MOLECULAR CONSTANTS OF SOME TETRAHALIDE MOLECULES OF GROUP IV A

By P. C. Sarkar*, G. C. Singh and Km. S. Roy Choudhury**

Department of Physics, St. Andrew's College, Gorakhpur

(Received July 5, 1977)

Molecular constants viz. potential constants, mean amplitudes of vibration, Coriolis coupling constants of (2×2) f_2 species and kinetic constants of some tetrahalide molecules of Group IV A calculated by kinetic constant method has been reported and analysed.

1. Introduction

In molecular dynamics, Thirugnanasambandam and Srinivasan [1, 2] have introduced a very interesting set of quantities called kinetic constants. These are certain reduced masses and are related to inverse elements of Wilson's [3] G-matrices in the same way as the valence force constants are related to symmetry force constants.

Apart from studying the salient features of the kinetic constants, Thirugnanasambandam and Srinivasan [1, 2] proposed certain relation between the ratio of a pair of symmetry force constants and the corresponding pair of kinetic constants for the solution of second and third order secular equations of molecular systems belonging to $XY_3(D_{3h})$, $XY_3(C_{3v})$, $XY_4(D_{4h})$, $XYZ_2(C_{2v})$, $XYZ_3(C_{3v})$, $XY_4(T_d)$ and $XY_6(O_h)$ symmetry [2, 4–8].

In the present communication, valence force constants calculated by the kinetic constant method [1, 2] have been reported along with mean amplitudes of vibration calculated by an extension of kinetic constant method proposed by Sarkar and Singh [9, 10]. Furthermore, effect of atomic mass-ratio on the Coriolis coupling constants have also been examined graphically. Similar to kinetic constants, some interesting mutual relations between the valence force constants as well as between bonded mean square amplitude quantities have been pointed out and discussed.

* Address: Department of Physics, St. Andrew's College, Gorakhpur, India 273 001.
** Present address: Department of Chemistry, University of Gorakhpur, India 273 001.

2. Theoretical consideration

Tetrahalides of Group IV A under the present study belong to T_d point group and their fundamental vibrations are distributed among different species as

$$\Gamma = a_1 + e + 2f_2 .$$

Symmetry force constants and symmetrized mean square amplitude matrices of a_1 and e species can be calculated directly, whereas those for the second order f_2 species involve solution of the following equations:

$$F_{33}G_{33} + F_{44}G_{44} + 2F_{34}G_{34} = \lambda_3 + \lambda_4,$$

$$(F_{33}F_{44} - F_{34}^2)(G_{33}G_{44} - G_{34}^2) = \lambda_3\lambda_4, \tag{1}$$

$$\Sigma_{33}G_{33}^{-1} + \Sigma_{44}G_{44}^{-1} + 2\Sigma_{34}G_{34}^{-1} = \Delta_3 + \Delta_4,$$

$$(\Sigma_{33}\Sigma_{44} - \Sigma_{34}^2)[G_{33}^{-1}G_{44}^{-1} - (G_{34}^{-1})^2] = \Delta_3\Delta_4, \tag{2}$$

where

$$\Delta_i = \frac{h}{8\pi^2 \nu_i} \coth \frac{h\nu_i}{2KT},$$

the rest of the symbols have the usual meaning.

For the solution of first set of equations involving three symmetry force constants, exponents of kinetic constant method [1, 2, 4–8] have proposed the following relations as postulates:

$$\frac{F_{ij}}{F_{jj}} = \frac{K_{ij}}{K_{jj}} = \frac{G_{ij}^{-1}}{G_{jj}^{-1}}. \tag{3}$$

Recently Alix, Müller and Mohan [11] have pointed out that this method is just equivalent to Peacock and Müller's L matrix method [12] viz. $L_{ij} = 0$, $i < j$. Sarkar and Singh [9, 10] extended the kinetic constant method for the evaluation of symmetrized mean square amplitude matrices by proposing the following as postulate:

$$-\frac{\Sigma_{ij}}{\Sigma_{ii}} = \frac{K_{ij}}{K_{jj}} = \frac{G_{ij}^{-1}}{G_{jj}^{-1}}. \tag{4}$$

