A new look at molecular vibrations

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An overlooked category of internal coordinates has been recognised in a recent study of molecular vibrations Taking this aspect into account, a fresh study of the force constants and the mean amplitudes of twelve molecules of the pyramidal XY_3 type is presented here with interesting results

1 Introduction

A recent study of the bent symmetrical XY_2 molecules (Thirugnanasambandam *et al* 1974a) appears to have brought out significant results in the understanding of molecular vibrations The reflex angle in the simple planar structure associated with these molecules provides an internal coordinate which demands our attention from considerations of molecular dynamics This additional internal coordinate obviously increases the number of such coordinates from the usual three to four in number Such a reasonable set of four internal coordinates naturally throws up seven force constants but, fortunately all of them are not independent More- over, a new symmetry coordinate has incidentally presented itself and it turns to be a redundant symmetry coordinate This redundant coordinate easily elimi- nates three of the seven force constants, leaving us with the well known four independent force constants to be evaluated from the three spectral frequencies characterising the structure Such a new approach has led to very interesting results relating to the force constants of these molecules

This new procedure is now extended to another basically important type of molecules viz., the pyramidal XY_3 molecules Naturally, there are three bonds and three interbond angles in this structure. At the same time, we are now called upon to recognise the three reflex angles also as not of unimportance in this regard Thus there are nine parameters which provide an equal number of internal coordinates All these nine internal coordinates are taken into account in framing a new set of symmetry coordinates consistent with Wilson's group theoretical method of analysis. It is interesting to note that three of these sym- metry coordinates are redundant and they are used to work out six redundancy constraints relating to force constants. Consequently, out of the total number of twelve force constants, only six are independent and these are the usual force

constants recognised in this molecular type over the years All these six independent force constants are evaluated here in twelve molecules, making use of the four spectral frequencies distributed in the two species associated with this molecular type

The procedure adopted here in the solution of the secular equation is the same as the one adopted in the study of the bent symmetrical triatomic molecules as well as the earlier study relating to planar tetratomic molecules (Thirugnanasambandam *et al* 1969, 1974a) The values of the force constants obtained here appear to be interesting from many points of view The results are found to provide a pleasing verification of the fundamental statement of Herzberg which has been the guiding principle in the evaluation of force constants in isotopic molecules all these years · *Since the isotopic molecules have the same electronic structure, the potential function under the influence of which the nuclei are moving is the same to a very high degree of approximation.*

The highly acceptable sets of force constants, as obtained here, are in turn utilised to find the mean amplitudes of the twelve molecules under consideration The results are again equally interesting and indicate that the present comprehensive procedure, involving all the internal coordinates, is reasonable and at the same time capable of leading to refreshingly significant results in the study of molecular vibrations

2. THEORETICAL CONSIDERATIONS

The pyramidal XY_3 structure comes under 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
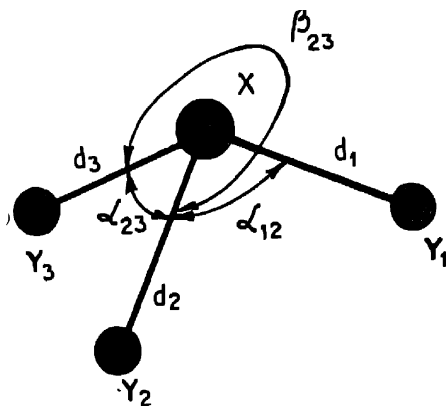

Fig 1. Geometry of the pyramidal XY_3 type structure, the equilibrium bond distances, bond angles and reflex angles.

