

## Isotopic invariants of pyramidal symmetrical $XY_3$ molecules and evaluation of molecular constants

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**Abstract.** The isotopic invariants of pyramidal symmetrical  $XY_3$  molecules are calculated in terms of frequencies, Coriolis coupling constants, molecular geometry parameters and masses of the constituent atoms. These invariants are used to evaluate force constants, compliance constants and mean amplitudes of vibration of four sets of 12 isotopic molecules.

**Keywords.** Isotopic invariants; pyramidal  $XY_3$  molecules; force constants; mean amplitudes of vibration.

### 1. Introduction

The theory of isotopic substitution of nonlinear triatomic molecules of Parker (1975) has been generalised recently by Jagannathan *et al* (1980) applicable to molecules of the type  $X_mY_n$  whose  $G$  matrix contains  $1 \times 1$  and  $2 \times 2$  diagonal blocks in a mass-independent coordinate system. The same has been applied (Chinnappan *et al* 1978; Chinnappan and Savariraj 1979) for the nonlinear symmetrical  $XY_2$  molecules and the planar symmetrical  $XY_3$  molecules to derive expressions involving vibrational frequencies, Coriolis coupling constants, molecular geometry and masses of the constituent atoms that are invariant under symmetrical isotopic substitution. These invariants have been used to calculate the molecular constants such as force constants, centrifugal distortion constants and mean amplitudes of vibration for these molecules. In this paper, the expressions for the isotopic invariants of pyramidal  $XY_3$  molecules are derived based on the theory of Jagannathan *et al* (1980). The numerical values are computed using the harmonic frequencies, the Coriolis coupling constants, geometry parameters and the masses of the constituent atoms for 4 sets of 12 isotopic molecules and these invariants are used to calculate the force constants, the compliance constants and the mean amplitudes of vibration of these molecules.

### 2. Theory

Throughout this paper, the symbols, definitions of standard matrices, molecular geometry parameters and the orientation of coordinate axes are as in Cyvin (1968). The regular pyramidal  $XY_3$  molecule belongs to  $C_{3v}$  point

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group symmetry giving rise to six fundamental normal modes of vibration which are distributed among the different species according to

$$\Gamma_{\text{vib}} = 2A_1 + 2E \quad (1)$$

where  $E$  is doubly degenerate.

The  $G$  matrix of such a regular pyramidal  $XY_3$  molecule in the internal symmetry coordinate system has two diagonal blocks each of them being of order  $2 \times 2$  and they are

$$G(A_1) = \begin{bmatrix} (4 \cos^2 A - 1)\mu_X + \mu_Y & -2(4 \cos^2 A - 1) \tan A \mu_X \\ -2(4 \cos^2 A - 1) \tan A \mu_X & (4 - \sec^2 A)(4 \sin^2 A \mu_X + \mu_Y) \end{bmatrix} \quad (2)$$

$$\text{and } G(E) = \begin{bmatrix} 2 \sin^2 A \mu_X + \mu_Y & 2 \sin^2 A \tan A \mu_X \\ 2 \sin^2 A \tan A \mu_X & 2 \sin^2 A \tan^2 A \mu_X + (1 + \frac{1}{2} \sec^2 A) \mu_Y \end{bmatrix} \quad (3)$$

where  $\mu_{XY}$  and  $\mu_{YX}$  are the reciprocal masses of the atoms  $X$  and  $Y$  respectively and  $2A$  is the  $YXY$  bond angle. Incidentally, angle  $B$  which is the angle between the symmetry axis and the  $X-Y$  bond is related to the  $YXY$  bond angle according to

$$3 \sin^2 B = 2(1 - \cos 2A)$$

$$\text{or } \sin B = (2/\sqrt{3}) \sin A \quad (4)$$

Following the notation and theory of Jagannathan *et al* (1980), the explicit expressions for  $g$ ,  $d$  and  $\Gamma$  matrices for  $A_1$  and  $E$  species are given by

$$g(A_1) = \begin{bmatrix} 1 & -2 \tan A \\ -2 \tan A & (\sec^2 A - 4) \end{bmatrix},$$

