FORCE CONSTANTS, GENERALISED MEAN-SQUARE AMPLITUDES OF VIBRATION, SHRINKAGE CONSTANTS AND CORIOLIS COUPLING COEFFICIENTS OF GeH_3CCH AND GeD_3CCH

By Prof. K. Venkateswarlu, F.A.Sc., Dr. V. Malathy Devi

and

A. Natarajan

(Department of Physics, Kerala University Centre, Cochin-22)

Received April 6, 1968

Abstract

General valence force constants have been evaluated for GeH_3CCH and GeD_3CCH. Generalised mean-square amplitudes of vibration have been obtained and the shrinkage constants have been calculated using the perpendicular mean-square amplitudes of vibration. Coriolis coupling constants have also been determined.

1. Introduction

Thomas and Laurie[1] have made the first precise structural study of the molecule GeH_3CCH from the microwave spectrum and reported the various parameters. Lovejoy and Baker[2] have obtained the infrared spectra of GeH_3CCH and GeD_3CCH in the gaseous state and assigned all their fundamentals. These molecules belong to the point group C_{3v} consisting of five totally symmetric a_1 modes and five doubly degenerate e modes, all the ten fundamentals being infrared active.

Very recently, Rao and Rai[3] have determined the general valence force constants of these molecules but they have transferred many of the bending and interaction force constants from the previous work.[4, 5] Further, they have not made use of the latest parameters available from microwave data[1] but borrowed from the earlier work on similar molecules.[4, 5] Hence, the force constants have been reinvestigated on the basis of general valence force field using the latest parameters pertaining to germylacetylene. The generalised mean-square amplitudes of vibra-

tion, shrinkage constants and the Coriolis coupling coefficients have also been obtained for the first time in this investigation.

2. Potential Constants, Mean-Square Amplitudes of Vibration and Shrinkage Effect

The symmetry co-ordinates, satisfying the orthogonality and normalization conditions and which transform according to the characters of the point group C_{3v} have been constructed. The kinetic energy matrix G has been obtained using the relation $G = BM^{-1}B'$, where M^{-1} is a diagonal matrix of the reciprocal masses and B is the transformation matrix from Cartesian displacement co-ordinates to internal co-ordinates. The force constant matrix F has been derived assuming a general valence type of potential function. By solving the secular equation[6] $|FG - E\lambda| = 0$, a reasonable set of force constants has been evaluated.

The elements of the symmetrised mean-square amplitude matrix Σ have been obtained using the relation,[7] $\Sigma = L\triangle L'$, where L and $\triangle$ have their usual significance. The L matrix has been determined from the general valence force constants.

The generalised mean-square amplitudes which include the mean-square parallel amplitudes $\langle(\triangle z)^2\rangle$, the mean-square perpendicular amplitudes, $\langle(\triangle x)^2\rangle$ and $\langle(\triangle y)^2\rangle$ and the mean cross products $\langle(\triangle z\ \triangle x)\rangle$, $\langle(\triangle x\ \triangle y)\rangle$ and $\langle(\triangle y\ \triangle z)\rangle$ have been obtained by the method of Morino and Hirota.[8] In order to compute these quantities, the symmetry co-ordinates S are to be expressed in terms of Cartesian displacement co-ordinates X. They are related through the relation, $X = AS$, where A is the transformation matrix given by $A = M^{-1}B'G^{-1}$. Here G^{-1} is the inverse of the kinetic energy matrix and B is such that $S = BX$. Expressions have been derived for the paralleled and perpendicular mean-square amplitudes for the various bonded and non-bonded atom pair. Making use of the elements of Σ and A matrices in the above expressions, the generalised mean-square amplitudes have been evaluated.