The new set of symmetry coordinates appropriate to this molecular type has been obtained as follows

$$S_1(A_1) = (1/\sqrt{3})(\Delta d_1 + \Delta d_2 + \Delta d_3),$$
$$S_2(A_1) = (1/\sqrt{6})(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} - \Delta\beta_{12} - \Delta\beta_{23} - \Delta\beta_{31}),$$
$$S_{r1}(A_1) = (1/\sqrt{6})(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} + \Delta\beta_{12} + \Delta\beta_{23} + \Delta\beta_{31}) \equiv 0 \text{ (Redundant)},$$
$$S_{3a}(E) = (1/\sqrt{6})(\Delta d_1 - \Delta d_2 - \Delta d_3),$$
$$S_{3b}(E) = (1/\sqrt{2})(\Delta d_2 - \Delta d_3),$$
$$S_{4a}(E) = (1/\sqrt{12})(2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{31} - 2\Delta\beta_{23} + \Delta\beta_{12} + \Delta\beta_{31}),$$
$$S_{4b}(E) = (1/\sqrt{4})(\Delta\alpha_{31} - \Delta\alpha_{12} - \Delta\beta_{31} + \Delta\beta_{12}),$$
$$S_{r2}(E) = (1/\sqrt{12})(2\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{31} + 2\Delta\beta_{23} - \Delta\beta_{12} - \Delta\beta_{31}) \equiv 0 \text{ (Redundant)},$$
$$S_{r3}(E) = (1/\sqrt{4})(\Delta\alpha_{31} - \Delta\alpha_{12} + \Delta\beta_{31} - \Delta\beta_{12}) \equiv 0 \text{ (Redundant)},$$

where Δd_j is the change o in the jth $X-Y$ bond, $\Delta\alpha_{jk}$ and $\Delta\beta_{jk}$ are the changes in the interior and exterior angles between the jth and k^{th} $X-Y$ bonds respectively

4   F Matrix

On the basis of the most general quadratic potential function, there are twelve force constants and they are given in table 1.

Table 1   Description of the force constants

Force constant	Nature
f_d	Stretching
f_{dd}	Bond-bond interaction
f_α	Interior bending
$f_{\alpha\alpha}$	Interior-interior adjacent angle interaction
$f_{\alpha\alpha}'$	Bond-interior distant angle interaction
$f_{\alpha\alpha}''$	Bond-interior adjacent angle interaction
f_β	Exterior bending
$f_{\beta\beta}$	Exterior-exterior adjacent angle interaction
$f_{\alpha\beta}'$	Interior-exterior non reflex angle interaction
$f_{\alpha\beta}''$	Interior-exterior reflex angle interaction
$f_{d\beta}'$	Bond-exterior distant angle interaction
$f_{d\beta}''$	Bond-exterior adjacent angle interaction

The general F matrix elements may be obtained by the usual procedure in wilson's F-G matrix method   The redundant symmetry coordinates lead to the following relations among the force constants concerned.

$$(f'_{d\alpha} + 2f''_{d\alpha}) + (f'_{d\beta} + 2f''_{d\beta}) = 0,$$

$$(f'_{d\alpha} - f''_{d\alpha}) + (f'_{d\beta} - f''_{d\beta}) = 0,$$

$$(f_a+2f_{\alpha\alpha})+(f_\beta+2f_{\beta\beta})+2(2f'_{\alpha\beta}+f''_{\alpha\beta}) = 0,$$

$$(f_a-f_{\alpha\alpha})+(f_\beta-f_{\beta\beta})-2(f'_{\alpha\beta}-f''_{\alpha\beta}) = 0,$$

$$(f_a-f_{\alpha\alpha})-(f_\beta-f_{\beta\beta}) = 0,$$

$$(f_a+2f_{\alpha\alpha})+(f_\beta+2f_{\beta\beta}) = 0.$$

Making use of the constraints, the F matrix elements may be reduced to the following condensed forms involving the six independent force constants viz., f_d, f_{dd}, f_α, $f_{\alpha\alpha}$, $f'_{d\alpha}$ and $f''_{d\alpha}$ only