$$d(A_1) = \begin{bmatrix} [(4 \cos^2 A - 1)(\mu_X + \frac{1}{3}\mu_Y)]^{1/2} & 0 \\ 0 & (\frac{1}{3}\mu_Y \cos^2 A)^{1/2} \end{bmatrix},$$

$$\Gamma(A_1) = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix},$$

$$g(E) = \begin{bmatrix} 1 & \tan A \\ \tan A & -(1 + \frac{1}{2} \sec^2 A) \end{bmatrix},$$

$$d(E) = \begin{bmatrix} [2\mu_X \sin^2 A + \frac{1}{3}\mu_Y(2\cos^2 A) + 1]^{1/2} & 0 \\ 0 & (\frac{2}{3}\mu_Y \cos^2 A)^{1/2} \end{bmatrix},$$

$$\Gamma(E) = \begin{bmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{bmatrix}, \quad (5)$$

where  $\theta$  and  $\alpha$  are the two parameters introduced for  $A_1$  and  $E$  species respectively. It can be easily verified that

$$G(A_1) = g(A_1) d(A_1)^2 g(A_1)^\dagger,$$

and

$$G(E) = g(E) d(E)^2 g(E)^\dagger. \quad (6)$$

The parameters  $\theta$  and  $\alpha$  can be determined from the Coriolis coupling constants as follows. According to the choice of the coordinate axes, there exists the Coriolis coupling matrix elements for the  $A_1 \otimes E$  coupling with respect to  $Y$  axis and for the  $E \otimes E$  coupling with respect to  $X$  axis and  $Z$  axis. Now the relation for the Coriolis coupling constant matrix  $\zeta^\alpha$  and  $L$  matrix (Cyvin 1968) is

$$\zeta^\alpha = L^{-1} C^\alpha L^{-1\dagger} \quad (7)$$

where  $\alpha = x, y, z$ .

Making use of the explicit values of  $C^\alpha$  (skew symmetric matrix) for the various couplings from Cyvin (1968) and the relation (Jagannathan *et al* 1980).

$$L = g d \Gamma \quad (8)$$

we get the  $\zeta$  elements in terms of the parameters  $\theta$  and  $\alpha$  as

$$\begin{aligned} \zeta_{1,3a}^Y &= -C(D \cos \theta + E \sin \theta) \cos \alpha; & \zeta_{1,4a}^Y &= -C(D \cos \theta + E \sin \theta) \sin \alpha; \\ \zeta_{2,3a}^Y &= -C(E \cos \theta - D \sin \theta) \cos \alpha; & \zeta_{2,4a}^Y &= C(E \cos \theta - D \sin \theta) \sin \alpha; \\ \zeta_{3a,4b}^X &= -(m_X/6MI_{XX})^{1/2} R \cos B; & \zeta_{3a,3b}^Z &= K \cos^2 \alpha - \sin^2 \alpha; \\ \zeta_{3a,4b}^Z &= \zeta_{4a,3b}^Z = -(K+1) \sin \alpha \cos \alpha; & \zeta_{4a,4b}^Z &= K \sin^2 \alpha - \cos^2 \alpha \end{aligned} \quad (9)$$

where

$$C = \left( \frac{6R^2 m_Y}{MI_{XX}} \right)^{1/2}, \quad D = \left( \frac{M}{4 \cos^2 A - 1} \right)^{1/2} \sin A \cos B,$$

$$E = \frac{1}{2} m_X^{1/2} \cos B, \quad K = I_{ZZ}/2I_{XX}$$

$$\text{with } I_{XX} = \frac{R^2 m_Y}{M} [6m_Y \sin^2 A + m_X(2 \cos^2 A + 1)],$$

$$I_{ZZ} = 4R^2 m_Y \sin^2 A; \quad M = m_X + 3m_Y$$

Here  $m_X$  and  $m_Y$  are the masses of the X and Y atoms respectively and  $R$  the X–Y bond length.