3. Results and discussion

The relevant expressions for the evaluation of the molecular constants have been presented in Table I. Frequencies reported by Bosworth and Clark [13] have been used for the present work. Kinetic constants have been presented in Table II. Symmetry force constants for the $(2 \times 2)f_2$ species calculated by the present method are listed in Table III along with the Coriolis coupling constant ξ_3 and ξ_4 calculated by Cyvin's [14] comprehensive equation. For the sake of comparison, symmetry force constants calculated by adopting orbital valence force field (Sanyal, Ganguli and Dixit [15]) and Urey Bradley force field

TABLE I

Molecular constants in terms of reciprocals of atomic masses, symmetry force constants and symmetrized mean square amplitude matrices

Kinetic constants	Valence force constants	Mean square amplitude quantities
$K_d = \dfrac{\mu_y+3\mu_x}{\mu_y(\mu_y+4\mu_x)}$	$f_d = \frac{1}{4}(F_{11}+3F_{33})$	$\sigma_d = \frac{1}{4}(\Sigma_{11}+3\Sigma_{33})$
$K_{dd} = \dfrac{\mu_x}{3\mu_y(\mu_y+4\mu_x)}$	$f_{dd} = \frac{1}{4}(F_{11}-F_{33})$	$\sigma_{dd} = \frac{1}{4}(\Sigma_{11}-\Sigma_{33})$
$K_\alpha = \dfrac{13\mu_y+28\mu_x}{36\mu_y(\mu_y+4\mu_x)}$	$f_\alpha = \frac{1}{3}F_{22}+\frac{1}{2}F_{44}$	$\sigma_\alpha = \frac{1}{3}\Sigma_{22}+\frac{1}{2}\Sigma_{44}$
$K_{\alpha\alpha} = -\dfrac{1}{18\mu_y}$	$f_{\alpha\alpha} = -\frac{1}{6}F_{22}$	$\sigma_{\alpha\alpha} = -\frac{1}{6}\Sigma_{22}$
$K'_{\alpha\alpha} = \dfrac{4\mu_x-5\mu_y}{36\mu_y(\mu_y+4\mu_x)}$	$f'_{\alpha\alpha} = \frac{1}{3}F_{22}-\frac{1}{2}F_{44}$	$\sigma'_{\alpha\alpha} = \frac{1}{3}\Sigma_{22}-\frac{1}{2}\Sigma_{44}$
$K_{d\alpha} = \dfrac{\sqrt{2}\mu_x}{3\mu_y(\mu_y+4\mu_x)}$	$f_{d\alpha} = \dfrac{F_{34}}{2\sqrt{2}}$	$\sigma_{d\alpha} = \dfrac{\Sigma_{34}}{2\sqrt{2}}$

TABLE II

Kinetic constant (in $\times 10^{-23}$ g) of some XY_4 type molecule

Mol.	K_d	K_{dd}	K_α	$-K_{\alpha\alpha}$	$-K'_{\alpha\alpha}$	$K_{d\alpha} = -K'_{d\alpha}$	$\Sigma K_{ij} = \dfrac{4}{\mu_y}$
CF_4	2.4731	0.2270	0.6850	0.1752	−0.0159	0.3210	12.6160
SiF_4	2.5783	0.1919	0.7551	0.1752	0.0543	0.2714	12.6160
CCl_4	4.5284	0.4521	1.2208	0.3269	−0.0869	0.6394	23.5392
$SiCl_4$	4.6568	0.4093	1.3064	0.3269	−0.0013	0.5789	23.5392
$GeCl_4$	4.9117	0.3244	1.4764	0.3269	0.1686	0.4587	23.5392
$SnCl_4$	5.0839	0.3669	1.5911	0.3269	0.2834	0.3775	23.5392
$SiBr_4$	10.2157	1.0160	2.7577	0.7369	−0.1898	1.4369	53.0552
$GeBr_4$	10.5626	0.9008	2.9885	0.7369	0.0407	1.2739	53.0600
$SnBr_4$	10.8473	0.8061	3.1782	0.7369	0.2303	1.1400	53.0624
SiI_4	16.0757	1.6634	4.2803	1.1703	−0.4011	2.3525	84.2640
GeI_4	16.4589	1.5359	4.5356	1.1703	−0.1459	2.1721	84.2664
SnI_4	16.7995	1.4229	4.7621	1.1703	0.0803	2.0123	84.2732