A_1 Type	E Type
$F_{11} = f_d+2f_{dd}$	$F_{33} = f_d-f_{dd}$
$F_{22} = 2d^2(f_\alpha+2f_{\alpha\alpha})$	$F_{44} = 2d^2(f_\alpha-f_{\alpha\alpha})$
$F_{12} = \sqrt{2}d(f'_{d\alpha}+2f''_{d\alpha})$	$F_{34} = \sqrt{2}d(f'_{d\alpha}-f''_{d\alpha})$

5. G MATRIX

The G matrix elements are

A_1 Type ·

$$G_{11} = \mu_y+\mu_x(1+2\cos\alpha),$$

$$G_{22} = 4[\mu_y+2\mu_x(1-\cos\alpha)](1+2\cos\alpha)/d^2(1+\cos\alpha),$$

$$G_{12} = -2\sqrt{2}\mu_x(1+2\cos\alpha)(1-\cos\alpha)/d\sin\alpha,$$

E Type :

$$G_{33} = \mu_y+\mu_x(1-\cos\alpha),$$

$$G_{44} = 2[\mu_y(2+\cos\alpha)+\mu_x(1-\cos\alpha)^2]/d^2(1+\cos),$$

$$G_{34} = \sqrt{2}\mu_x(1-\cos\alpha)^2/d\sin\alpha,$$

where μ_x and μ_y are the reciprocal masses of the X and Y atoms respectively.

6. KINETIC CONSTANTS

Making use of the G matrix elements, the following kinetic constants are obtained

$$K_d = (1/3)[(\mu_y+2\mu_x E)/A+2(\mu_y F+\mu_x E^2)/B],$$

$$K_{dd} = (1/3)[(\mu_y+2\mu_x E)/A-2(\mu_y F+\mu_x E^2)/B],$$

$$K_\alpha = (1/6)[(\mu_y+\mu_x F)(C/A)-2(\mu_y+\mu_x E)(D/B)],$$

$$K_{\alpha\alpha} = (1/6)[(\mu_y+\mu_x F)(C/A)-(\mu_y+\mu_x E)(D/B)],$$

$$K'_{d\alpha} = (\mu_x\sin\alpha/\sqrt{18}B)[(1/2)-2E\sin\alpha],$$

$$K''_{d\alpha} = -(\mu_x\sin\alpha/\sqrt{18}B)[(1/2)+2E\sin\alpha],$$

where $A = \mu_y(\mu_y + 3\mu_x)$,

$B = \mu_y[\mu_y(2 + \cos \alpha) + 3\mu_x(1 - \cos \alpha)]$,

$C = (1 + \cos \alpha)/4(1 + 2\cos \alpha)$,

$D = (1 + \cos \alpha)/2$,

$E = (1 - \cos \alpha)$,

$F = (2 + \cos \alpha)$

Further these independent kinetic constants are related to the dependent kinetic constants in the following manner, in similarity with the corresponding force constants.

$$(K'_{d\alpha} + 2K''_{d\alpha}) + (K'_{d\beta} + 2K''_{d\beta}) = 0,$$

$$(K'_{d\alpha} - K''_{d\alpha}) + (K'_{d\beta} - K''_{d\beta}) = 0,$$

$$(K_\alpha + 2K_{\alpha\alpha}) + (K_\beta + 2K_{\beta\beta}) + 2(2K'_{\alpha\beta} + K''_{\alpha\beta}) = 0,$$

$$(K_\alpha - K_{\alpha\alpha}) + (K_\beta - K_{\beta\beta}) - 2(K'_{\alpha\beta} - K''_{\alpha\beta}) = 0,$$

$$(K_\alpha - K_{\alpha\alpha}) - (K_\beta - K_{\beta\beta}) = 0,$$

$$(K_\alpha + 2K_{\alpha\alpha}) + (K_\beta + 2K_{\beta\beta}) \neq 0.$$

7 FORCE CONSTANTS

The six independent GQVFF force constants are evaluated using wilson's F-G matrix method (Wilson *et al* 1955)   The secular equations have been solved with the help of kinetic constants on the basis of the procedure outlined in our earlier papers   (Thirugnanasambandam *et al* 1969, 1974a, 1974b)

8 MEAN AMPLITUDES

Utilising Cyvin's equation $|\Sigma F - \lambda \Delta E| = 0$, the symmetrized mean square amplitude matrices (Σ) are obtained.

