Normal Coordinate Analysis of Nitrogentrichloride

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The intramolecular force fields of nitrogen trichloride have been determined using the recent experimental data on the vibrational frequencies. Three different methods have been used for the evaluation of force constants. The results obtained are quite consistent.

Introduction

In a general program [1, 2] of determining the intramolecular force field of Group V trihalides the NCl_3 molecule could not be studied for the lack of experimental data. Nitrogentrichloride belongs to the C_{3v} point group having pyramidal structure with two nondegenerate vibrations belonging to A_1-species and two degenerate vibrations belonging to E-species. Carter et al. [3] have, recently, reported the fundamental frequencies of this molecule and it was thought worthwhile to calculate its force constants and related properties.

Duncan [4] has shown that the simple Urey-Bradley Force Field (UBFF) is not capable of satisfactorily explaining the vibrations of pyramidal XY_3 molecules, as it does not take into account the interactions between two angle bendings and bond stretching and angle bending when the bond is not continuous, with the angle. A modified UBFF was suggested by Shimanouchi et al. [5] to improve this situation by introducing cross terms for bond-angle and angle-angle interactions. In a recent paper Carter et al. [6] have proved the utility of this modified UBFF for NCl_3. In an attempt to describe the normal vibrations of NH_3 Pariseau et al. [7] suggested the inclusion in the potential field of the repulsion between a ligand atom and the lone-pair of electrons on the central atom. The lone-pair acts as a virtual atom of zero mass. The same method has been applied to NF_3 by Curtis and Muirhead [8] and to the group V trihalides by King and Overend [9]. These studies have proven the general superiority of the lone-pair model in describing the vibrations of pyramidal molecules over the simple UBFF. Our aim is to see how well this model works in the case of NCl_3.

While this work was in process, Bayersdorfer et al. [10] caried out GVFF calculations for this molecule. In the present communication we have applied three different models for the potential field, namely, an approximate GVFF, simple UBFF and lone-pair model, for the evaluation of force constants of the molecule.

Methods of Calculations

The symmetry coordinates used in the present calculations are the same as those given in [1] and [2]. There have not been any structural investigations on this molecule and the bond length was estimated from the relation:

$$\text{N-Cl (in NCl}_3\text{)/N-F (in NF}_3\text{)} = \text{P-Cl (in PCl}_3\text{)/P-F (in PF}_3\text{)}, = \text{As-Cl (in AsCl}_3\text{)/As-F (in AsF}_3\text{)}.$$

The mean value of the N-Cl bond length is thus found to be 1.78 Å. This is in good agreement with its approximate value (1.73 Å) obtained from the relation [11]:

$$r = r_N + r_{Cl} - 0.06 \, | \chi_N - \chi_{Cl} |$$

where r_N and r_{Cl} are the atomic radii and χ_N and χ_{Cl} are the electronegativities. The bond angle has been assumed to be 100°. The bond angle has also been estimated like the bond length i. e. from the relation

$$< \text{ClNCl (in NCl}_3\text{)} / < \text{FNF (in NF}_3\text{)} = < \text{ClPCl (in PCl}_3\text{)} / < \text{FPF (in PF}_3\text{)} \quad \text{etc.}$$

The expressions for symmetrized force constants in terms of the parameters entering in the three methods are given in Table 1, where "r" refers to the N-Cl bond and "α" to Cl – N – Cl angle.

Table 1. F-Matrix Elements in Different Force Fields for NCl_3.

F-Matrix Elements	GVFF	Simple UBFF	Lone Pair Model
A_1 Species			
F_{11}	$f_r + 2 f_{rr}$	$K + 4 F \sin^2 \frac{1}{2} \alpha$	$K_r + 4 F_r \sin^2 \frac{1}{2} \alpha$
F_{12}	$r (2 f_{r\alpha} + f_{r\alpha}')$	$1.8 \, r F \sin \frac{1}{2} \alpha \cos \frac{1}{2} \alpha$	$r [0.9 F_r \sin \frac{1}{2} \alpha \cos \frac{1}{2} \alpha + 3 F_{r\alpha}]$
F_{22}	$r^2 (f_\alpha + 2 f_{\alpha\alpha})$	$r^2 [H + F (\cos^2 \frac{1}{2} \alpha + 0.1 \sin^2 \frac{1}{2} \alpha)]$	$[H_\alpha + F_r (\cos^2 \frac{1}{2} \alpha + 0.1 \sin^2 \frac{1}{2} \alpha)] \, r^2$
E Species			
F_{33}	$f_r - f_{rr}$	$K + F [\sin^2 \frac{1}{2} \alpha - 0.3 \cos^2 \frac{1}{2} \alpha]$	$K_r + F_r [\sin^2 \frac{1}{2} \alpha - 0.3 \cos^2 \frac{1}{2} \alpha]$
F_{34}	$r (- f_{r\alpha} + f_{r\alpha}')$	$r [0.9 F_r \sin \frac{1}{2} \alpha \cos \frac{1}{2} \alpha]$	$r [0.9 F_r \sin \frac{1}{2} \alpha \cos \frac{1}{2} \alpha]$
F_{44}	$r^2 (f_\alpha - f_{\alpha\alpha})$	$r^2 [H + F (\cos^2 \frac{1}{2} \alpha + 0.1 \sin^2 \frac{1}{2} \alpha)]$	$[H_\alpha + F_r (\cos^2 \frac{1}{2} \alpha + 0.1 \sin^2 \frac{1}{2} \alpha)] \, r^2$