The shortening or shrinkage of the internuclear distances can be calculated from spectroscopic data, using the perpendicular mean-square amplitudes of vibration as has been pointed out by Morino.[9] For the molecules under study, the following shrinkages are found to exist:

$$-\delta_{46} = \frac{\tau_{46}}{R + r_c} - \frac{\tau_{45}}{R} - \frac{\tau_{56}}{r_c},$$

$$-\delta_{47} = \frac{\tau_{47}}{R + r_c + D} - \frac{\tau_{45}}{R} - \frac{\tau_{56}}{r_c} - \frac{\tau_{67}}{D},$$

$$-\delta_{57} = \frac{\tau_{57}}{r_c + D} - \frac{\tau_{56}}{r_c} - \frac{\tau_{67}}{D},$$

where

$$\tau_{ij} = \frac{\langle(\triangle x_{ij})^2\rangle + \langle(\triangle y_{ij})^2\rangle}{2},$$

$\langle(\triangle x_{ij})^2\rangle$ and $\langle(\triangle y_{ij})^2\rangle$ representing the respective perpendicular mean-square amplitude values.

3. Coriolis Coupling Constants

Applying Jahn's rule,[10] the non-vanishing zeta values are found to be of the type ζ^z arising from the coupling $e \times e$ and ζ^x and ζ^y due to the coupling $a_1 \times e$. These constants have been estimated using the matrix relation, $\zeta^\alpha = L^{-1} C^\alpha L'^{-1}$, where L is the normal co-ordinate transformation matrix and C^α ($\alpha = x, y, z$) is the skew symmetric matrix obtained by the vector method of Meal and Polo.[11] The C^α matrix elements are given below:

$e \times e$ Coupling:

$$C^z_{6a,6b} = \frac{4}{3}\mu_{Ge}$$

$$C^z_{7a,7b} = \frac{3}{2}\left(\frac{1}{a} + \frac{a}{3}\right)^2 \mu_{Ge} + \frac{3}{2a^2}\mu_C$$

$$C^z_{8a,8b} = b^2\mu_C + \left(b + \frac{1}{b}\right)^2 \mu_C + \frac{1}{b^2}\mu_H$$

$$C^z_{9a,9b} = \frac{8}{3}\mu_{Ge} - \frac{\mu_X}{2}$$

$$C^z_{10a,10b} = c^2\mu_{Ge} + \left(c + \frac{1}{c}\right)^2 \mu_C + \frac{1}{c^2}\mu_C$$

$$C^z_{6a,7b} = -\sqrt{2}\,\mu_{Ge}\left(\frac{1}{a}+\frac{a}{3}\right)$$

$$C^z_{6a,8b} = 0$$

$$C^z_{6a,9b} = \sqrt{2}\,\mu_X + \frac{4}{3}\sqrt{2}\,\mu_{Ge}$$

$$C^z_{6a,10b} = -\frac{2}{\sqrt{3}}\,c\,\mu_{Ge}$$

$$C^z_{7a,8b} = -\sqrt{\frac{3}{2}}\frac{b}{a}\mu_C$$

$$C^z_{7a,9b} = -\frac{a}{2}\mu_X - 2\left(\frac{1}{a}+\frac{a}{3}\right)\mu_{Ge}$$

$$C^z_{7a,10b} = \sqrt{\frac{3}{2}}\left(\frac{1}{a}+\frac{a}{3}\right)c\mu_{Ge} + \sqrt{\frac{3}{2}}\frac{\mu_C}{a}\left(c+\frac{1}{c}\right)$$

$$C^z_{8a,9b} = 0$$

$$C^z_{8a,10b} = -b\left(c+\frac{1}{c}\right)\mu_C - \frac{1}{c}\left(b+\frac{1}{b}\right)\mu_C$$

$$C^z_{9a,10b} = -\sqrt{\frac{8}{3}}\,c\mu_{Ge};$$

$a_1 \times e$ Coupling:

$$C^y_{1,6a} = -C^x_{1,6b} = 0$$

$$C^y_{1,7a} = -C^x_{1,7b} = 0$$

$$C^y_{1,8a} = -C^x_{1,8b} = -\mu_C\left(b+\frac{1}{b}\right) - \frac{1}{b}\mu_H$$