Incidentally the following sum rules are evident:

$$\begin{aligned}
 \text{(i)} \quad & (\zeta_{1,3a}^Y)^2 + (\zeta_{1,4a}^Y)^2 + (\zeta_{2,3a}^Y)^2 + (\zeta_{2,4a}^Y)^2 = \frac{I_{ZZ}}{4I_{XX}} + \frac{1}{2} \\
 \text{(ii)} \quad & \zeta_{1,3a}^Y \zeta_{2,4a}^Y = \zeta_{1,4a}^Y \zeta_{2,3a}^Y \\
 \text{(iii)} \quad & \zeta_{3a,3b}^Z \zeta_{4a,4b}^Z = \frac{R^2 m_X m_Y}{MI_{XX}} (1 - 4 \cos^2 A), \\
 \text{(iv)} \quad & \zeta_{3a,3b}^Z \zeta_{4a,4b}^Z - (\zeta_{3a,4b}^Z)^2 = -\frac{I_{ZZ}}{2I_{XX}} \\
 \text{(v)} \quad & \sum_{i=1}^2 \sum_{t=3}^4 (\zeta_{i,ta}^Y)^2 + \frac{1}{2} [\zeta_{3a,3b}^Z \zeta_{4a,4b}^Z - (\zeta_{3a,4b}^Z)^2] = \frac{1}{2} \quad (10)
 \end{aligned}$$

The sum rules (i) and (ii) are given by Hoy *et al* (1972) and the rules (iii) and (iv) are given in Cyvin (1968 p. 341). The rule (v) is another sum rule of the Coriolis coupling constants and it is obtained by using the sum rules (i) and (iv).

According to (21)–(23) of Jagannathan *et al* (1980) and from (5), the invariants of the regular pyramidal  $XY_3$  molecules in terms of the parameters  $\theta$  and  $\alpha$  are given by

$$\begin{aligned}
 I_{11} &= \frac{3m_X m_Y}{M(4 \cos^2 A - 1)} (\lambda_1 \cos^2 \theta + \lambda_2 \sin^2 \theta), \\
 I_{12} &= \frac{3m_Y}{\cos A} \left( \frac{m_X}{M[4 \cos^2 A - 1]} \right)^{1/2} (\lambda_1 - \lambda_2) \sin \theta \cos \theta, \\
 I_{22} &= \frac{3m_Y}{\cos^2 A} (\lambda_1 \sin^2 \theta + \lambda_2 \cos^2 \theta), \quad (11) \\
 I_{33} &= \frac{3m_X m_Y}{6m_Y \sin^2 A + m_X (2 \cos^2 A + 1)} (\lambda_3 \cos^2 \alpha + \lambda_4 \sin^2 \alpha), \\
 I_{34} &= \frac{3m_Y}{\cos A} \left[ \frac{m_X}{12m_Y \sin^2 A + 2m_X (2 \cos^2 A + 1)} \right]^{1/2} \sin \alpha \cos \alpha (\lambda_3 - \lambda_4), \\
 I_{44} &= \frac{3m_Y}{2 \cos^2 A} (\lambda_3 \sin^2 \alpha + \lambda_4 \cos^2 \alpha), \quad (12)
 \end{aligned}$$

where  $\lambda_i = 4\pi^2 c^2 \omega_i^2$  with  $\omega_i$  the vibrational frequency of the  $i$ th mode of vibration.

The parameter  $\theta$  in (11) is determined using the geometry parameters of the molecule and the Coriolis coupling constants from the relation

$$\theta = \tan^{-1} \left\{ \frac{[m_X (4 \cos^2 A - 1)]^{1/2} \zeta_{1,3a}^Y - 2M^{1/2} \sin A \zeta_{2,3a}^Y}{2M^{1/2} \sin A \zeta_{1,3a}^Y + [m_X (4 \cos^2 A - 1)]^{1/2} \zeta_{2,3a}^Y} \right\} \quad (13)$$

and the parameter  $\alpha$  in (12) is eliminated and the equations are rewritten as