TABLE III

Values of symmetry force constants (in mdyne/Å) and Coriolis coupling constants

Force field	Symmetry force constants			Coriolis coupling constant		Mass ratio m_x/m_y
	F_{33}	F_{34}	F_{44}	ξ_{33}	ξ_{44}	
			CF_4			
K. C.	7.6676	1.2837	0.9461	1.0460	−0.5460	0.6321
O. V. F. F.	6.7547	0.7333	0.7742			
U. B. F. F.	6.5494	0.6341	0.7541			
			SiF_4			
K. C.	6.6296	0.4116	0.4340	0.6360	−0.1360	1.4784
O.V.F. F.	6.1377	0.1653	0.4432			
U. B. F. F.	6.0614	0.1370	0.4497			
			CCl_4			
K. C.	3.4823	0.6308	0.3955	1.0258	−0.5258	0.3388
O. V. F. F.	1.8447	0.3773	0.4467			
U. B. F. F.	2.5604	0.3591	0.4603			
			$SiCl_4$			
K. C.	3.3126	0.2820	0.2248	0.7902	−0.2902	0.7924
O. V. F. F.	2.9473	0.1467	0.2328			
U. B. F. F.	2.9222	0.1387	0.2340			
			$GeCl_4$			
K. C.	2.7708	0.1346	0.1707	0.5365	−0.0365	2.0477
O. V. F. F.	2.7237	0.1053	0.1712			
U. B. F. F.	2.7074	0.0955	0.1712			
			$SnCl_4$			
K. C.	2.5231	0.0602	0.1058	0.3614	+0.1386	3.3484
O. V. F. F.	2.5663	0.0507	0.1158			
U. B. F. F.	2.6021	0.1349	0.1082			
			$SiBr_4$			
K. C.	2.8042	0.2574	0.1626	0.8881	−0.3881	0.3516
O. V. F. F.	2.3913	0.0987	0.1648			
U. B. F. F.	2.2627	0.1026	0.1768			
			$GeBr_4$			
K. C.	2.2904	0.1578	0.1308	0.7322	−0.2322	0.9085
O. V. F. F.	2.5313	0.1067	0.0183			
U. B. F. F.	2.0860	0.0733	0.1738			
			$SnBr_4$			
K. C.	2.0775	0.0844	0.0892	0.5718	−0.0718	1.4856
O. V. F. F.	2.1417	0.0693	0.0422			
U. B. F. F.	2.0155	0.0509	0.0898			
			SiI_4			
K. C.	2.0794	0.1913	0.1115	0.9230	−0.4230	0.2214
O. V. F. F.	1.7423	0.0747	0.1168			
U. B. F. F.	1.6440	0.0761	0.1222			

TABLE III (continued)

Force field	Symmetry force constants			Coriolis coupling constant		Mass ratio m_x/m_y
	F_{33}	F_{34}	F_{44}	ξ_{33}	ξ_{44}	
			GeI_4			
K. C.	1.8536	0.1303	0.0930	0.8018	−0.3018	0.5720
O. V. F. F.	1.5977	0.0453	0.0987			
U. B. F. F.	1.5704	0.0370	0.0999			
			SnI_4			
K. C.	1.4525	0.0801	0.0681	0.6962	−0.1962	0.9354
O. V. F. F.	1.3777	0.0493	0.0687			
U. B. F. F.	1.3745	0.0457	0.0692			