$$C^y_{1,9a} = -C^x_{1,9b} = 0$$

$$C^y_{1,10a} = -C^x_{1,10b} = \frac{1}{c}\mu_C$$

$$C^y_{2,6a} = -C^x_{2,6b} = 0$$

$$C^{y}_{2,7a} = -C^{x}_{2,7b} = -\sqrt{\frac{3}{2}}\frac{1}{a}\mu_C$$

$$C^{y}_{2,8a} = -C^{x}_{2,8b} = b\mu_C + \left(\frac{1}{b} + b\right)\mu_C$$

$$C^{y}_{2,9a} = -C^{x}_{2,9b} = 0$$

$$C^{y}_{2,10a} = -C^{x}_{2,10b} = -\left(c + \frac{1}{c}\right)\mu_C - \frac{1}{c}\mu_C$$

$$C^{y}_{3,6a} = -C^{x}_{3,6b} = \frac{2}{3}\mu_{Ge}$$

$$C^{y}_{2,7a} = -C^{x}_{3,7b} = -\frac{a}{\sqrt{2}}\mu_X - \frac{1}{\sqrt{2}}\left(\frac{1}{a} + \frac{a}{3}\right)\mu_{Ge}$$

$$C^{y}_{3,8a} = -C^{x}_{3,8b} = 0$$

$$C^{y}_{3,9a} = -C^{x}_{3,9b} = \frac{\sqrt{8}}{3}\mu_{Ge}$$

$$C^{y}_{3,10a} = -C^{x}_{3,10b} = -\frac{c}{\sqrt{3}}\mu_{Ge}$$

$$C^{y}_{4,6a} = -C^{x}_{4,6b} = -\frac{1}{2}(1+a)\mu_X - \frac{4}{3}(1+a)\mu_{Ge}$$

$$C^{y}_{4,7a} = -C^{x}_{4,7b} = \sqrt{2}(1+a)\left(\frac{1}{a} + \frac{a}{3}\right)\mu_{Ge}$$

$$C^{y}_{4,8a} = -C^{x}_{4,8b} = 0$$

$$C^{y}_{4,9a} = -C^{x}_{4\ 9b} = -\frac{1}{\sqrt{2}}(1+a)\mu_X - \frac{4}{3}\sqrt{2}(1+a)\mu_{Ge}$$

$$C^{y}_{4,1.a} = -C^{x}_{4,10b} = \frac{2}{\sqrt{3}}(1+a)c\mu_{Ge}$$

$$C^{y}_{5,6a} = -C^{x}_{5,6b} = -\frac{2}{\sqrt{3}}\mu_{Ge}$$

$$C^{y}_{5,7a} = -C^{x}_{5,7b} = \sqrt{\frac{3}{2}}\left(\frac{1}{a} + \frac{a}{3}\right)\mu_{Ge} + \sqrt{\frac{3}{2}}\frac{1}{a}\mu_C$$

$$C^{y}_{5,8a} = -C^{x}_{5,8b} = -b\mu_C$$

$$C^{y}_{5,9b} = -C^{x}_{5,9b} = -\sqrt{\frac{8}{3}}\,\mu_{Ge}$$

$$C^{y}_{5,10a} = -C^{x}_{5,10b} = c\mu_{Ge} + \left(c + \frac{1}{c}\right)\mu_C$$

where μ_X (X = H or D), μ_{Ge}, μ_C and μ_H represent the reciprocal masses of the respective atoms and

$$a = \sqrt{\frac{R}{r}}, \quad b = \sqrt{\frac{D}{r_c}}, \quad c = \sqrt{\frac{r_c}{R}}.$$

4. Results and Discussion

The molecular parameters[1] are given in Table I. The angles α and β are taken to be tetrahedral. The internal co-ordinates, numbering of atoms and orientation of the principal axes are shown in Fig. 1.

TABLE I

Molecular parameters (Å) of germylacetylene

Distance	GeH_3CCH
r	1·521
R	1·896
r_c	1·208
D	1·056

The angles α and β are tetrahedral

The secular equations have been solved to obtain the F matrix elements. The frequencies have been finally calculated which agreed reasonably well with the observed values. The calculated and the observed fundamental frequencies are given in Table II. The appropriate set of force constants is presented in Table III. The mean amplitudes of vibration are given in Table IV.

