MOLECULAR CONSTANTS OF GERMYL CYANIDE AND GERMYL CYANIDE-d₃

K. Venkateswarlu[†] and P. Bhamambal

Department of Physics, Kerala University*

Normal coordinate analysis of the germyl cyanide and germyl cyanide-d_3 based on the general valence and Urey Bradley force fields is presented. Generalised mean-square amplitudes of vibration and shrinkage effect are obtained from the fundamental frequencies as observed in the infrared. The zeta values for the degenerate species are also reported. The thermodynamic properties have been calculated for the ideal gaseous state at one atmospheric pressure for eleven temperatures ranging from 100° to 1000° K assuming a rigid rotor harmonic oscillator approximation.

1. Introduction

Molecules of the $XY_3 ZW$ type belonging to the symmetry group C_{3v} have been subjected to spectroscopic studies by several investigators [1–13]. The complete infrared spectra of germyl cyanide and its deuterated analogue have been reported by Goldfarb [14]. From the rotational structure of two of the perpendicular bands he has also reported the values of ζ_5 and ζ_6 for GeH_3CN. From the observed frequency for the CN stretching vibration, it has been concluded that the molecule is the normal cyanide only unlike in the case of alkyl, germyl cyano and silyl cyano compounds, which are equilibrium mixtures of the normal and isocyanides. So far no normal coordinate analysis has been carried out for these molecules though such studies are available for the methyl cyanide, methyl isocyanide [3, 6, 9, 10] and silyl cyanide [10]. Hence in the present investigation an attempt is made to obtain the force constants, generalised mean-square amplitudes of vibration, shrinkage effect and Coriolis coupling constants of these molecules. The thermodynamic properties are also reported here.

The C_{3v} symmetry of GeH_3CN requires eight fundamental vibrational modes, all infrared and Raman active, four belonging to the type a_1 and the other four belonging to the doubly degenerate e type. Fig. 1 shows the numbering of atoms, internal coordinates and the orientation of the principal axes for the GeX_3CN (X = H or D) molecules.
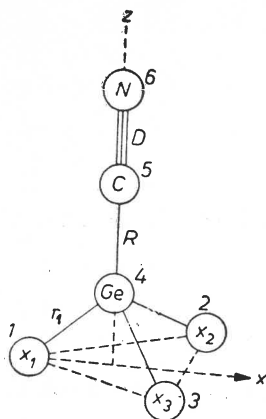
Fig. 1. Internal coordinates, numbering of atoms and orientation of the principal axes

2. Potential energy constants

Following the FG matrix method of Wilson [15], the potential constants have been obtained for both the general valence and Urey Bradley type of force fields. The symmetry coordinates and frequencies are from references [1] and [14] respectively. The Ge—H distance (1.53 Å) is taken as the average value based on the microwave and infrared data on germane and several of its derivatives [16–18]. The Ge–C distance (1.95 Å) is the microwave value reported for methyl germane [18] and C ≡ N distance (1.16 Å) is based on the microwave value in methyl cyanide [19].

3. Generalised mean-square amplitudes

The generalised mean-square amplitudes which include both the parallel and perpendicular mean-square amplitudes are evaluated by the method of Morino and Hirota [20]. The Σ values are obtained solving the secular equation of Cyvin [21]. Using the transformation matrix A derivable from the s vectors, the generalised mean-square amplitudes are computed in terms of the Σ elements.

Shrinkage effect

The shrinkage effect in linear molecules which has been observed experimentally from electron diffraction studies by Bastiansen et al. [22–24] may be calculated theoretically from spectroscopic data using the perpendicular mean-square amplitudes as pointed out by Morino [25]. For the type of molecules under study, the only linear shrinkage is that of the Ge...N distance. When the mean-square perpendicular amplitudes, $\langle (\Delta x)^2 \rangle$ and $\langle (\Delta y)^2 \rangle$ are known in the case of a bond having an equilibrium length r_e, the constant K has been defined as $K = [\langle (\Delta x)^2 \rangle + \langle (\Delta y)^2 \rangle]/2r_e$. In the present case, the shrinkage for the Ge...N bond length is found from the relation,

$$-\delta_{\text{GeN}} = K_{\text{GeN}} - (K_{\text{GeC}} + K_{\text{CN}})$$

Coriolis coupling constants

The force constants of the e species can be used to calculate the Coriolis constants for the interaction of the vibrations of this species with molecular rotation. The procedure of Meal and Polo [26] is adopted here. In this the zetas are obtained as the diagonal elements of the matrix $\zeta = L^{-1}C^Z\tilde{L}^{-1}$, where L^{-1} is the inverse of the L matrix, which may be obtained from force constants. The elements of C^Z can be found from the s vectors using the relation.