TABLE IV

Valence force constants (in mdyne/Å) of some XY_4 type molecules

Mol.	f_d	f_{dd}	f_α	$-f_{\alpha\alpha}$	$-f'_{\alpha\alpha}$	$f_{d\alpha} = -f'_{d\alpha}$	$\Sigma f_{ij}/\lambda_1 = \frac{4}{\mu_y}$
CF_4	8.0600	0.3923	0.7078	0.1173	0.2384	0.4539	76.0001
SiF_4	6.7668	0.1372	0.3038	0.0434	0.1302	0.1455	76.0001
CCl_4	3.7166	0.2342	0.3042	0.0532	0.0913	0.2230	141.8002
$SiCl_4$	3.4191	0.1065	0.1613	0.0245	0.0635	0.0997	141.8002
$GeCl_4$	2.8973	0.1265	0.1216	0.0181	0.0491	0.0476	141.8002
$SnCl_4$	2.7115	0.1884	0.0738	0.0105	0.0319	0.0213	141.8002
$SiBr_4$	2.8194	0.0152	0.1189	0.0188	0.0437	0.0910	319.6011
$GeBr_4$	2.3716	0.0812	0.0946	0.0146	0.0362	0.0558	319.6011
$SnBr_4$	2.1387	0.0611	0.0631	0.0093	0.0261	0.0298	319.6011
SiI_4	2.0764	−0.0030	0.0833	0.0138	0.0282	0.0676	507.6013
GeI_4	1.8450	−0.0085	0.0686	0.0111	0.0244	0.0461	507.6013
SnI_4	1.4977	0.0444	0.0490	0.0075	0.0191	0.0283	507.6013

(Pandey, Sharma and Kumar [16]) have also been presented in Table III in parenthesis. Valence force constants calculated by the present method have been presented in Table IV. Symmetrized mean square amplitude quantities, calculated from the symmetrized mean square amplitude matrices by the kinetic constant method proposed by Sarkar, Singh [9, 10] at three different temperatures are given in Table V whereas mean amplitude of vibration for bonded as well as non-bonded atom pairs at three different temperatures are presented in Table VI.

It is quite evident from Table III that the various symmetry force constants calculated by the present method are in reasonable agreement with those calculated by O. V. F. F. and U. B. F. F. methods.

TABLE V

Mean square amplitude quantities (in $10^{-4} \times$ Å^2) of some XY_4 type molecules

Mol.	Temp.	σ_d	$-\sigma_{dd}$	σ_α	$-\sigma_{\alpha\alpha}$	$-\sigma'_{\alpha\alpha}$	$\sigma_{d\alpha} = -\sigma'_{d\alpha}$	$\Sigma\sigma_{ij}/\Delta_1 = 4\mu_y$
	0	18.5683	2.9338	73.3431	10.2122	32.4944	10.3144	2105.260
CF_4	298	18.6946	2.8949	82.4426	13.0707	30.1597	10.3564	2105.260
	500	19.7786	2.8226	103.6233	18.4136	29.9690	10.8417	2105.260
	0	15.0614	1.3274	85.4259	16.7909	18.2621	5.4953	2105.260
SiF_4	298	15.3466	1.2645	127.6267	29.8029	8.4151	5.5699	2105.260
	500	17.0152	1.1596	188.3779	46.2823	3.2488	6.0942	2105.260
	0	24.8098	4.8241	99.2431	11.1001	54.8428	16.7088	1128.348
CCl_4	298	26.4313	4.5258	147.6350	23.3460	54.2509	17.4549	1128.348
	500	31.7546	4.6397	213.6688	37.1490	65.0727	20.5206	1128.348
	0	18.3291	2.3633	97.6955	16.3749	32.1958	9.1776	1128.348
$SiCl_4$	298	20.8331	2.0817	197.2082	48.6164	2.7427	10.1633	1128.348
	500	27.0329	2.1151	340.6029	79.5233	22.5098	12.9279	1128.348
	0	15.8308	1.2752	93.1049	19.0211	17.0204	4.7701	1128.348
$GeCl_4$	298	20.0109	1.2813	263.7447	64.9275	4.0347	5.9374	1128.348
	500	27.9969	1.5662	429.2002	106.8696	1.7216	8.2438	1128.348
	0	15.2174	1.0707	111.7821	24.9752	11.8814	3.2801	1128.348
$SnCl_4$	298	20.1235	1.3489	425.0906	110.5886	−17.2639	4.3422	1128.348
	500	28.9632	1.8883	701.7480	183.4396	−32.0105	6.2129	1128.348
	0	17.4894	2.9791	91.3015	12.4399	41.5417	11.4535	500.6240
$SiBr_4$	298	22.4693	2.1505	284.8932	61.6180	38.4211	13.7764	500.6240
	500	31.3912	2.0990	461.7008	102.4721	51.8124	18.7399	500.6240
	0	13.9988	1.6825	69.8229	14.1291	13.3352	6.5948	500.624
$GeBr_4$	298	22.0375	1.5479	333.7801	79.1714	17.0945	9.9188	500.624
	500	33.2337	1.9442	550.8754	131.8723	23.3862	14.7941	500.624
	0	12.9471	1.1492	46.5459	17.7295	24.3722	4.7146	500.624
$SnBr_4$	298	22.6096	1.0758	282.5972	124.3122	−214.6517	7.9217	500.624
	500	34.9804	1.4175	470.4057	207.6262	−360.0992	12.1734	500.624
	0	19.2493	3.7538	96.9766	11.5313	50.8515	13.9497	315.208
SiI_4	298	28.1582	2.4017	399.1414	83.4331	65.4088	18.5324	315.208
	500	41.3480	2.4442	654.4486	139.4171	96.7802	26.5569	315.208
	0	14.2849	1.9232	82.8857	12.8888	31.3306	8.0200	315.208
GeI_4	298	26.9597	1.0965	458.6964	103.8416	43.3301	13.8828	315.208
	500	42.1639	1.1994	762.4020	173.7970	67.2141	21.4571	315.208
	0	13.7335	1.5799	87.7795	15.6651	25.1190	6.3638	315.208
SnI_4	298	31.0949	1.6045	633.5228	153.5140	19.4667	13.5889	315.208
	500	49.8337	2.2914	1057.9418	257.1240	29.4459	21.6616	315.208

