ij} - R_{ij}^e)^2 \rangle^{1/2} \quad (11)$$

The symmetrised mean square amplitude matrix is given by $\Sigma = \langle SS' \rangle = U \sigma U'$, where U matrix connects the valency coordinates and the symmetry coordinates as $S = UR$ and $UU' = E$. Then, $\Sigma = L \Delta L'$, where $\Delta = \langle Q Q' \rangle$.

For application of Wilson's GF matrix to XY_3 pyramidal type molecules for solving force field problem, the changes in the three Y-X-Y inter bond angles and the changes in the three X-Y bond distances will be selected as the necessary and sufficient set of coordinates. From these, the symmetry coordinates will be calculated. The general valency force field is assumed for the molecule and the f matrix and symmetrised F matrix elements can be calculated. The G matrix can be constructed using the Wilson's vector method.

To evaluate the correct set of E species force constants, Coriolis coupling constants (mainly ζ_{44}) can be used with good advantage. According to Krishnamurthy [33], the centrifugal distortion constants are insensitive to the variation of A_1 species force constants. Hence, in evaluating the A_1 species force constants, the usual method of selecting physically reasonable value of interaction force constant (F_{ij}) has been adopted to reproduce the experimental centrifugal distortion constants (mainly D_J). The D_J is related to the force constants by the equation,

$$D_J = (677.31/8.(I_x)^4) \sum_{ij} J^i_{xx} J^k_{xx} F^{-1}_{ij} \quad (12)$$

Where I_x is the moment of intertia and J^i_{xx} and J^k_{xx} are the elements of the compliance matrix expressed in terms of symmetry coordinates.

For XY_3 type molecules, the E-species Coriolis coupling constants (ζ_{33} , ζ_{44}) can be obtained from the following equation,

$$F_{33} - \frac{2N}{d} F_{34} + \frac{3}{d^2} F_{44} = m_y \lambda_3 (1 - (\zeta_{33}) + \lambda_4 (1 - \zeta_{44}) \quad (13)$$

where $N = (1-\cos\alpha)/\sin\alpha$, and $\lambda_i = 4 \pi^2 \nu_i^2 c^2$ and m_y is the mass of Y atom.
With each set of force constants, the Centrifugal distortion constants D_J, D_{JK} and D_K can be evaluated and the set which gives the distortion

constant values agreeing with the experimental values can be considered as the correct set.

The mean square amplitudes are expressed as

$$l^2_{X\text{-}Y} = (\Sigma_{11} + 2\,\Sigma_{33})/3 \qquad (14)$$

$$l^2_{Y\ldots Y} = 2\,s^2\,(2\Sigma_{11} + \Sigma_{33})/3 + c^2\,(\Sigma_{22} + 2\,\Sigma_{44})/3 + 4\,cs\,(\Sigma_{12} + 2\,\Sigma_{34})/3 \qquad (15)$$

where the mean square amplitude matrix elements $\Sigma_{ii} = \langle S_i^2 \rangle$ and $\Sigma_{ij} = \langle S_i\,S_j \rangle$ and $c = \cos(\alpha/2)$ and $s = \sin(\alpha/2)$. The mean amplitudes of vibration are calculated with the above formula using the best set of force constants obtained for the molecules.

When experimental values for any of the molecular constants mentioned above are not available, certain approximation methods can still be used to obtain the correct set of force constants. Various approximation methods have been used [34] for evaluation of such molecular constants. The different approximation methods used for the present work include L-matrix approximation method developed by Muller and Peacock [35], Kinetic constants method by Thirugnanasambandam and Mohan [36], Parametric representation method by Pfeiffer [37] and L-F approximation method by Pandey et al [38].