It is found that the stretching force constants of Ge—x and C≡C, obtained in the present study, are in good agreement with the values reported

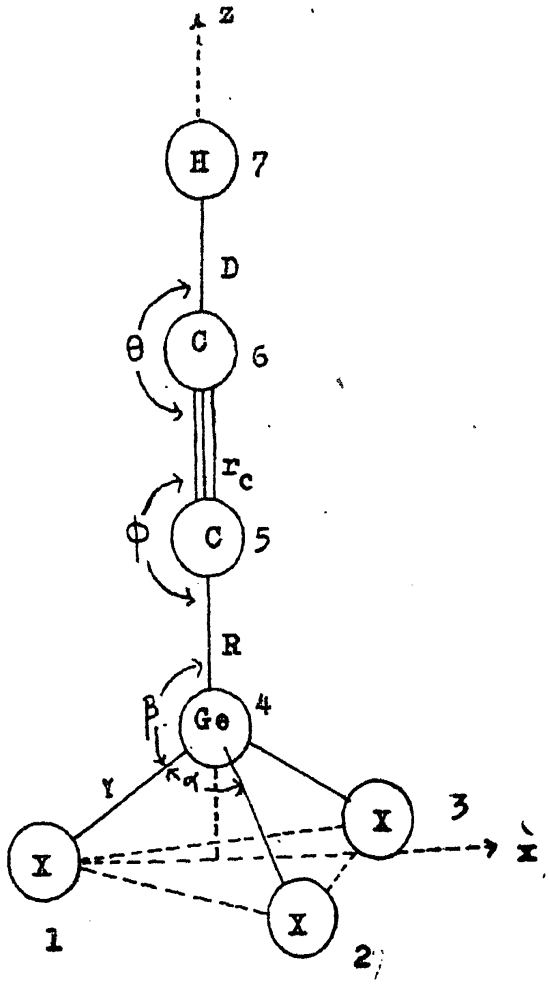

FIG. 1. The internal co-ordinates, numbering of atoms and orientation of the principal axes of germylacetylene.

for corresponding bonds in related molecules.[12–14] The infrared spectra[15] and electron diffraction[16] studies have shown that single bonds adjacent to triple bonds in the acetylenes and cyanides are significantly shorter than the normal tetrahedral carbon bond. Microwave studies of the linear acetylenes[17, 18] and cyanides[18, 19] also show the same effect. The higher force constants and the smaller mean amplitude values of the Ge—C≡bond may be attributed to this shortening. The Ge—C bond is 0·05 Å shorter[1] than the value reported for methyl germane[20] and is consistent with a change in carbon hybridization from sp^3 to sp.

The generalised mean-square amplitudes of vibration are reported in Table V. Substitution of deuterium does not affect the parallel mean amplitudes of the other bonds, but the perpendicular mean amplitudes are

very much altered. The shrinkage constants are presented in Table VI. The shrinkage effect in GeD_3CCH is found to be slightly more than in GeH_3CCH, since the perpendicular mean-square amplitudes are found to be higher in the former case.

TABLE II

Observed and calculated vibrational frequencies ($cm.^{-1}$) of GeH_3CCH and GeD_3CCH

Species	Designation	GeH_3CCH		GeD_3CCH	
		Observed	Calculated	Observed	Calculated
a_1	ν_1	3313·5	3314	3316·5	3316
	ν_2	2160	2065	2052·5	2065
	ν_3	2120	2120	1525	1505
	ν_4	843·8	843	608	607
	ν_5	530	528	518	524
e	ν_6	2117·2	2117	1525	1525
	ν_7	886	885	643·2	643
	ν_8	673	700	673	678
	ν_9	643·8	643	484	485
	ν_{10}	216·4	218	202·8	203