$$\begin{aligned} I_{33} &= m_X m_Y R^2 \left[ \frac{(\lambda_3 - \lambda_4)(1 + \zeta_{3a,3b}^Z)}{I_{ZZ} + m_X R^2} + \frac{3m_Y \lambda_4}{MI_{XX}} \right] \\ &= m_X m_Y R^2 \left[ \frac{3m_Y \lambda_3}{MI_{XX}} - \frac{(\lambda_3 - \lambda_4)(1 + \zeta_{4a,4b}^Z)}{I_{ZZ} + m_X R^2} \right], \\ I_{34} &= \frac{(\lambda_3 - \lambda_4) R \zeta_{3a,4b}^Z}{(I_{ZZ} + m_X R^2) \cos A} \left( \frac{1}{2} M m_X m_Y I_{XX} \right)^{1/2} \\ I_{44} &= \frac{1}{2 \cos^2 A} \left[ \frac{(\lambda_3 - \lambda_4) MI_{XX} (1 + \zeta_{4a,4b}^Z)}{I_{ZZ} + m_X R^2} + 3m_Y \lambda_4 \right] \\ &= \frac{1}{2 \cos^2 A} \left[ 3m_Y \lambda_3 - \frac{(\lambda_3 - \lambda_4) MI_{XX} (1 + \zeta_{3a,3b}^Z)}{I_{ZZ} + m_X R^2} \right] \end{aligned} \quad (14)$$

It can be noticed that these invariants are calculated using observable quantities in addition to the molecular parameters.

### 3. Applications of the invariants

#### 3.1 Calculation of force constants

From (19) of Chinnappan *et al* (1978), viz.,  $F = g^{-1} I g^{-1}$  the symmetrised force constants of the regular pyramidal  $XY_3$  molecule are worked out to be

$$F_{11} = \frac{1}{9} [(4 \cos^2 A - 1)^2 I_{11} + \sin^2 2A I_{22} - 2(4 \cos^2 A - 1) \sin 2A I_{12}]$$

$$F_{12} = \frac{1}{9} [-(4 \cos^2 A - 1) \sin 2A I_{11} + \sin 2A \cos^2 A I_{22} + (\sin^2 2A - \overline{4 \cos^2 A - 1 \cos^2 A}) I_{12}]$$

$$F_{22} = \frac{1}{9} [\sin^2 2A I_{11} + \cos^4 A I_{22} + 2 \sin 2A \cos^2 A I_{12}]$$

$$F_{33} = \frac{1}{9} [(2 \cos^2 A + 1)^2 I_{33} + \sin^2 2A I_{44} + 2 \sin 2A (2 \cos^2 A + 1) I_{34}]$$

$$F_{34} = \frac{1}{9} [\sin 2A [(2 \cos^2 A + 1) I_{33} - 2 \sin 2A \cos^2 A I_{44} + (\sin^2 2A - 2 \cos^2 A + 1 \cdot 2 \cos^2 A) I_{34}]]$$

$$F_{44} = \frac{1}{9} [\sin^2 2A I_{33} + 4\cos^4 A I_{44} - 4\sin 2A \cos^2 A I_{34}] \quad (15)$$

### 3.2 Calculation of compliance constants

The compliance constant matrix is given by (Cyvin 1968)

$$N = L\sigma L^\dagger \quad (16)$$

where  $\sigma_i = 1/\lambda_i$ . Using (5), (8), (11) and (14) in (16) the elements of the symmetrised compliance constants are found to be

$$N_{11} = P \{Q[4m_X \sin^2 A - M(4\cos^2 A - 1)] + 2Mm_X I_{12}(4\cos^2 A - 1) \sin 2A + 3m_X m_Y [M\lambda_1(4\cos^2 A - 1) + 4m_X \lambda_2 \sin^2 A]\},$$

$$N_{12} = P(4\cos^2 A - 1) \{2Q(M + m_X) \tan A + Mm_X I_{12}(4\cos^2 A - 1) - 6m_X m_Y \tan A (M\lambda_1 - m_X \lambda_2)\},$$

$$N_{22} = P(4 - \sec^2 A) \{Q[m_X(4\cos^2 A - 1) - 4M\sin^2 A] - 2Mm_X I_{12}(4\cos^2 A - 1) \sin 2A + 3m_X m_Y [4M\lambda_1 \sin^2 A + m_X \lambda_2(4\sin^2 A - 1)]\},$$

$$N_{33} = T\{(3m_X m_Y \lambda_4 - SI_{33})(S - 2m_X \sin^2 A) - 2SI_{34} \sin 2A - 3m_X m_Y [S\lambda_3 + 2m_X \lambda_4 \sin^2 A]\},$$

$$N_{34} = T\{S(3m_X m_Y \lambda_4 - SI_{33}) \tan A + Sm_X I_{34}(2\cos^2 A + 1) + 3m_X m_Y \tan A [S\lambda_3 - m_X \lambda_4(2\cos^2 A + 1)]\},$$