L-Matrix approximation method

In this method, one of the off-diagonal elements L_{ij} or L_{ji} $(i < j)$ will be assumed to be equal to zero. This method has the advantage that L-matrix can be evaluated in terms of G matrix elements and does not require the knowledge of F matrix. Further, the method enables the mean square amplitudes to be expressed in terms of G and Δ matrix elements. By this method, the force constants of the XY_3 pyramidal type molecules can be evaluated using the following equations :

$$F_{ii} = (\lambda_i\,|G| + \lambda_j\,G_{ij}^2)/\,G_{ii}\,|G|$$
$$F_{ij} = -\lambda_j G_{ij}/|G| \qquad (16)$$
$$F_{jj} = \lambda_j\,G_{ii}\,/\,|G|, \quad \text{where } |G| = (G_{ii}\,G_{jj} - G_{ij}^2)$$

Kinetic constants method

In this method, the required n(n-1)/2 force constants were developed by assuming that the off-diagonal elements, F_{ij}, may be related to the corresponding off-diagonal elements K_{ij} of kinetic constants matrix, as

$$F_{ij} / F_{jj} = K_{ij} / K_{jj} \qquad (i < j)$$

The reasonable set of solutions obtained from this method is given below:

$$F_{ii} = G_{ii}^{-1}\,(\lambda_i - \lambda_j G_{ij}\,K_{ij}),$$
$$F_{ij} = \lambda_j\,K_{ij} \qquad (17)$$
$$F_{jj} = \lambda_j\,K_{jj}\,.$$

Parametric representation method

Pfeiffer [37] investigated a special single parameter (L_o) representation of the solution of the inverse eigen value problem of n=2 and derived equations for the force constants for A_1 and E modes of XY_3 pyramidal type molecules. The relevant equations are given below :

$$F_{ii} = (\lambda_i + \lambda_j)/2 + \cos2(\theta - \psi)\,(\,G_{jj}/|G|\,)(\lambda_i + \lambda_j)/2$$
$$F_{ij} = -\,(\lambda_i + \lambda_j)\,(\,G_{ij}/|G|\,)/2 + \sin2\theta\,(\sqrt{G_{ii}G_{jj}}\,)\,/\,|G|\,(\lambda_i - \lambda_j)/2 \qquad \ldots.(18)$$
$$F_{jj} = (\lambda_i + \lambda_j)/2 - \cos2(\theta + \psi)\,(\,G_{ii}/|G|\,)(\lambda_i - \lambda_j)/2$$

where, $\sin2\,\psi = G_{ij}/(\sqrt{G_{ii}G_{jj}}\,)$.

L-F approximation method

This method has been formulated on the ground that the magnitude of the square of non-diagonal elements, for example, squares of F_{12} and L_{12} appearing in F and L matrices are very small as compared to F_{12} and L_{12} respectively. Thus, element F_{11} which is larger in magnitude than F_{12} or F_{22} is fixed as the principal force constant. The method resulted the following set of expressions for the force constants:

$$F_{ii} = \lambda_i\,/\,G_{ii}$$
$$F_{ij} = \lambda_j\,G_{ij}\,/\,(2\,|G|\,) \qquad (19)$$
$$F_{jj} = G_{ii}\,\lambda_j\,/\,|G|$$

Once the value of the principal symmetrised force constant F_{ii} is fixed, the other two force constants F_{ij} and F_{jj} can be evaluated easily. Pandey *et al.* [38] applied this method to 35 molecules of various types, XY_6 (O_h), XY_4 (T_d), XY_3 (D_{3h}), and XY_2(C_{2v}) and their results were validated by comparing with other methods. The present work applied this method to XY_3 (C_{3v}) type group V trihalides.

RESULTS AND DISCUSSION

Figure 1 (a) and 1(b) are providing a greater support even when both bond distance and bond angle values are not available from literature for some molecules. Using the bond distance value estimated from these figures, the vibrational

frequencies can be easily estimated from the other figures. Following the graphs and assuming that the linear relationship holds rigorously, a least squares fit method has been developed between the bond distances and bond angles on one hand and bond distances and vibrational frequencies on the other hand. Though there are slight deviations in some cases, this method furnishes reliable information to estimate the bond distances, bond angles and vapour phase vibrational frequencies of some group V trihalides. When slight deviations occur (in the case of vibrational frequencies), by many iterations of varying the frequencies and adjusting the deviations to nearly ± 20 cm^{-1}, best fit values have been taken from the least squares fit method. The linear relationships (like $y = mx + c$) between bond angles (α) and bond distances (d) and between vibrational frequencies (ν) and bond distances expressed by equations have been obtained. In the case of vibrational frequencies, a separate formula has been derived for each of the four vibrational modes in each case of trifluorides, trichlorides, etc. The values of the slope (m) and intercept (c) for all the above linear relationships are given in Table 2. All the estimated values of bond parameters and vapour phase vibrational frequencies of group V trihalides are listed in Table 3.