$$C_{ij}^{\zeta} = \sum_a \mu_a(s_{ia} \times s_{ja})\, e_Z$$

Here e_Z is the unit vector along the Z axis, s_{ia} and s_{ja} are the s vectors and μ_a, the reciprocal mass of the atom "a". The vector sum is carried over all atoms in the molecules, though of course symmetry may require some of the s vectors to be zero. The elements of C^Z so derived for the molecules investigated here are:

$$C_{5a,5b} = \frac{4}{3}\,\mu_{Ge}$$

$$C_{5a,6b} = -\sqrt{2}\,\mu_{Ge}\left(\frac{a}{3} + \frac{1}{a}\right)$$

$$C_{5a,7b} = \sqrt{2}\,\mu_X + \frac{4}{3}\sqrt{2}\,\mu_{Ge}$$

$$C_{5a,8b} = \frac{2}{\sqrt{3}}\,b\mu_{Ge}$$

$$C_{6a,6b} = \frac{3}{2}\left(\frac{1}{a} + \frac{a}{3}\right)^2 \mu_{Ge} + \frac{3}{2a^2}\,\mu_C$$

$$C_{6a,7b} = -\frac{a}{2}\,\mu_X - 2\mu_{Ge}\left(\frac{1}{a} + \frac{a}{3}\right)$$

$$C_{6a,8b} = -\sqrt{\frac{3}{2}}\,b\left(\frac{1}{a} + \frac{a}{3}\right)\mu_{Ge} - \sqrt{\frac{3}{2}}\frac{1}{a}\left(\frac{1}{b} + b\right)\mu_C$$

$$C_{7a,7b} = -\frac{1}{2}\,\mu_X + \frac{8}{3}\,\mu_{Ge}$$

$$C_{7a,8b} = 2b\sqrt{\frac{2}{3}}\,\mu_{Ge}$$

$$C_{8a,8b} = b^2\mu_{Ge} + \left(\frac{1}{b} + b\right)^2 \mu_C + \frac{1}{b^2}\,\mu_N.$$

Where $a = \left(\dfrac{R}{r}\right)^{\frac{1}{2}}$ and $b = \left(\dfrac{D}{R}\right)^{\frac{1}{2}}$, $^\mu\text{Ge}$, $^\mu\text{X}$ and $^\mu\text{N}$ are the reciprocal masses of Ge, X and N atoms respectively. In the case of the coupling between the degenerate pair, C and ζ are symmetric submatrices so that $C_{ia,jb} = C_{ib,ja}$ and $\zeta_{ia,jb} = \zeta_{ib,ja}$. For a six atomic molecule belonging to the point group C_{3v}, the zeta sum vule [27] is $\displaystyle\sum_{i=5}^{8}\zeta_i = 1 + \dfrac{I_A}{2I_B}$ where ζ_i are the diagonal elements of the matrix ζ and I_A and I_B are the monents of inertia about the symmetry axis and any one of the two perpendicular axes respectively.

Thermodynamic properties

Making use of the observed frequencies and molecular parameters, the molar thermodynamic properties *viz.*, heat content, entropy, free energy and heat capacity have been calculated for both germyl cyanide and germyl cyanide d_3. The calculations are for the ideal gaseous state at normal pressure, based on a rigid rotor, harmonic oscillator approximation with no interaction between vibrational and rotational energies.

Results and discussion

The force constants of GeH_3CN and GeD_3CN for both the general valence and Urey Bradly type of force fields are given in Table I. The solutions of the secular equations for germyl cyanide and its deuterated analogue were attempted separately and slightly differ-

TABLE I

General valence and Urey Bradley force constants (md/Å) of germyl cyanide and germyl cyanide-d_3