TABLE VI

Mean amplitude of vibration (in Å) of some XY_4 type molecules

Mol.	0 Å		298 Å	500 Å
CF_4	C–F	0.0430	0.0432	0.0445
	F–F	0.0508	0.0539	0.0659
SiF_4	Si–F	0.0388	0.0392	0.0413
	F–F	0.0604	0.0713	0.0851
CCl_4	C–Cl	0.0505	0.0523	0.0576
	Cl–Cl	0.0531	0.0675	0.0829
$SiCl_4$	Si–Cl	0.0428	0.0456	0.0520
	Cl–Cl	0.0605	0.0846	0.1106
$GeCl_4$	Ge–Cl	0.0398	0.0447	0.0529
	Cl–Cl	0.0644	0.1008	0.1276
$SnCl_4$	Sn–Cl	0.0390	0.0450	0.0538
	Cl–Cl	0.7067	0.1260	0.1607
$SiBr_4$	Si–Br	0.0418	0.0474	0.0560
	Br–Br	0.0531	0.0980	0.1255
$GeBr_4$	Ge–Br	0.0374	0.0469	0.0576
	Br–Br	0.0522	0.1095	0.1405
$SnBr_4$	Sn–Br	0.0360	0.0476	0.0591
	Br–Br	0.0473	0.1039	0.1336
SiI_4	Si–I	0.0439	0.0531	0.0643
	I–I	0.0517	0.1157	0.1483
GeI_4	Ge–I	0.0377	0.0519	0.0649
	I–I	0.0538	0.1270	0.1638
SnI_4	Sn–I	0.0371	0.0558	0.0706
	I–I	0.0578	0.1500	0.1937

4. Behavioural pattern of molecular constants

(a) Kinetic and potential constants: From Tables II and IV, it is seen that for systems with common central atom, kinetic constants increase with the mass of ligand atoms whereas valence force constants show opposite trend, this may be due to the increased separation between constituent atoms. In the case of valence force constant $f'_{\alpha\alpha}$ is negative and the rest of the force constants are all positive except for SiI_4 and GeI_4 for which bond-bond interaction constants are negative.

(b) Mean square amplitude quantities: Mean square amplitude quantities exhibit common features with kinetic constants in general i. e. these quantities increase with mass of ligand atoms when the mass of central atom remains constant.