Table 2. Values of slope (m) and intercept (c) from least squares fit method*

Type of group V trihalide		Values of 'm' and 'c' for vibrational modes and bond angle				
		Vibrational modes				Bond angle
		ν_1	ν_2	ν_3	ν_4	∝
Trifluorides,	m	-818.8 2155.9	-862.6	-630.1	-651.9	-20.2
	c		1826.5	1793.3	1376.9	129.8
Trichlorides,	m	-361.9	-314.2	-437.9	-215.1	-10.9
	c	1229.5	889.8	1384.5	638.1	122.5
Tribromides,	m	-405.5	-205.3	-420.8	-121.6	-9.8
	c	1269.6	612.4	1301.1	380.0	122.7
Triiodides,	m	-401.4	-123.5	-335.2	-87.1	-10.2
	c	1262.5	410.0	1058.8	292.2	126.6

* : $y = m.x + c$, where 'y' is the vibrational mode (ν) or bond angle (∝), and 'x' is bond distance (d).

Table 3. Estimated vapour phase vibrational frequencies and bond parameters of group V trihalides

Molecule	Vibrational frequencies, cm^{-1}				Bond distance	Bond angle
	ν_1	ν_2	ν_3	ν_4	d. A	∝°
SbF_3	698	290	664	218	1.78	94
BiF_3	580	168	575	122	1.93	90.75
NCl_3	590	340	625	257.5		103.4
$BiCl_3$						95.5
NBr_3	505	225	510	150	1.90	104
$BiBr_3$						96.85
NI_3	405	145	335	105		104.75
PI_3	290	112	250	84		
BiI_3	135	65	115	50		98

With the help of Figure 1(a) and Figure 1(b) and least squares fit method as well, the bond distance and bond angle values of BiF_3 have been estimated. Same procedure has been followed in the case of SbF_3. The vapour phase vibrational frequencies of BiF_3 and SbF_3 have been estimated first by the help of Figure 2 and then refined by least squares fit method.

As the reported experimental value [14] of bond angle (107.367°) of NCl_3 is very high (highest of all group V trihalides), it was felt that it is better to estimate it. The vibrational frequencies of NCl_3 and the bond angles of NCl_3 and $BiCl_3$ have been estimated. In literature [20], same bond angle (100° $\pm$6°) was reported for $BiCl_3$, $BiBr_3$ and BiI_3 and a bond angle value of 100° was used

for all these three molecules to estimate their force field. As this seems to be not proper, their bond angles have been estimated from the least squares fit method. The estimated values are well agreeing with the reported range (100° ±6°).

For group V tribromides, the least squares fit method has been used to estimate the structural parameters and vibrational frequencies of NBr_3 and the bond angle of $BiBr_3$. A value of 1.82 A was reported [39] for N-Br distance in N-Bromoacetamide by X-ray analysis. The present estimated bond distance value of 1.9 A for NBr_3 is in good agreement with that value. Masuko and Hamada [40] estimated the single N-Br stretching frequency in NH_2Br molecule by high resolution FTIR study as 569 cm^{-1}. In the present work, for the NBr_3 molecule, the estimated values of two N-Br stretching vibrations are 505 and 510 cm^{-1}, somewhat in agreement with the experimental value in NH_2Br, which is a light molecule when compared with NBr_3. The same authors reported a value of 678 cm^{-1} as observed and 659 cm^{-1} as calculated frequency for N-Cl stretching bond in NH_2Cl molecule. The present work estimated the values for two N-Cl stretchings in NCl_3 molecule as 590 and 625 cm^{-1}.