Generala valence force field			Urey Bradley force field		
Designation	GeH_3CN	GeD_3CN	Designation	GeH_3CN	GeD_3CN
f_D	17.780	17.820	K_D	17.020	17.030
f_R	3.196	3.203	K_R	2.577	2.563
f_r	2.710	2.758	K_r	2.521	2.587
f_α	0.1270	0.1466	H_{XX}	0.1638	0.1702
f_β	0.2230	0.2236	H_{CX}	0.1301	0.1219
f_Φ	0.0645	0.0646	H_{GeN}	0.0603	0.0637
f_{RD}	0.3398	0.3171	F_{XX}	−0.0308	−0.0469
f_{rD}	0.1184	0.1184	F_{CX}	0.2382	0.2460
f_{Rr}	0.2206	0.2201	F_{NX}	0.0807	0.0856
f_{rr}	0.0207	0.0127	F_{GeN}	0.0398	0.0425
$(f_{D\alpha}-f_{D\beta})$	0.0099	0.0099			
$(f_{R\alpha}-f_{R\beta})$	0.0135	0.0138			
$f_{r\alpha}$	0.0551	0.0555			
$f_{r\beta}$	0.0429	0.0410			
$f'_{r\alpha}$	0.0242	0.0217			
$f_{\alpha\alpha}$	−0.0245	−0.0090			
$f_{\alpha\beta}$	−0.0102	0.0048			

ing sets of force constants have been obtained. The major force constants, obtained by different methods show satisfactory agreement. The Urey Bradley force field gives the repulsion force constants also, which are of the van der waals type. H...H and D...D repulsion forces are found to be negative in conformity with what has been reported by Venkateswarlu and Thanalakshmi [9] for CH_3CN and CH_3NC molecules. Table II shows a comparison of the main force constants of germyl cyanide obtained in the present investigation with

TABLE II

Comparison of force constants (md/Å) in germyl cyanide, methyl cyanide and methyl isocyanide

Force constant	General valence			Urey Bradley		
	GeH_3CN	CH_3CN	CH_3NC	GeH_3CN	CH_3CN	CH_3NC
f_D	17.7800	17.8800	16.8500	17.0200	17.2480	16.2460
f_R	3.1960	5.1300	5.1300	2.5770	5.1300	5.1300
f_r	2.7100	4.9430	4.9160	2.5210	4.5519	4.6069
f_α	0.1270	0.4608	0.4591	0.1638	0.5099	0.5819
f_β	0.2230	0.5384	0.5310	0.1301	0.2739	0.2024
f_Φ	0.0645	0.3210	0.1879	0.0603	0.1880	0.1197

these of methyl cyanide and methyl isocyanide reported in the literature [6,9]. From this Table it may be noted that $C = N$ force constant is almost the same in GeH_3CN and CH_3CN but is a little lower in CH_3NC. This suggests that the CN groups in the normal cyanide and isocyanide are not exactly identical. If the germyl cyanide were an equilibrium mixture of the normal and isocompounds, the force constant might have been less then what is obtained here. The perfect agreement in the $C = N$ force constants of germyl cyanide and methyl cyanide leads to the conclusion that the molecule is normal cyanide only as suggested by Goldfarb [14]. The substitution of germanium for carbon produces a substantial decrease in all the other major force constants. This is to be anticipated since germanium is heavier and less electronegative than carbon.

The generalised mean-square amplitudes of vibration for GeH_3CN and GeD_3CN are summarised in Table III. Owing to the symmetry of the molecule the perpendicular amplitudes $\langle(\Delta x)^2\rangle = \langle(\Delta y)^2\rangle$ and all the mean cross-products vanish for $Ge-C$, $Ge...N$ and $C \equiv N$ distances. The mean-square amplitudes obtained here for the bonded atom pairs compare well with the values reported for similar bonds. Again the $Ge-C$ and $C \equiv N$ mean-square amplitudes are almost the same in GeH_3CN and GeD_3CN. This shows that the mean amplitude is characteristic of the bond and is little affected by the bond environments. Even though the $Ge-X$ force constant is very nearly the same in GeH_3CN and GeD_3CN, the corresponding mean-square amplitude is widely different. By the deuterium substitution all the other nonbonded mean-square amplitudes (except $Ge...N$) are also affected considerably. The general observation is that for these nonbonded distances both the parallel and perpendicular amplitudes are less in the deuterated molecule. These mean-square amplitudes may prove useful in the interpretation of electron diffraction data.