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The set of symmetrized force constants using the *L*-matrix approximation method have been calculated from the following relations given by PEACOCK and MÜLLER[12]:

$$F_{ii}=\frac{D\,\lambda_i+G_{ij}^2\,\lambda_j}{G_{ii}\,D}\,;\qquad F_{ij}=-\frac{G_{ij}\,\lambda_j}{D}\,;\qquad F_{jj}=\frac{G_{ii}\,\lambda_j}{D}$$

where $D=\det|G|$ and λ_i, λ_j are the eigenvalues of the secular equation related to the vibrational frequencies ν_i, ν_j. The approximate GVFF calculated from these relations are quite reliable in the XY_n type molecules with $m_X > m_Y$ [13] but in the present case ($m_Y > m_X$) it is not very accurate and a slight correction[14] is needed. However, this correction leads to imaginary force constants in A_1-species in the present case. The limiting values of the force constants are obtained and given in parantheses in Table 3 which contains the results obtained from the above relations. In E-species the correction yields real force constants and Table 3 includes them also (in parantheses).

Table 2. Observed and calculated vibrational frequencies (cm^{-1}) for NCl_3.

i	ν_i Observed	ν_i Calculated Lone Pair Model	ν_i Calculated Simple UBFF	$\Delta\nu_i\,\%$ Lone Pair Model	$\Delta\nu_i\,\%$ Simple UBFF
1	538	519.7	592.7	3.41	−10.17
2	349	336.7	343.1	3.52	1.70
3	642	659.5	659.1	−2.72	−2.67
4	258	266.5	254.5	−3.31	1.35

N. B.: $\Delta\nu_i\,\% = \frac{\nu_{\text{obs.}}-\nu_{\text{calc.}}}{\nu_{\text{obs.}}}\times 100$.

Table 3. Symmetrized force constants in mdyn/A (constants have been scaled with bond length) for NCl_3.

	F_{11}	F_{12}	F_{22}	F_{33}	F_{34}	F_{44}
L Matrix approximation method	3.54	0.79	0.51	2.50	0.37	0.42
	(2.58)	(0.60)	(0.61)	(2.19)	(0.22)	(0.44)
Simple UBFF	2.67	0.49	0.62	1.62	0.24	0.62
Lone Pair Model	2.94	0.63	0.49	2.18	0.18	0.49

In UBFF, we have to determine only three force constants from four known frequencies and therefore the problem is overdetermined. An iterative least squares treatment suggested by MANN et al.[15], was employed using a judiciously chosen initial set of force constants. It was, however, not possible to get satisfactory results since the choice of different sets of initial constants led to slightly different converged force constants. The constants summarized in Table 4 refer to the mean values of a number of such attempts. In the lone-pair model, there are four constants to be determined from four known vibrational frequencies but the direct solution of the problem leads to complex values for the force constants. We have, therefore, used the least squares adjustment technique referred to above for evaluating the force constants. The force constants thus obtained are expected to be more reliable than those obtained from the simple UBFF since the same set of converged force constants was obtained with different choices of the initial set in the present method.

Table 4. Force constants for NCl_3.