The Coriolis coupling constants are given in Tables VII and VIII. These constants for the degenerated coupling have been obtained from the spectral analysis by Lovejoy and Baker.[2] They have shown that $\zeta_8 + \zeta_{10} = 1{\cdot}975$ and both ζ_8 and ζ_{10} might be positive and approximately equal but slightly less than the unity. The values determined in this investigation for ζ_8 and ζ_{10} are in good agreement with the observation made by them. Further, they have predicted a value of $-0{\cdot}052$ for ζ_6, $-0{\cdot}248$ for ζ_7 and $0{\cdot}364$ for ζ_9. Though the numerical values obtained in the present study are not widely different from those values, the signs of these constants are found to be exactly reverse.

TABLE III

Force constants (md/Å) of GeH_3CCH and GeD_3CCH

Force constant	GeH_3CCH	GeD_3CCH
f_r	2·631	2·663
f_R	3·273	3·273
f_{rc}	15·140	15·140
f_D	5·888	5·888
f_α	0·1291	0·1408
f_β	0·3373	0·3540
f_ϕ	0·1396	0·1228
f_θ	0·1461	0·1241
f_{rr}	0·0160	0·0001
f_{rcD}	0·0398	0·0398
f_{rcR}	0·0050	0·0050
f_{Rr}	0·0018	0·0018
$f_{r\alpha}$	0·0055	0·0117
$f_{r\beta}$	0·0102	0·0212
$f_{\alpha\beta}$	0·0616	0·0660
$f_{\phi\theta}$	−0·0722	−0·0595
$(f_{R\alpha} - f_{R\beta})$	−0·0515	−0·0515

TABLE IV

Mean-square amplitudes of vibration (Å²) of GeH_3CCH and GeD_3CCH

Designation	GeH_3CCH	GeD_3CCH
σ_r	0·008005	0·005645
σ_R	0·002166	0·002210
σ_{rc}	0·001329	0·001330
σ_D	0·005645	0·005514
σ_α	0·070530	0·052749
σ_β	0·030830	0·023912
σ_ϕ	0·046620	0·050676
σ_θ	0·058480	0·061626
σ_{rr}	−0·000040	−0·000052
σ_{rcD}	−0·000285	−0·000269
$\sigma_{\phi cR}$	−0·000515	−0·000503
σ_{Rr}	−0·000037	−0·000051
$\sigma_{r\alpha}$	−0·000207	−0·000287
$\sigma_{r\beta}$	−0·000197	−0·000273
$\sigma_{\alpha\beta}$	0·009650	0·007178
$\sigma_{\phi\theta}$	0·015460	0·016810
$(\sigma_{R\alpha} - \sigma_{R\beta})$	0·000567	0·000843

TABLE V

Generalised mean-square amplitudes (10^{-4} Å^2) of vibration in GeH_3CCH and GeD_3CCH