$$N_{44} = T\{(SI_{33} - 3m_X m_Y \lambda_4) [\frac{1}{2} m_X (2\cos^2 A + 1)^2 - S \tan^2 A] + Sm_X I_{34}(2\cos^2 A + 1) \sin 2A + 3m_X m_Y [S\lambda_3 \tan^2 A + \frac{1}{2} m_X \lambda_4 (2\cos^2 A + \sec A)^2]\}, \quad (17)$$

where  $P = (9m_X^2 m_Y^2 \lambda_1 \lambda_2)^{-1}$ ,  $Q = MI_{11}(4\cos^2 A - 1) - 3m_X m_Y \lambda_2$ ,

$$T = (9m_X^2 m_Y^2 \lambda_3 \lambda_4)^{-1}, \quad S = 6m_Y \sin^2 A + m_X(2\cos^2 A + 1).$$

### 3.3 Calculation of mean amplitudes of vibration

The matrix of the mean square amplitudes of vibration is given as (Cyvin 1968)

$$\Sigma = L \delta L^\dagger \quad (18)$$

Substituting (5), (8), (11) and (14) in (18), the elements of the symmetrised mean square amplitudes of vibration are as follows:

$$\Sigma_{11} = U\{V[4m_X \sin^2 A - M(4\cos^2 A - 1)] + 2Mm_X I_{12}(4\cos^2 A - 1) \sin 2A\} + (3m_X m_Y)^{-1} [M \delta_2 (4\cos^2 A - 1) + 4m_X \delta_1 \sin^2 A],$$

$$\Sigma_{12} = U(4\cos^2 A - 1) \{2V(M + m_X) \tan A + Mm_X I_{12}(4\cos^2 A - 1)\} - (3m_X m_Y)^{-1} 2 \tan A (M \delta_2 - m_X \delta_1),$$

$$\begin{aligned}\Sigma_{22} &= U(4 - \sec^2 A) \{V[m_X(4\cos^2 A - 1) - 4M\sin^2 A] - 4Mm_X I_{12} \cos^2 A(4\cos^2 A - 1) \tan A\} + (3m_X m_Y)^{-1} (4 - \sec^2 A) [m_X \delta_1 (4\cos^2 A - 1) + 4M \delta_2 \sin^2 A] \\ \Sigma_{33} &= W\{(3m_X m_Y \lambda_4 - S I_{33}) (S - 2m_X \sin^2 A) - 2S m_X I_{34} \sin^2 A\} + (3m_X m_Y)^{-1} (2m_X \delta_3 \sin^2 A + S \delta_4), \\ \Sigma_{34} &= W\{S(3m_X m_Y \lambda_4 - S I_{33}) \tan A + S m_X I_{34} (2\cos^2 A + 1)\} + (3m_X m_Y)^{-1} \tan A [S \delta_4 - m_X \delta_3 (2\cos^2 A + 1)] \\ \Sigma_{44} &= W \sec^2 A \{(S I_{33} - 3m_X m_Y \lambda_4) [\frac{1}{2} m_X (2\cos^2 A + 1)^2 - S \sin^2 A] + S m_X I_{34} (2\cos^2 A + 1) \sin 2A\} + (3m_X m_Y)^{-1} \sec^2 A [\frac{1}{2} m_X \delta_3 (2\cos^2 A + 1)^2 + S \delta_4 \sin^2 A],\end{aligned}\quad (19)$$

$$\text{where } U = [9m_X^2 m_Y^2 (\lambda_1 - \lambda_2)]^{-1} (\delta_2 - \delta_1),$$

$$V = M I_{11} (4\cos^2 A - 1) - 3m_X m_Y \lambda_2,$$

$$W = [9m_X^2 m_Y^2 (\lambda_3 - \lambda_4)]^{-1} (\delta_4 - \delta_3),$$

$$\delta_i = h/8\pi^2 c \omega_i \cot h(hc/kT) \omega_i,$$

$$= 16.85748/\omega_i \cot h(0.719399/T) \omega_i.$$

The mean amplitudes of vibration of the bonded and the non-bonded atoms are given as (Cyvin 1968)

$$1(X \text{---} Y) = [\frac{1}{3}(\Sigma_{11} + 2\Sigma_{33})]^{1/2},$$

$$1(Y \cdots Y) = \{\frac{1}{3}[(4\Sigma_{11} + 2\Sigma_{33}) \sin^2 A + 2(\Sigma_{12} - \Sigma_{34}) \sin^2 A + (\Sigma_{22} + 2\Sigma_{44}) \cos^2 A]\}^{1/2}.\quad (20)$$