In the case of group V triiodides, only PI_3 and AsI_3 are having the reported vapour phase frequencies and so in Fig. 5, it was not possible to draw standard lines. Therefore, after estimating the frequencies of other three triiodides from least squares fit method, lines were drawn for the five molecules. All the points are well agreeing with the linear relationship between the bond distances and frequencies. This procedure has been used rarely. The structural parameters of NI_3 and frequencies of NI_3 , SbI_3 and BiI_3 and the bond angle of BiI_3 have been estimated.

Using the available experimental values of vapour phase vibrational frequencies, bond distance and bond angle, coriolis coupling constants (ζ_{44}) and centrifugal distortion constants (D_J) of some molecules and the present estimated data of the rest of the group V trihalides and also by the application of different approximation methods, the force constants have been evaluated for all the group V trihalides. The unknown values of centrifugal distortion constants (D_J, D_{JK}) and mean amplitudes of vibration (l_{x-y}, $l_{y..y}$) of A_1-species (at 300 K) and coriolis coupling constants (ζ_{33}, ζ_{44}) of E-species of vibration for some molecules have also been evaluated. The calculated values of force constants and other molecular constants are given in Table 4 and Table 5. From the experimental values given in Table 1, it can be observed that the ζ_{44} and D_J values decrease from nitrogen to bismuth. The same trend has been observed from the present calculated values as listed in Table 5.

The percentage of potential energy distribution (PED) for all the group V trihalides are calculated and given in Table 6. All the estimated structural and vibrational spectroscopic values seem to be appropriate as they are reproducing the expected PED. From Table 6, it can be observed that the bond stretching and bond bending characters of both A_1 and E species are increasing from nitrogen to bismuth. Pure vibrations are occurring for the heavy central atoms. This is supporting the present calculations of force fields of group V trihalides. That same trend has been observed in the case of some other group V trihalides where the structural parameters and vapour phase vibrational frequencies estimated by the least squares fit method have been used and where the force constants have been determined by using approximation methods, that is, in the case of SbF_3 , BiF_3 , $BiCl_3$, $BiBr_3$ and BiI_3. The estimation of structural or spectroscopic or both data of SbF_3 , BiF_3 , $BiCl_3$, $BiBr_3$ and BiI_3 from least squares fit method is well supported by the above observations from the application of PED. The estimation of vapour phase frequencies and structural parameters by least squares fit method for NCl_3 , NBr_3 , NI_3 and PI_3 is also well justified.

Table 4. Calculated force constants of all group V trihalides

Molecule	A species of vibration			E species of vibration		
	F_{11} (md/A)	F_{12} (md)	F_{22} (md.A)	F_{33} (md/A)	F_{34} (md)	F_{44} (md.A)
NF_3	6.4182	0.921	2.336	3.3972	-0.4509	1.6657
PF_3	5.73	0.1475	2.1323	4.8973	-0.2481	1.2249
AsF_3	5.3784	1.08	1.5661	4.3422	-0.3463	0.9492
SbF_3	4.8058	0.0936	1.2468	4.2255	-0.0336	0.7523
BiF_3	3.46	0.022	0.5105	3.389	-0.0067	0.2955
NCl_3	4.0579	1.1987	1.4548	2.3296	-0.6541	1.2032
PCl_3	3.1745	0.41	1.4843	2.2603	-0.1881	0.9929
$AsCl_3$	2.7147	0.06	1.2538	2.1397	-0.1234	0.8479
$SbCl_3$	2.4553	0.0873	0.9641	2.0025	-0.0414	0.6706
$BiCl_3$	2.1234	0.0446	0.812	1.8052	-0.0224	0.6325
NBr_3	4.4096	1.3657	1.3621	1.8614	-0.5933	1.0057
PBr_3	3.2606	0.7623	1.1383	1.8501	-0.3579	0.8686
$AsBr_3$	2.4889	0.4237	1.0137	1.7352	-0.2033	0.7175
$SbBr_3$	2.0797	0.1363	0.8876	1.6501	-0.0623	0.6139
$BiBr_3$	1.7487	0.0661	0.6686	1.4966	-0.0332	0.5084
NI_3	3.2925	1.0508	1.0662	0.9798	-0.5435	0.9791
PI_3	2.3491	0.6872	0.9586	0.9431	-0.373	0.8816
AsI_3	1.8125	0.4208	0.8612	1.07	-0.1963	0.6297
SbI_3	1.6161	0.2781	0.772	0.7604	-0.1311	0.5536
BiI_3	0.9481	0.1024	0.7698	0.5844	-0.0485	0.5498

