A new look at molecular vibrations : Part II

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A new look at molecular vibrations, developed in relation to pyramidal XY_3 molecules, resulted in fresh results with respect to force constants and mean amplitudes of vibration of twelve such molecules. Extending this study to fourteen more molecules in this paper, it is found that the new procedure leads to interesting results in these cases as well.

1. INTRODUCTION

Wilson's group theoretical method has been a powerful tool in the evaluation of force constants of polyatomic molecules. However, there have been some imperfections inasmuch as some internal coordinates have not been taken into account so far. Additional internal coordinates naturally mean additional force constants but it is possible to separate secondary force constants from primary force constants and the latter force con tants may be evaluated from spectral frequencies. Further, the evaluation of these primary force constants may be carried out easily through an understanding and application of the kinetic constants of molecules. Such a comprehensive application of the group theoretical method has led to satisfactory results which were presented under the title *A new look at molecular vibrations* (Thirugnanasambandam & Mohan 1975a). This procedure, is now extended to fourteen more cases of the pyramidal type of molecules in this paper forming Part II of the series while the earlier paper will be referred to as Part I of this series. Of these fourteen cases, three are oxygenated cases and the eleven are halogenated molecules. The symmetry coordinates, the F matrix, the G matrix, the K matrix and other details of the procedure are the same as those given in Part I. The results of the present investigation are once again interesting and confirm the potentialities of the new procedure in leading to satisfactory results in the study of molecular vibrations. The validity of the force field has also been tested by evaluating the mean amplitudes of vibration, using the present values of the force constants. The mean amplitudes appear to be reasonable and they are in the expected range.

2. RESULTS AND DISCUSSION

Results relating to three oxygenated molecules and eleven halogenated molecules of the pyramidal XY_3 type under investigations discussed here. Table 1 gives the structural parameters and the vibrational frequencies of these

molecules. Their kinetic constants are tabulated in table 2. Table 3 deals with the force constants evaluated here. The mean amplitudes evaluated in the present investigation are reported in table 4. The results and those of the earlier workers are compared in table 5.

Table 1. Structural parameters and vibrational frequencies.

Sl. No.	Molecule	d Å	α deg.	$\nu_1(A_1)$	$\nu_2(A_2)$	$\nu_3(E)$	$\nu_4(E)$	Ref.
						cm^{-1}		
1.	ClO_3	1·60	89°	933	652	963	480	$a-c$
2.	BrO_3	1·68	89°	800	442	828	350	$a-c$
3.	IO_3	1·79	89°	780	357	809	362	$a-c$
4.	$SbCl_3$	2·325	99°30′	377	164	356	128	$d-f$
5.	$SbBr_3$	2·51	97°	227	110	236	92	d, g
6.	SbI_3	2·67	99°	177	89	147	71	d, e
7.	$BiCl_3$	2·48	100°	288	130	242	100	d, h, e
8.	$BiBr_3$	2·63	100°	196	104	165	90	d, e
9.	BiI_3	2·81	100°	145·4	90·2	115·2	71	e
10.	CF_3	1·32	109°	937	697	1116	508	h
11.	NF_3	1·371	102°6′	1031·97	647·18	908·4	492·59	a, d
12.	$^{14}NCl_3$	1·7	106°	540·5	349	643	257	i, j
13.	$SiCl_3$	2·01	110°	489	249	587	179	h
14.	$SiBr_3$	2·15	110°	362	166	470	11	h

a Wilson & Polo (1952)
b Mckean & Schatz (1956)
c Landolt-Bornstein (1951)
d Sutton (1958)
e Manley & Williams (1965)

f Davis & Oetjen (1958)
g Cross & Ginsburg (1956)
h Venkateswarlu & Sundaram (1956)
i Otake et al (1968)
j Bayersdorfer (1968)

Table 2. Kinetic constants (10^{-23} g).