#### 4. Results and discussion

The isotopic invariants for the four sets of 12 molecules of regular pyramidal  $XY_3$  type (the trihydrides of the group V elements  $X = \text{N, P, As, Sb}$  and  $Y = \text{H, D, T}$ ) are calculated taking the frequencies and the Coriolis coupling constants from Cyvin (1968) and the geometrical parameters as given by Thyagarajan *et al* (1969) and are given in table 1. These invariants show a very good consistency thereby justifying the assumption that the molecular force field and the geometry remain unaltered under isotopic substitution. The calculated symmetrised force constants using these invariants are listed in table 2 and they show agreement with the values given by Periseau *et al* (1963). It is noted that the force constant  $F_{33}$  which involves the stretching constant is nearly 10 times  $F_{44}$  which involves the bending constant. Similar relation is noticed between  $F_{11}$  and  $F_{22}$ . Also, the stretching and bending force constants decrease characteristically with the increase in the mass of the apex atom. The calculated values of the compliance constants are presented in table 3. It is quite striking to observe the invariance of the compliance constants due to the isotopic substitution from table 3 thereby conforming the basic assump-

**Table 1.** The isotopic invariants of pyramidal  $XY_3$  molecules.

Molecule	$I_{11}$	$-I_{12}$	$I_{22}$	$I_{33}$	$I_{34}$	$I_{44}$
NH <sub>3</sub>	6.7720	12.6044	56.7034	7.7658	7.4110	17.6267
ND <sub>3</sub>	6.7213	12.6007	56.6811	7.7692	7.4093	17.6210
NT <sub>3</sub>	6.7208	12.5859	56.7119	7.7679	7.4026	17.6211
PH <sub>3</sub>	5.7895	6.4059	14.9647	3.8049	2.8937	5.6973
PD <sub>3</sub>	5.7900	6.4085	14.9627	3.8024	2.8927	5.6891
PT <sub>3</sub>	5.7921	6.4106	14.9625	3.8048	2.8942	5.6935
AsH <sub>3</sub>	5.1569	5.0644	11.0072	3.0074	2.4441	4.7322
AsD <sub>3</sub>	5.1586	5.0669	10.9929	3.0076	2.4471	4.7317
AsT <sub>3</sub>	5.1558	5.0670	10.9999	3.0069	2.4425	4.7334
SbH <sub>3</sub>	3.9653	4.2498	8.7431	2.4748	1.9434	3.3438
SbD <sub>3</sub>	3.9739	4.2538	8.7295	2.4760	1.9435	3.3397
SbT <sub>3</sub>	3.9771	4.2536	8.7227	2.4759	1.9442	3.3400

**Table 2.** The symmetrised force constants (md/A) of pyramidal  $XY_3$  molecules.

Molecule	$F_{11}$	$-F_{12}$	$F_{22}$	$F_{33}$	$-F_{34}$	$F_{44}$
NH <sub>3</sub>	7.0721 (7.018)	-0.7792 (-1.098)	0.5313 (0.6401)	7.0388 (6.881)	0.1758 (0.195)	0.6650 (0.680)
PH <sub>3</sub>	3.4004 (3.439)	0.0618 (0.057)	0.3402 (0.290)	3.4639 (3.283)	0.0399 (0.163)	0.3763 (0.410)
AsH <sub>3</sub>	2.7758 (2.850)	0.0069 (0.077)	0.3135 (0.270)	2.8904 (2.865)	0.0976 (0.237)	0.3021 (0.330)
SbH <sub>3</sub>	2.2735 (2.184)	0.1990 (0.374)	0.2113 (0.213)	2.2983 (2.215)	0.2005 (0.131)	0.2075 (0.224)

The values in parentheses are from Pariseau (1963).