Table 5. Calculated values of various molecular constants of some group V trihalides

Molecule	Coriolis coupling constants		Centrifugal distortion constants (K.Hz)		Mean amplitudes of vibration	
	ζ_{33}	ζ_{44}	D_J	D_{JK}	l_{x-y}	l_{y-y}
SbF_3	0.1538	-0.05068	3.778	-5.1464	0.03946	0.06314
BiF_3	0.0865	-0.5163	4.8276	-6.1431	0.04236	0.08874
NCl_3	0.7548	-0.8034	1.9005	-3.1593	0.0535	0.06997
$SbCl_3$	0.2657	-0.5282	0.56024	-0.85128	0.04814	0.07015
$BiCl_3$	0.1665	-0.4953	0.3673	-0.5388	0.05019	0.07348
NBr_3	0.875	-0.8976	0.3324	-0.5716	0.05596	0.0734
PBr_3	0.7523	-0.8088	0.21302	-0.36203	0.0508	0.06844
$AsBr_3$	0.5528	-0.6708	0.1685	-0.2819	0.0501	0.07004
$SbBr_3$	0.457	-0.6312	0.1251	-0.2047	0.0506	0.07292
$BiBr_3$	0.3152	-0.5566	0.0951	-0.1476	0.05307	0.0793
NI_3	0.9193	-0.9329	0.08474	-0.1424	0.0741	0.09134
PI_3	0.832	-0.867	0.06143	-0.1026	0.0683	0.0838
AsI_3	0.6662	-0.7487	0.0591	-0.1001	0.06174	0.08097
SbI_3	0.5485	-0.6729	0.0457	-0.07662	0.06972	0.08787
BiI_3	0.4702	-0.653	0.03707	-0.05832	0.0798	0.096

Table 6. Percentage of Potential Energy Distribution (PED) of group *V* trihalides

Molecule	ν_1		ν_2		ν_3		ν_4	
	S_1	S_2	S_1	S_2	S_1	S_2	S_1	S_2
NF_3	69.2	30.8	20.65	79.35	80.52	19.48	10.00	90.00
PF_3	87.11	12.89	10.81	89.19	97.52	2.48	0.35	99.65
AsF_3	99.82	0.18	10.11	89.89	99.76	0.24	1.47	98.53
SbF_3	99.43	0.57	0.16	99.84	99.83	0.17	0.05	99.95
BiF_3	99.88	0.12	0.03	99.97	99.98	0.02	0.0045	99.9955
NCl_3	80.46	19.54	0	100	87.49	12.51	0	100
PCl_3	86.79	13.21	4.51	95.49	94.71	5.29	1.29	98.71
$AsCl_3$	95.36	4.64	3.46	96.54	98.51	1.49	0.1	99.9
$SbCl_3$	98.61	1.39	0.39	99.61	99.46	0.54	0.15	99.85
$BiCl_3$	99.51	0.49	0.13	99.87	99.81	0.19	0.05	99.95
NBr_3	76.3	23.7	0	100	84.17	15.83	0	100
PBr_3	86.46	13.54	0	100	92.62	7.38	0	100
$AsBr_3$	93.36	6.64	0	100	96.79	3.21	0	100
$SbBr_3$	95.78	4.22	1.24	98.76	98.41	1.59	0.43	99.57
$BiBr_3$	98.43	1.57	0.43	99.57	99.4	0.6	0.16	99.84
NI_3	76.08	23.92	0	100	76.41	3.59	0	100
PI_3	82.69	17.31	0	100	85.67	14.33	0	100
AsI_3	89.82	10.18	0	100	94.59	5.41	0	100
SbI_3	94.16	5.84	0	100	96.08	3.92	0	100
BiI_3	93.81	6.19	1.96	98.04	96.84	3.16	0.92	99.08

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