	K or K_r (mdyn/A)	H or H_α (mdyn-A/r^2)	F or F_r (mdyn/A)	$F_{r\alpha}$ (mdyn/A)
Simple UBFF	1.36	0.35	0.55	
Lone Pair Model	2.00	0.30	0.40	0.15

Results and Discussions

The symmetrized force constants calculated by *L*-matrix approximation method, the simple UBFF and the lone-pair model have been summarized in Table 3. The symmetrized force constants obtained by *L*-matrix approximation are considerably larger than those obtained by the other two methods. This may be due to the appreciable mixing of two modes in the same species. An empirical correction[14] has already been suggested to calculate force constants in such cases. However, in the preceding section we have seen that this correction leads to imaginary force constants in A_1-species. Interestingly in E-species this correction gives real force constants which are in good agreement with the results obtained by the lone-pair model. The limiting values of the force constants in A_1-species also lead to the same conclusion. Indeed, still more modifications are needed to improve the applicability of *L*-matrix approximation method but due to the non-availability of additional data we can not suggest any such modification at present.

The results of the lone-pair model are nearer to the results of GVFF (approximate) than the results of simple UBFF. The percentage deviations between the observed and calculated frequencies are shown in Table 2. We are led to the conclusion that the lone-pair model is a better approximation than the simple UBFF to fix the vibration frequencies.

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On the Application of OVFF to MX_6 Type Ions

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Force constants for nine ions belonging to O_h point group have been evaluated by using Orbital Valence Force Field. The constants have been compared with their values obtained by using Urey-Bradley Force Field. The validity of the two methods has been discussed.

Introduction

Simplified force fields such as Urey-Bradley Force Field (UBFF) and Orbital Valence Force Field (OVFF) play very important roles in the determination of molecular force fields of polyatomic molecules, specially when additional experimental data e. g. Coriolis coupling constants or frequencies of isotopic species are not available. Thus it becomes necessary to test carefully the validity of these model force fields and to assess their relative merits. Recently, Kim et al. [1] have emphasized the applicability of OVFF and have shown its superiority over UBFF in hexafluorides. We have also been interested in the studies of MX_6 type molecules and ions possessing O_h symmetry to see whether the superiority of the OVFF over UBFF claimed by Kim et al. [1] in hexafluorides holds in hexachlorides and hexabromides also and have shown in a recent paper [2] that it does not hold. However, in the previous paper [2] only a limited number of ions and one molecule were studied, it was thought worthwhile to extend the work. In the present communication the OVFF has been applied to nine ions. Thakur et al. [3] have already reported the UBFF constants for these ions. An attempt has been made to judge the suitability of these two model force fields for different hexahalides.

Method of Calculations

The elements of the kinetic and potential energy matrices used by us are the same as reported in our earlier paper [2]. The vibrational frequencies for the first six ions i. e. PF_6^-, AsF_6^-, SbF_6^-, SiF_6^{--}, GeF_6^{--}, SnF_6^{--}, have been given by Begun and Rutenberg [4], and data for the remaining ions i. e. $ReCl_6^{--}$, $ReBr_6^{--}$, $OsCl_6^{--}$ were taken from Nagarajan's paper [5]. An initial set of force constants was obtained by an educated guess. This set was refined using the weighted least squares process described by Mann et al. [6]. The elements of the Jacobian matrix were calculated by giving an increment of 0.01 mdyn/A to each of the force constants in turn and determining the corresponding changes in frequencies. A new Jacobian was constructed after each iteration and the process repeated. Convergence was obtained usually after three or four itera-

Table 1. OVFF constants (in mdyn/A) for some MX_6 type ions.

Molecule	*K*	*D*	*F*	*F′*
PF_6^-	2.71	0.86	0.88	0.03
	(2.95)	(0.11)	(0.92)	(−0.14)
AsF_6^{--}	3.12	0.49	0.52	0.00
	(3.46)	(0.13)	(0.42)	(−0.11)
SbF_6^{--}	3.69	0.00	0.32	−0.19
	(3.69)	(−0.03)	(0.33)	(−0.22)
SiF_6^{--}	2.03	0.27	0.72	−0.07
	(2.06)	(0.05)	(0.73)	(−0.10)
GeF_6^{--}	2.16	0.16	0.52	−0.06
	(2.16)	(0.00)	(0.55)	(−0.09)
SnF_6^{--}	2.41	0.01	0.35	−0.07
	(2.55)	(0.06)	(0.33)	(−0.15)
$ReCl_6^{--}$	1.38	−0.07	0.27	−0.03
	(1.37)	(−0.03)	(0.27)	(−0.06)
$ReBr_6^{--}$	1.06	0.10	0,23	0.00
	(1.03)	(−0.03)	(0.29)	(−0.04)
$OsCl_6^{--}$	1.31	0.04	0.28	−0.01
	(1.52)	(0.00)	(0.21)	(−0.07)

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