9. RESULTS AND DISCUSSION

Results relating to the twelve pyramidal XY_3 molecules under consideration are discussed here   Table 1 gives the description and the distribution of the force constants relating to this molecular type. The structural parameters and the vibrational frequencies of the molecules are tabulated in table 2. Table 3 deals with the kinetic constants while table 4 gives the force constants evaluated here The mean amplitudes of the molecules studied here are collected in table 5.

The kinetic constants of the molecules studied here may be grouped under three heads   Based on the properties of these constants, they may be grouped as complementary kinetic constants or supplementary kinetic constants

The four bond-angle interaction kinetic constants from the first group of complementary kinetic constants as they vanish among themselves when added together   Thus

$$K'_{d\alpha} + 2K''_{d\alpha} + K'_{d\beta} + 2K''_{d\beta} = 0.$$

The second group of complementary kinetic constants is provided by the two bending kinetic constants K_α, K_β and the four angle-angle interaction kinetic constants inasmuch as they also become zero when added together Thus,

$$K_\alpha + 2K_{\alpha\alpha} + K_\beta + 2K_{\beta\beta} + 2(2K'_{\alpha\beta} + K''_{\alpha\beta}) = 0$$

The remaining two kinetic constants, viz, the stretching kinetic constant K_d and the bond-bond interaction kinetic constant K_{dd} are together called supplementary kinetic constants as they lead to a characteristic constant typical of the molecule concerned.

Thus,
$$\Sigma K_{ij} = \Sigma K_d + \Sigma K_{dd}$$
$$= 3[\mu_y + 2\mu_x(1 - \cos\alpha)]/\mu_y(\mu_y + 3\mu_x)$$

The interesting procedure evolved here in the solution of the symmetrized force constants (Thirugnanasambandam *et al* 1969, 1974a, 1974b) is based on a detailed study of the kinetic constants of molecules. Extending the procedure to the molecules under study, it will be seen that there are two equations given by the two frequencies as against three unknown quantities F_{11}, F_{22} and F_{12} associated with the A_1 species The new procedure gives a constraint-relation governing F_{12} and F_{22} viz.,

$$F_{12} = (K_{12}/K_{22})F_{22}$$

Thus the two equations are readily solved with the help of this third equation

The force constants F_{33}, F_{44} and F_{34} associated with the E species are similarly obtained with the help of the equation

$$F_{34} = (K_{34}/K_{44})F_{44}$$

The symmetry force constants are combined to yield the individual force constants listed in table 4.

Reference may be made to the different workers of the earlier investigators in studying the force constants of these molecules In general, it may be mentioned that the present values of the force constants are more systematic than the earlier values. The values of f_d and f_{dd} remain in the respective ranges given by the concerned authors On the other hand, the bending force constant and the interaction force constants are found to be considerably reduced as a result of the recognition of the reflex angles and therefore additional force constants

Turning to the nature of the results obtained here, the following observations may be made The stretching force constant f_d and the bending force constant f_α are found to be practically identical among the three members forming each of the four sets of isotopic molecules studied here. This is indeed a striking and at the same time independent verification of the behaviour of such molecules as anticipated by Herzberg years ago