Coriolis coupling constants

Coriolis coupling constants have been plotted against mass ratio m_x/m_y in Fig. 1 showing the general behaviour ξ_3 decreases with the increase in the mass ratio. This has been previously reported by many workers (Sanyal, Verma, Dixit [17]) in the case of $XY_4(T_d)$ symmetry molecules, and in the case of XY_6 octahedral system by Ahmad, Dixit

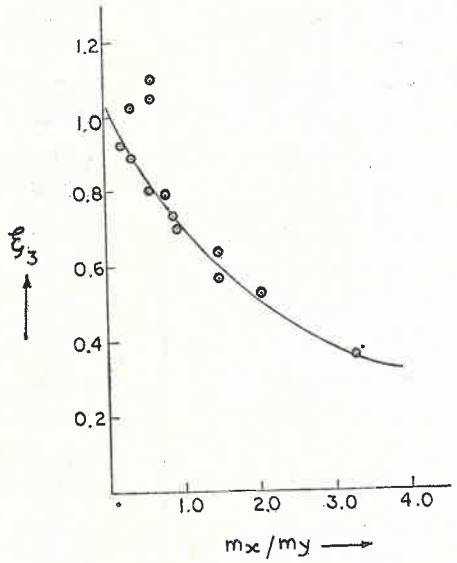

Fig. 1. Variation of Coriolis coupling with mass ratio of different systems

and Sanyal [18], Sanyal, Verma and Dixit [19]. The expected trend of ξ_3 values shows the correctness of symmetry force constants of $[2\times 2]f_2$ species which is further supported by the reasonable agreement between the present values of symmetry force constant and those reported in the literature adopting other force fields [15, 16].

Mutual relationships between molecular constants

Consideration of redundancy constraints due to Ford, Orville–Thomas [20] gives rise to some interesting mutual relationships between the molecular constants.

(a) Bond angle, bending, and angle-angle interaction constants are complementary i. e., their algebraic sums are zero.

(b) Stretching and bond-bond interaction constants exhibit supplementary behaviour as given below.

Bond angle interaction

Kinetic constant	Valence force-constant	Mean square amplitude quantities
$\Sigma K_{d\alpha}+\Sigma K'_{d\alpha}=0$	$\Sigma f_{d\alpha}+\Sigma f'_{d\alpha}=0$	$\Sigma\sigma_{d\alpha}+\Sigma\sigma'_{d\alpha}=0$
$12(2K_{d\alpha})+12(2K'_{d\alpha})=0$	$12(2f_{d\alpha})+12(2f'_{d\alpha})=0$	$12(2\sigma_{d\alpha})+12(2\sigma'_{d\alpha})=0$
$K_{d\alpha}+K'_{d\alpha}=0$	$f_{d\alpha}+f'_{d\alpha}=0$	$\sigma_{d\alpha}+\sigma'_{d\alpha}=0$

Bending and angle-angle interaction

Kinetic constant	Valence force constant	Mean square amplitude quantities
$\Sigma K_\alpha+\Sigma K_{\alpha\alpha}+\Sigma K'_{\alpha\alpha}=0$	$\Sigma f_\alpha+\Sigma f_{\alpha\alpha}+\Sigma f'_{\alpha\alpha}=0$	$\Sigma\sigma_\alpha+\Sigma\sigma_{\alpha\alpha}+\Sigma\sigma'_{\alpha\alpha}=0$
$6K_\alpha+24K_{\alpha\alpha}+6K'_{\alpha\alpha}=0$	$6f_\alpha+24f_{\alpha\alpha}+6f'_{\alpha\alpha}=0$	$6\sigma_\alpha+24\sigma_{\alpha\alpha}+6\sigma'_{\alpha\alpha}=0$
$K_\alpha+4K_{\alpha\alpha}+K'_{\alpha\alpha}=0$	$f_\alpha+4f_{\alpha\alpha}+f'_{\alpha\alpha}=0$	$\sigma_\alpha+4\sigma_{\alpha\alpha}+\sigma'_{\alpha\alpha}=0$