TABLE III

Generalised mean-square amplitudes of vibration (Å)^2 of germyl cyanide and germyl cyanide-d_3

Atom pair	Mean-square amplitude quantity	GeH$_3$CN	GeD$_3$CN	Atom pair	Mean-square amplitude quantity	GeH$_3$CN	GeD$_3$CN
Ge—X	$\langle(\Delta z)^2\rangle$	0.008020	0.005627	C...X	$\langle(\Delta z)^2\rangle$	0.015235	0.011502
	$\langle(\Delta x)^2\rangle$	0.027790	0.021754		$\langle(\Delta x)^2\rangle$	0.035183	0.029270
	$\langle(\Delta y)^2\rangle$	0.019041	0.018735		$\langle(\Delta y)^2\rangle$	0.031822	0.026989
	$\langle(\Delta z)(\Delta x)\rangle$	0.000016	0.000048		$\langle(\Delta z)(\Delta x)\rangle$	0.005243	0.005866
Ge—C	$\langle(\Delta z)^2\rangle$	0.002355	0.002344	N...X	$\langle(\Delta z)^2\rangle$	0.023395	0.018953
	$\langle(\Delta x)^2\rangle$	0.009148	0.008654		$\langle(\Delta x)^2\rangle$	0.012901	0.008847
	$\langle(\Delta y)^2\rangle$				$\langle(\Delta y)^2\rangle$	0.017335	0.013288
					$\langle(\Delta z)(\Delta x)\rangle$	0.007259	0.004487
C≡N	$\langle(\Delta z)^2\rangle$	0.001211	0.001207	X...X	$\langle(\Delta z)^2\rangle$	0.026185	0.020276
	$\langle(\Delta x)^2\rangle$	0.021270	0.021970		$\langle(\Delta x)^2\rangle$	0.016945	0.013610
	$\langle(\Delta y)^2\rangle$				$\langle(\Delta y)^2\rangle$	0.056554	0.043383
					$\langle(\Delta y)(\Delta x)\rangle$	0.000261	0.001168
Ge...N	$\langle(\Delta z)^2\rangle$	0.002296	0.002278				
	$\langle(\Delta x)^2\rangle$						
	$\langle(\Delta y)^2\rangle$	0.002632	0.003366				

TABLE IV

K values and shrinkage constant (Å) in GeH$_3$CN and GeD$_3$CN

Atom pair	K or δ	GeH$_3$CN	GeD$_3$CN
Ge—C	K	0.004692	0.004438
C—N	K	0.018320	0.018930
Ge...N	K	0.000846	0.001080
Ge...N	δ	0.022166	0.022288

The K values and shrinkage constants are presented in Table IV. Since the perpendicular mean-square amplitudes for C = N, Ge-C and Ge...N distances on which the shrinkage is ultimately dependent are very nearly the same for GeH$_3$CN and GeD$_3$CN, the shrinkage is not altered considerably by the substitution of D for H. The zeta values for the coupling within the degenerate pair are given in Table V. From high resolution studies of the rotational structure of the perpendicular bands Goldfarb has reported a value of —0.03 for ζ_5, corresponding to a vibrational wave number 2147.7 cm^{-1} and —0.31 for ζ_6 corresponding, vibrational wave number being 893.7 cm^{-1}. The present study yields a value of —0.01 for ζ_5 ($\zeta_{5a,5b}$ in the Table) and in magnitude it is less than the experimental value. However, the value of —0.31 for ζ_{b6} obtained in the present study exactly coincides with the experimental value. This suggests the validity of the force field (general valence type) used in the present study. The sum of the zetas for both the molecules is in agreement with what is expected from the zeta sum rule.

TABLE V

Coriolis coupling constants of GeH_3CN and GeD_3CN

Coupling	$\zeta^z_{i,j}$	GeH_3CN	GeD_3CN
	$\zeta^z_{5a,5b}$	−0.0105	0.0618
		0.6553	0.6515
	$\zeta^z_{5a,6b}$	0.6663	0.6528
	$\zeta^z_{5a,7b}$	−0.0762	−0.1513
	$\zeta^z_{5a,8b}$	−0.3127	−0.3229
exe	$\zeta^z_{6a,6b}$	−0.0480	−0.1254
	$\zeta^z_{6a,7b}$	−0.1471	−0.1779
	$\zeta^z_{6a,8b}$	0.3944	0.4207
	$\zeta^z_{7a,8b}$	0.1353	0.2130
	$\zeta^z_{8a,8b}$	0.9506	0.8835

TABLE VI

Thermodynamic functions of GeH_3CN and GeD_3CN (Cal deg^{-1} mole^{-1})