Atom Pair	Designation	GeH_3CCH	GeD_3CCH
Ge—X	$\langle(\triangle z)^2\rangle$	79·960	56·410
	$\langle(\triangle x)^2\rangle$	277·524	221·876
	$\langle(\triangle y)^2\rangle$	183·775	137·600
	$\langle(\triangle z\ \triangle x)\rangle$	0·280	0·230
Ge—C_5	$\langle(\triangle z)^2\rangle$	21·660	22·120
	$\langle(\triangle x)^2\rangle = \langle(\triangle y)^2\rangle$	78·236	83·701
$C_5 \equiv C_6$	$\langle(\triangle z)^2\rangle$	13·310	13·360
	$\langle(\triangle x)^2\rangle = \langle(\triangle y)^2\rangle$	136·549	159·200
C_6—H_7	$\langle(\triangle z)^2\rangle$	56·450	55·140
	$\langle(\triangle x)^2\rangle = \langle(\triangle y)^2\rangle$	726·700	782·029
$X_2 \cdots X_3$	$\langle(\triangle z)^2\rangle$	284·470	208·970
	$\langle(\triangle x)^2\rangle$	191·250	141·400
	$\langle(\triangle y)^2\rangle$	568·184	455·165
	$\langle(\triangle x\ \triangle y)\rangle$	75·919	62·621
$X_1 \cdots C_5$	$\langle(\triangle z)^2\rangle$	155·684	118·670
	$\langle(\triangle x)^2\rangle$	333·705	293·808
	$\langle(\triangle y)^2\rangle$	296·884	248·942
	$\langle(\triangle z\ \triangle x)\rangle$	−79·140	−61·268
$X_1 \cdots C_6$	$\langle(\triangle z)^2\rangle$	225·670	188·427
	$\langle(\triangle x)^2\rangle$	142·976	99·355
	$\langle(\triangle y)^2\rangle$	171·502	122·856
	$\langle(\triangle z\ \triangle x)\rangle$	−92·056	−69·525
$X_1 \cdots H_7$	$\langle(\triangle z)^2\rangle$	415·539	384·023
	$\langle(\triangle x)^2\rangle$	663·107	683·834
	$\langle(\triangle y)^2\rangle$	829·888	873·083
	$\langle(\triangle z\ \triangle x)\rangle$	197·658	246·950
Ge $\cdots$ C_6	$\langle(\triangle z)^2\rangle$	24·650	25·430
	$\langle(\triangle x)^2\rangle = \langle(\triangle y)^2\rangle$	11·987	17·272
Ge $\cdots$ H_7	$\langle(\triangle z)^2\rangle$	75·400	75·200
	$\langle(\triangle x)^2\rangle = \langle(\triangle y)^2\rangle$	765·058	853·468
$C_5 \cdots H_7$	$\langle(\triangle z)^2\rangle$	64·040	64·420
	$\langle(\triangle x)^2\rangle = \langle(\triangle y)^2\rangle$	1228·190	1360·686

TABLE VI

Shrinkage effect (Å) in GeH_3CCH and GeD_3CCH

Designation	GeH_3CCH	GeD_3CCH
δ_{4-6}	0·015051	0·017039
δ_{4-7}	0·065877	0·070975
σ_{5-7}	0·025900	0·027000

TABLE VII

Zeta values for GeH_3CCH and GeD_3CCH ($e \times e$) coupling

ζ^{α}_{ij}	GeH_3CCH	GeD_3CCH
ζ^{α}_{66}	0·01818	0·03568
ζ^{α}_{77}	0·45327	0·48789
ζ^{α}_{88}	0·88880	0·89773
ζ^{α}_{99}	−0·29980	−0·31169
$\zeta^{\alpha}_{10,10}$	0·96134	0·91825
$\zeta^{\alpha}_{6,7}$	−0·47820	−0·48395
$\zeta^{\alpha}_{6,8}$	−0·30180	0·19220
$\zeta^{\alpha}_{6,9}$	0·75010	0·77970
$\zeta^{\alpha}_{6,10}$	0·06990	0·09152
$\zeta^{\alpha}_{7,8}$	−0·22190	0·22664
$\zeta^{\alpha}_{7,9}$	−0·11160	−0·03680
$\zeta^{\alpha}_{7,10}$	0·13730	0·17423
$\zeta^{\alpha}_{8,9}$	0·11670	0·05246
$\zeta^{\alpha}_{8,10}$	0·04521	−0·08020
$\zeta^{\alpha}_{9,10}$	0·10350	0·12844