3

P. Thirugnanasambandam and S. Mohan

Table 2   Structural parameters and vibrational frequencies

S No.	Molecule	d Å	α in deg	$\nu_1(A_1)$	$\nu_2(A_2)$ cm^{-1}	$\nu_3(E)$	$\nu_4(E)$	Ref
1	NH$_3$	1 0116	106' 42'	3506	1022	3577	1691	a
2	ND$_3$			2495	793	2652	1225	a
3	NT$_3$			2090	695	2204	1019	b, c
4	PH$_3$	1 419	93 '30'	2452	1041	2457	1154	a
5	PD$_3$			1761	756	1766	822	a
6	PT$_3$			1443	643	1424	679	b, d
7	AsH$_3$	1 523	91 36'	2209	973	2226	1012	a
8	AsD$_3$			1571	696	1582	719	a
9	AsT$_3$			1289	578	1294	593	b, d
10.	SbH$_3$	1.712	91 31'	1989	796	1975	845	a
11	SbD$_3$			1409	569	1404	600	a
12	SbT$_3$			1152	471	1153	490	b, d

a) Duncan et al (1964)   b) Sutton (1958)
c) Sundaram et al (1960)   d) Altı et al (1964)

Table 3   Kinetic constants (10^{-23}g)

S No	Molecule	K_d	K_{dd}	K_α	$K_{\alpha x}$	$K'_{d\alpha}$	$K''_{d\alpha}$
1	NH$_3$	0 1571	0 0030	0 0208	0 0044	0.0009	0 0028
2	ND$_3$	0 2987	0 0108	0 0381	0 0069	0 0034	0 0097
3	NT$_3$	0 4302	0 0220	0 0532	0 0083	−0 0070	0 0193
4	PH$_3$	0 1623	0 0004	0 0203	0 0004	−0 0001	0.0013
5	PD$_3$	0 3155	0 0016	0.0393	0 0002	−0.0006	0 0018
6	PT$_3$	0 4611	0 0039	0.0573	−0 0005	0.0014	0 0102
7	AsH$_3$	0 1652	0 0001	0 0206	0 0002	−0 0002	0 0006
8	AsD$_3$	0 3262	0 0003	0 0407	0 0001	−0 0001	0 0021
9.	AsT$_3$	0 4833	0 0008	0 0604	−0 0003	−0 0003	0 0047
10.	SbH$_3$	0 1660	0 00001	0 0207	0 0002	−0.0001	0 0003
11	SbD$_3$	0 3294	0 0002	0 0412	0 0002	−0.0001	0.0013
12	SbT$_3$	0 4902	0 0004	0 0612	0.0001	−0 0002	0 0030

Table 4   Force constants (10^5 dynes cm

S No	Molecule	f_d	f_{dd}	f_α	$f_{\alpha\alpha}$	$f'_{d\alpha}$	$f'_{d\alpha}$
1	NH_3	7 0081	0.0410	0 1475	0 0187	0 0194	0 0185
2	ND_3	7 0484	−0.0329	0 1494	0 0167	0 0345	0 0352
3	NT_3	6 9408	0 1079	0 1501	-0 0153	0 0465	0 0503
4	PH_3	3 4701	0 0022	0 0896	0 0045	0 0013	0 0054
5.	PD_3	3 4759	0 0073	0 0894	0 0045	0.0024	0.0104
6	PT_3	3 3291	0 0496	0 0907	-0 0040	-0 0033	0 0516
7.	AsH_3	2.8907	-0 0136	0 0732	0 0013	-0 0002	0 0019
8.	AsD_3	2 8834	-0 0111	0 0732	-0 0015	0 0004	0 0038
9	AsT_3	2 8627	-0 0039	0.0741	0 0016	-0 0006	0 0006
10	SbH_3	2 3098	0 0114	0 0506	-0 0015	0 0001	0 0008
11.	SbD_3	2 3101	0 0065	0 0508	0 0015	-0 0002	0 0016
12	SbT_3	2 3114	0 0002	0 0509	0 0012	-0.0003	0 0024