**Table 3.** The compliance constants (A/md) of pyramidal  $XY_3$  molecules.

Molecule	$N_{11}$	$N_{12}$	$N_{22}$	$N_{33}$	$N_{34}$	$N_{44}$
NH <sub>3</sub>	0.1687	-0.2475	2.2453	0.1429	0.2002	1.5123
ND <sub>3</sub>	0.1687	-0.2473	2.2454	0.1428	0.2001	1.5122
NT <sub>3</sub>	0.1686	-0.2473	2.2450	0.1429	0.2001	1.5117
PH <sub>3</sub>	0.3045	0.1797	3.0443	0.2894	0.2770	2.6609
PD <sub>3</sub>	.03046	0.1798	3.0456	0.2892	0.2767	2.6620
PT <sub>3</sub>	0.3048	0.1793	3.0457	0.2891	0.2767	2.6619
AsH <sub>3</sub>	0.3881	0.3114	3.4383	0.3509	0.4287	3.3589
AsD <sub>3</sub>	0.3881	0.3114	3.4368	0.3510	0.4287	3.3573
AsT <sub>3</sub>	0.3881	0.3113	3.4364	0.3507	0.4282	3.3563
SbH <sub>3</sub>	0.4803	0.4528	5.1687	0.4345	0.4992	4.7967
SbD <sub>3</sub>	0.4799	0.4518	5.1635	0.4344	0.4990	4.7992
SbT <sub>3</sub>	0.4801	0.4527	5.1669	0.4344	0.4991	4.7974



**Table 4.** The mean amplitudes of vibration ( $\text{\AA}$  units) of pyramidal  $XY_3$  molecules.

Molecules	T = 0 K		T = 298 K	
	$l(\text{X}—\text{Y})$	$l(\text{Y}\cdots\cdots\text{Y})$	$l(\text{X}—\text{Y})$	$l(\text{Y}\cdots\cdots\text{Y})$
$\text{NH}_3$	0.07144 (0.07146)	0.11048 (0.11569)	0.07146 (0.07147)	0.11060 (0.11578)
$\text{ND}_3$	0.06113 (0.06113)	0.09311 (0.09755)	0.06116 (0.06116)	0.09389 (0.09790)
$\text{NT}_3$	0.05613 (0.05614)	0.08421 (0.08837)	0.05615 (0.05618)	0.08484 (0.08906)
$\text{PH}_3$	0.08414 (0.0841)	0.14548 (0.1498)	0.08416 (0.0841)	0.14601 (0.1503)
$\text{PD}_3$	0.07130 (0.0713)	0.12245 (0.1261)	0.07132 (0.0713)	0.12434 (0.1282)
$\text{PT}_3$	0.06491 (0.0649)	0.11080 (0.1142)	0.06499 (0.0650)	0.11417 (0.1179)
$\text{AsH}_3$	0.08807 (0.0880)	0.15390 (0.1586)	0.08809 (0.0880)	0.15472 (0.1596)
$\text{AsD}_3$	0.07425 (0.0743)	0.12286 (0.1335)	0.07436 (0.0744)	0.13105 (0.1368)
$\text{AsT}_3$	0.06736 (0.0673)	0.11706 (0.1207)	0.06760 (0.0676)	0.12210 (0.1264)
$\text{SbH}_3$	0.09279 (0.0928)	0.16832 (0.1735)	0.09283 (0.0929)	0.17061 (0.1760)
$\text{SbD}_3$	0.07819 (0.0782)	0.14175 (0.1459)	0.07836 (0.0784)	0.14777 (0.1528)
$\text{SbT}_3$	0.07085 (0.0708)	0.12808 (0.1320)	0.07125 (0.0713)	0.13775 (0.1427)

The values in parentheses are from Cyvin (1968).

tion of the isotopic invariants. In table 4, the calculated mean amplitudes of vibration at temperature 0 K and 298 K are given. These values agree very well with the values given by Cyvin (1968) at these temperatures. It is observed that as the end atoms are substituted by heavier atoms, the mean amplitudes of vibration decrease as expected.

It is interesting to note that when once the isotopic invariants of a pyramidal  $XY_3$  molecules are found using reliable observable quantities like frequencies, etc., the other molecular constants of the same molecule and its isotopic substituents can be easily calculated.

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