Stretching and bond-bond interaction

$\Sigma K_d+\Sigma K_{dd}$	$\Sigma f_d+\Sigma f_{dd}$	$\Sigma\sigma_d+\Sigma\sigma_{dd}$
$4K_d+12K_{dd}$	$4f_d+12f_{dd}$	$4\sigma_d+12\sigma_{dd}$
$4(K_d+3K_{dd})=\dfrac{4}{\mu_y}$	$4(f_d+3f_{dd})=\dfrac{4\lambda_1}{\mu_y}$	$4(\sigma_d+3\sigma_{dd})=4\Delta_1\mu_y$
$\Sigma K_{ij}=\dfrac{4}{\mu_y}$	$\dfrac{\Sigma f_{ij}}{\lambda_1}=\dfrac{4}{\mu_y}$	$\dfrac{\Sigma\sigma_{ij}}{\Delta_1}=4\mu_y$

From Tables II, IV and V the above relations are quite evident. It is found that for common central atom algebraic sum of the kinetic constant leads to $4\,m_y$ i. e. this is simply proportional to the mass of the y atoms. However, in the case of valence force constant and mean square amplitude quantities the situation is quite different because these quantities depend upon the frequencies of a species also. However the quotient of algebraic sums of valence force constants and λ_1 as well as the quotient of algebraic sums of mean square amplitude quantities and Δ_1 leads to four times the mass of ligand atom when the central atom remains the same in the case of the former and $4/m_y$ in the case of the latter. Similar observations have been made in the case of XY_3 molecules of D_{3h} symmetry by Sarkar and Singh [10].

REFERENCES

[1] P. Thirugnanasambandam, Proceedings of the Seminar on Raman and Infrared Spectroscopy, University of Kerala (India), p. 174 (1964).
[2] P. Thirugnanasambandam, S. Srinivasan, *J. Chem. Phys.* **50**, 2467 (1969).
[3] E. B. Wilson, *J. Chem. Phys.* **7**, 1047 (1939); **9**, 76 (1941).
[4] P. Thirugnanasambandam, S. Mohan, *J. Chem. Phys.* **61**, 470 (1974).
[5] P. Thirugnanasambandam, S. Mohan, *Indian J. Pure and Appl. Phys.* **12**, 206 (1974).
[6] P. Thirugnanasambandam, N. Karunanidhi, *Indian J. Phys.* **49**, 658 (1975).
[7] P. Thirugnanasambandam, S. Mohan, *Bull. Soc. Chim.* **84**, 987 (1975).
[8] P. Thirugnanasambandam, N. Karunanidhi, *Indian J. Phys.* **50**, 527 (1976).
[9] P. C. Sarkar, G. C. Singh, *Indian J. Phys.*, accepted for publication.
[10] P. C. Sarkar, G. C. Singh, *Spectrosc. Letter*, accepted for publication.
[11] A. J. P. Alix, A. Müller, N. Mohan, *J. Mol. Struct.* **27**, 440 (1975).
[12] C. J. Peacock, A. Müller, *J. Mol. Spectrosc.* **26**, 454 (1968).

[13] Y. M. Bosworth, R. J. H. Clark, *J. Chem. Soc.* (Dalton) 1749 (1974).
[14] S. J. Cyvin, L. Kristiansen, *Acta Chem. Scand.* **16**, 2453 (1962).
[15] N. K. Sanyal, A. K. Ganguli, L. Dixit, *Indian J. Phys.* **48**, 647 (1974).
[16] A. N. Pandey, D. K. Sharma, V. Kumar, *Indian J. Phys.* **50**, 871 (1976).
[17] N. K. Sanyal, D. N. Verma, L. Dixit, *Spectrosc. Letter* **9**, 697 (1976).
[18] Parvez Ahmad, L. Dixit, N. K. Sanyal, *Indian J. Pure and Appl. Phys.* **12**, 489 (1974).
[19] N. K. Sanyal, D. N. Verma, L. Dixit, *Acta Phys. Pol.* **A50**, 527 (1976).
[20] T. A. Ford, W. J. Orville-Thomas, *Spectrochim. Acta* **23A**, 579 (1967).