Table 5   Mean amplitudes (Å) at 298 16K

S No	Molecule	$(\sigma_d)^{\frac{1}{2}}$	$(\sigma_1)^{\frac{1}{2}}$
1.	NH_3	0 0710	0.1222
2.	ND_3	0 0606	0 1030
3.	NT_3	0.0559	0.0937
4.	PH_3	0 0838	0.1479
5.	PD_3	0 0710	0 1260
6	PT_3	0.0654	0 1178
7	AsH_3	0.0873	0.1564
8.	AsD_3	0.0738	0.1339
9	AsT_3	0 0671	0 1231
10.	SbH_3	0 0923	0 1710
11	SbD_3	0 0778	0 1480
12	SbT_3	0 0706	0 1378

The remaining four force constants are all interaction force constants and they are also found to reveal own their interesting characteristics   The angle-angle interaction force constans $f_{\alpha\alpha}$ is always found to be negative in this type of molecule but magnitude-wise insignificant when compared with the predominant bending force constant f_α.

The bond-distant angle interaction force constant f'_{d_α} is also negative whereas the bond-adjacent angle interaction force constant f''_{d_α} is always positive the latter being in general of greater significance than the former regarding their magnitudes

While a detailed discussion of the significance of the interaction force constants in molecules has to await further work in the field, it is tempting even now to compare the pyramidal structure studied here with the planar structure studied earlier (Thirugnanasambandam et al 1969).

The angle-angle interaction force constant $f_{\alpha\alpha}$ and the bond-distant angle interaction force constant f'_{d_α} are negative in the pyramidal as well as the planar structures Regarding the magnitudes of these force constants the pyramidal structure appears to differ from the planar structure Then, $f_{\alpha\alpha}$ is found to be considerably less than f_α in the pyramidal case whereas it is equal to half of f_α in the planar case However, f''_{d_α}, in general, appears to be larger than f'_{d_α} in the pyramidal molecules while it is equal to half of f''_{d_α} in the planar molecules

Thus it appears that the interaction force constants may be considered to be basically important in distinguishing the pyramidal from the planar structure relating to molecules It is quite probable that an understanding of all these aspects may throw further light on some of the recondite features of the pyramidal structure such as the inversion of the ammonia molecule

The present set of symmetrized force constants has been utilised in Cyvin s secular equation (Cyvin 1959) to arrive at the symmetrized mean square amplitudes at temperature 298 16K The mean amplitudes have been computed from the mean square amplitudes and they are given in table 5 The mean amplitudes evaluated in the present investigation appear to be reasonable for all the molecules

The mean amplitudes of vibration for both the bonded $\sigma^{\frac{1}{2}}_d$ and the non-bonded $\sigma_r^{\frac{1}{2}}$ distances appear to decrease as one proceeds from lower to higher isotopic cases The mean amplitudes obtained here agree favourably with the mean amplitudes obtained from the electron diffraction data as may be seen from the following cases

	$\sigma_d^{\frac{1}{2}}(X-Y)$	$\sigma_r^{\frac{1}{2}}(Y..Y)$	
NH$_3$	0.0710	0.1222	P W
	0 078$_9$±0 002$_7$	0.11 ±0.02	A
		0.09 ±0 02	
ND$_3$	0.0606	0 1030	P W
	0 066$_7$±0 002$_7$	0 10 ±0.02	A
		−0.08 ±0 02	
PH$_3$	0.0838	0.1479	P.W
	0.085 ±0.008	—	B

P.W–Present work   A–Bastianesen et al (1964)   B–Bartell et al (1959)

10. CONCLUSION

The quadratic force constants of twelve molecules of pyramidal XY_3 structure are evaluated here introducing a new type of internal coordinates and therefore a new set of symmetry coordinates. It may be seen that highly systematic and reasonable sets of independent force constants relating to these molecules have been obtained here for the first time. The interaction force constants seem to assume, in magnitude and sign, significant values characteristic of the molecules and the molecular type. The mean amplitudes studied here are found to be in the expected range.

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