TABLE VIII

Zeta values for GeH_3CCH and GeD_3CCH ($a_1 \times e$) coupling

$\zeta^a_{ij} = -\zeta^y_{ij}$	GeH_3CCH	GeD_3CCH
$\zeta^y_{1,6}$	0·0	0
$\zeta^y_{1,7}$	0·2638	−0·4704
$\zeta^y_{1,8}$	−0·8395	−0·7606
$\zeta^y_{1,9}$	−0·1309	−0·0568
$\zeta^y_{1,10}$	−0·4529	−0·4450
$\zeta^y_{2,6}$	0	0
$\zeta^y_{2,7}$	−0·3218	0
$\zeta^y_{2,8}$	0·3677	0·5064
$\zeta^y_{2,9}$	0·0072	−0·0450
$\zeta^y_{2,10}$	−0·8450	−0·8370
$\zeta^y_{3,6}$	0·0092	0·0181
$\zeta^y_{3,7}$	−0·6362	−0·6102
$\zeta^y_{3,8}$	−0·2464	0·2747
$\zeta^y_{3,9}$	−0·2234	−0·1860
$\zeta^y_{3,10}$	0·1652	0·2193
$\zeta^y_{4,6}$	−0·7136	−0·7196
$\zeta^y_{4,7}$	0·3274	0·3214
$\zeta^y_{4,8}$	0·2086	−0·1269
$\zeta^y_{4,9}$	−0·5293	−0·5473
$\zeta^y_{4,10}$	−0·0470	−0·0581
$\zeta^y_{5,6}$	0·0003	0·0008
$\zeta^y_{5,7}$	0·2045	0·2193
$\zeta^y_{5,8}$	0·0188	−0·1573
$\zeta^y_{5,9}$	0·0590	0·0780
$\zeta^y_{5,10}$	0·1785	0·1377

For germylacetylene molecule, the following zeta sum rule is found to be satisfied for the degenerate coupling:

$$\sum_{i=6}^{10} \zeta_i = \frac{I_A}{2I_B} + 2 = 2{\cdot}022.$$

Here I_A and I_B represent the moments of inertia about the symmetry axis and any other axis respectively.

ACKNOWLEDGEMENT

Two of the authors (V. M. and A. N.) are thankful to the Council of Scientific and Industrial Research and Ministry of Education, Government of India for the award of Senior and Junior Research Fellowships respectively.

REFERENCES

1. Thomas E. C. and Victor W. Laurie — *J. Chem. Phys.*, 1966, **44**, 2602.
2. Lovejoy, R. W. and Baker, D. R. — *Ibid.*, 1967, **46**, 658.
3. Rao, D. V. R. A. and Rai, D. K. — *Curr. Sci.*, 1968, **37**, 41.
4. Meister, A. G. .. *J. Chem. Phys.*, 1948, **16**, 950.
5. Krishna Pillai, M. G. and Perumal, A. — *Bull. Soc. Chim. Belg.*, 1954, **73**, 29.
6. Wilson, E. B. .. *J. Chem. Phys.*, 1939, **7**, 1047; 1941, **9**, 76.
7. Cyvin, S J. .. *Acta Polytechnica Scandinavica*, 1960, Ph. 6, p. 279.
8. Morino, Y and Hirota, E. .. *J. Chem. Phys.*, 1955, **23**, 737.
9. ———— .. *Acta Cryst.*, 1960, **13**, 1107.
10. Jahn, H. A. .. *Phys. Rev.*, 1939, **56**, 680.
11. Meal, J. H. and Polo, S. R. — *J. Chem. Phys.*, 1956, **24**, 1119, 1126.
12. Venkateswarlu, K. and Mariamma, P. Mathew — *Ind. Jour. Pure and Appl. Phys.*, 1967, **5**, 17.
13. Clark, E. A. and Weber, A. .. *J. Chem. Phys.*, 1966, **45**, 1759.
14. Venkateswarlu, K. and Natarajan, A. — (To be published).
15. Herzberg, G., Patat, F. and Verleger, H. — *J. Phys. Chem.*, 1937, **41**, 123.

16. Pauling, L., Springal, H. D. and Palmer, K. J. — *J. Am. Chem. Soc.*, 1939, **61**, 927.

17. Westernberg, A. A. and Wilson, E. B. Jr. .. *Ibid.*, 1950, **72**, 199.

18. ——, Goldstein, J. H. and Wilson E. B. Jr. .. *J. Chem. Phys.*, 1949, **17**, 1319.

19. Kessler, M., Ring, H., Trambarulo, R. and Cordy, W. — *Phys. Rev.*, 1950, **79**, 54.

20. Lauric, V. W. .. *J Chem. Phys.*, 1959, **30**, 1210.