S.No.	Molecule	k_d	k_{dd}	k_α	$k_{d\alpha}$	$k'_{d\alpha}$	$k''_{d\alpha}$
1.	ClO_3	2·0076	0·0609	0·2621	−0·0293	−0·0324	0·1435
2.	BrO_3	2·2723	0·0201	0·2888	−0·0213	0·0114	0·0888
3.	IO_3	2·3874	0·0088	0·3012	−0·0167	−0·0054	0·0635
4.	$SbCl_3$	4·8262	0·2239	0·5796	0·0027	−0·0798	0·2655
5.	$SbBr_3$	9·5349	0·7571	1·1484	−0·0889	−0·3056	0·8804
6.	SbI_3	14·1363	1·6402	1·6451	−0·1501	−0·6556	1·6421
7.	$BiCl_3$	5·1541	0·1594	0·6927	0·0280	−0·0501	0·1880
8.	$BiBr_3$	10·4702	0·6282	1·2420	−0·0099	−0·2284	0·6958
9.	BiI_3	15·4725	1·3193	1·8038	−0·0768	−0·4995	1·3657
10.	CF_3	2·1265	0·3625	0·2065	−0·0003	−0·1249	0·2677
11.	NF_3	2·2052	0·2296	0·2451	−0·0279	0·1703	0·2915
12.	$^{14}NCl_3$	3·7122	0·6981	1·0455	−0·0963	−0·4351	0·9260
13.	$SiCl_3$	4·0881	0·6543	0·4073	0·0203	−0·2203	0·4749
14.	$SiBr_3$	8·5813	1·7187	0·7640	−0·0380	−0·5901	1·2252

Table 3. Force constants (10^5 dynes cm^{-1}).

S.No.	Molecule			f_a	f_{ax}	f'_{d_a}	f''_d
1.	ClO$_3$	6·1109	−0·0362	0·2530	0·0146	0·0218	0·1657
2.	BrO$_3$	5·3046	−0·1131	0·1468	0·0120	0·0094	0·0529
3.	IO$_3$	5·3760	−0·1224	0·1192	−0·0007	0·0005	0·0265
4.	SbCl$_3$	2·1664	0·1764	0·0410	0·0074	0·0010	0·0211
5.	SbBr$_3$	1·6024	0·0569	0·0386	0·0015	−0·0029	0·0327
6.	SbI$_3$	1·0275	0·2413	0·0339	0·0020	−0·0026	0·0383
7.	BiCl$_3$	1·2062	0·1820	0·0280	0·0066	0·0009	0·0093
8.	BiBr$_3$	1·0997	0·1952	0·0397	0·0036	−0·0028	0·0238
9.	BiI$_3$	0·8158	0·2016	0·0382	0·0049	−0·0006	0·0326
10.	CF$_3$	6·0414	0·8538	0·2447	0·0552	−0·0038	0·3560
11.	NF$_3$	5·4521	1·2791	0·2507	0·0154	−0·0607	0·3372
12.	NCl$_3$	2·4896	0·3904	0·1135	0·0170	0·0050	0·1200
13.	SiCl$_3$	3·1553	0·3398	0·0622	0·0182	0·0008	0·0799
14.	SiBr$_3$	2·8164	0·4635	0·0475	0·0099	0·0038	0·0891

Table 4. Mean amplitudes of vibration at 298·16 K (A).

S.No.	Molecule	$(\sigma_d)^{\frac{1}{2}}$ (X−Y)	$(\sigma_q)^{\frac{1}{2}}$ (Y...Y)
1.	ClO$_3$	0·0466	0·0641
2.	BrO$_3$	0·0462	0·0842
3.	IO$_3$	0·0453	0·0841
4.	SbCl$_3$	0·0496	0·1156
5.	SbBr$_3$	0·0545	0·1160
6	SbI$_3$	0·0706	0·1196
7.	BiCl$_3$	0·0581	0·1420
8.	BiBr$_3$	0·0644	0·1177
9.	BiI$_3$	0·0784	0·1185
10.	CF$_3$	0·0546	0·0611
11.	NF$_3$	0·0562	0·0605
12.	^{14}NCl$_3$	0·0549	0·0687
13.	SiCl$_3$	0·0548	0·0911
14.	SiBr$_3$	0·0538	0·0958

The behaviour of the kinetic constants of the molecules studied here is in line with the observations in our earlier papers. Basically, there are two classes of kinetic constants which may be called complementary kinetic constants and supplementary kinetic constants. The complementary kinetic constants are themselves distributed in two groups. The first group of complementary kinetic constants is provided by positive and negative bond-angle interaction kinetic constants which annul themselves. The second group of complementary kinetic constants consists of bending kinetic constants and angle-angle interaction kinetic constants which neutralise themselves on summation. On the other hand, the remaining kinetic constants viz., stretching kinetic constants and

Table 5. Mean amplitudes of vibration at 298·16 K (Å).