Temp. °(K)	GeH₃CN				GeD₃CN			
	Heat capacity	Heat content	Free energy	Entropy	Heat capacity	Heat content	Free energy	Entropy
100	9.859	8.500	44.364	52.864	10.186	8.590	45.296	53.886
200	13.252	10.017	50.720	60.737	14.952	10.572	51.844	62.416
273.2	15.644	11.207	54.034	65.241	17.791	12.147	55.358	69.173
300	16.420	11.631	55.101	66.732	18.626	12.683	56.491	69.173
400	18.846	13.150	58.668	71.818	21.116	14.483	60.381	74.864
500	20.716	14.488	61.773	76.261	23.046	16.045	63.841	79.884
600	22.286	15.668	64.499	80.168	24.546	17.322	66.866	84.184
700	23.616	16.702	66.978	83.679	25.736	18.436	69.608	88.044
800	24.756	17.640	69.265	86.904	26.716	19.426	72.148	91.574
900	25.696	18.486	71.409	89.894	27.486	20.256	74.468	94.724
1000	26.486	19.236	73.378	92.614	28.116	21.016	76.668	97.684

The thermodynamic functions of GeH_3CN and GeD_3CN are tabulated in Table VI.

REFERENCES

[1] J. W. Linnett, *J. Chem. Phys.*, **8**, 91 (1940).
[2] B. L. Crawford Jr., and S. A. Brinkley, *J. Chem. Phys.*, **9**, 69 (1941).
[3] S. L. N. G. Krishnamachari, *Indian J. Phys.*, **28**, 463 (1954).
[4] R. C. Taylor, *J. Chem. Phys.*, **26**, 1131 (1957); **27**, 979 (1957).
[5] G. W. Bethke, and M. K. Wilson, *J. Chem. Phys.*, **26**, 1118 (1957); **27**, 978 (1957).
[6] M. G. Krishna Pillai, and F. F. Cleveland, *J. Molecular Spectrosc.*, **5**, 212 (1960).
[7] S. Sundaram, and F. F. Cleveland, *J. Chem. Phys.*, **32**, 166 (1960).
[8] K. Venkateswarlu, and R. Thanalakshmi, *Proc. Indian Acad. Sci.*, **56**, 247 (1962).

[9] K. Venkateswarlu, and R. Thanalakshmi, *Indian J. Pure Appl. Phys.*, **1**, 64 (1963).

[10] J. L. Duncan, *Spectrochim. Acta*, **20**, 1197, 1807 (1964).

[11] K. Venkateswarlu, and C. Purushothaman, *Indian J. Pure Appl. Phys.*, **3**, 377 (1965).

[12] K. Venkateswarlu, and C. Purushothaman, *Czech. J. Phys.*, **16**, 144 (1966).

[13] K. Venkateswarlu, K. V. Rajalakshmi and C. Purushothaman, *Bull. Soc. Roy. Sci. Liege*, **333** (1967).

[14] T. D. Goldfarb, *J. Chem. Phys.*, **37**, 642 (1962).

[15] E. B. Wilson Jr., J. C. Decius and P. C. Cross, *Molecular Vibrations*, Mc Graw Hill, New York 1955.

[16] L. P. Lindeman and M. K. Wilson, *J. Chem. Phys.*, **22**, 1723 (1954).

[17] B. P. Dailey, J. M. Mays and C. H. Townes, *Phys. Rev.*, **76**, 136 (1949).

[18] V. W. Laurie, *J. Chem. Phys.*, **30**, 1210 (1959).

[19] M. Kessler, H. Ring and R. Trambarulo. *Phys. Rev.*, **79**, 54 (1950).

[20] Y. Morino and E. Hirota, *J. Chem. Phys.*, **23**, 737 (1955).

[21] S. J. Cyvin, *Acta Polytech. Scandinavica*, **6**, 279 (1960).

[22] A. Alemenningen, O. Bastiansen and T. Munthe-Kaas, *Acta Chem. Scandynavica*, **10**, 261 (1956).

[23] A. Alemenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scandinavica*, **13**, 1699 (1959).

[24] O. Bastiansen and M. Traetteberg, *Acta Cryst.*, **13**, 1108 (1960).

[25] Y. Morino, *Acta Cryst.*, **13**, 1107 (1960).

[26] J. H. Meal and S. R. Polo, *J. Chem. Phys.*, **24**, 1119 (1956).

[27] R. D. Cowan, *J. Chem., Phys.*, **18**, 1101 (1950).