S.No.	Molecule	$(\sigma_d)^{\frac{1}{2}}$ $(X-Y)$	$(\sigma_q)^{\frac{1}{2}}$ $(Y...Y)$	
1.	$SbCl_3$	0·0496	0·1156	*P.W.*
		0·053	0·116	*a*
		0·0457	0·0988	*b*
2.	$SbBr_3$	0·0545	0·1160	*P.W.*
		0·052	0·131	*a*
		0·0483	0·0981	*b*
3.	SbI_3	0·0706	0·1196	*P.W.*
		0·0706	0·1490	*c*
4.	$BiCl_3$	0·0581	0·1420	*P.W.*
		0·0560	0·1208	*b*
5.	$BiBr_3$	0·0644	0·1176	*P.W.*
		0·0647	0·1280	*c*
6.	BiI_3	0·0784	0·1185	*P.W.*
		0·0789	0·1387	*c*
7.	NF_3	0·0562	0·0605	*P.W.*
		0·048	0·056	*a*

P.W.   Present Work.
  a   Cyvin (1968)
  b   Sundaram (1962)
  c   Manly *et al* (1965)

bond-bond interaction kinetic constants form the set of supplementary kinetic constants. Collectively, all these kinetic constants appear to determine the nature of molecular vibrations characteristic of the molecule concerned and the molecular type to which the molecule belongs.

From table 2, the following observations are made regarding the behaviour of kinetic constants.

1. The kinetic constants k_{d_x}' appears to assume negative sign in all molecules.

2. The bond-bond interaction kinetic constant k_{dd} is positive in all the cases studied here.

3. The angle-angle interaction kinetic constant $k_{\alpha\alpha}$ assumes positive sign in some cases and negative sign in most of the cases depending upon the molecule.

4. When the mass of the X atom increases (for the same Y atom) the stretching kinetic constant k_d increases while the interaction kinetic constant k_{dd} decreases in all the molecules.

5. The other kinetic constants follow their characteristic trends depending upon the molecules.

The equations relating to these molecules and ions have been solved by the procedures outlined in the earlier papers (Thirugnanasambandam *et al* 1969, 1974a, 1974b; 1975a, 1975b, 1975c, 1976a, 1976b). The symmetry force constants thus obtained are combined to yield the individual force constants. From table 3, the following observations are made.

1. The interaction force constant f_{dd} is negative for molecules which have oxygen as the Y atoms. The force constant $f_{\alpha\alpha}$ is positive in ClO_3 and BrO_3 molecules while it appears to be negative in IO_3 molecule.

2. The interaction force constants f_{dd} and $f_{\alpha\alpha}$ appear to assume positive signs in all the molecules having halogen as the Y atoms.

3. The bond-distant angle interaction force constant $f_{d\alpha}'$ appears to be negative in $SbBr_3$, $BiBr_3$, BiI_3, CF_3 and NF_3 molecules.

Considering the force constants in related molecules, it is interesting to note the extraordinary regularities in the values obtained here in relation to the oxygenated molecules as well as halogenated molecules. The force constants obtained here, in molecules $SbCl_3$, $SbBr_3$, SbI_3, $BiCl_3$, $BiBr_3$ and BiI_3, appear to exhibit uniform gradations.

The present values of the force constants stand in good comparison with earlier values. The bending force constant f_α and the interaction force constants $f_{\alpha\alpha}$, $f_{d\alpha}'$, $f_{d\alpha}''$ assume a considerable lowering of values as a consequence of the recognition of β in relation to the bending modes.

Using the present set of force constants, the values of the mean amplitudes of vibration for all the molecules at 298·16 K have been computed. The present values of the mean amplitudes relating to the bonded as well as the non-bonded distances of the pyramidal XY_3 molecules compare favourably with the calculated values of the earlier authors wherever such data are available. The mean amplitudes evaluated in the present investigation may be seen to be reasonable and in the expected range. These results are useful in the interpretation of electron diffraction data of these molecules.

3. Conclusion

All the G.Q.V.F.F. force constants have been evaluated for fourteen molecules using the new procedure developed in this laboratory. The force constants thus obtained seem to be highly reasonable. The interaction force constants seem to assume, in magnitude and in sign, significant values characteristic of the molecules studied here. The mean amplitudes of these molecules evaluated in the present study are also found to be reasonable.

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