

KINETIC CONSTANTS METHOD FOR THE VIBRATIONAL ANALYSIS OF MONO-AND-TRI-DEUTERO GERMANES

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A fresh study of the harmonic potential constants, compliance constants, vibrational mean amplitudes, Coriolis coupling constants and centrifugal distortion constants has been attempted in mono-and-tri-deutero-germanes. The values of all these molecular constants evaluated by 'Kinetic Constants' method, in general, is in agreement with the values in the literature.

Keywords : Kinetic Constants—Harmonic Potential Compliance & Coriolis Coupling; Mono & Tri-Deutero Germanes; Molecular Dynamics; Force Field for XYZ₃ Systems; Vibrational Analysis

INTRODUCTION

THE concept of kinetic constants has drawn the attention of molecular spectroscopists and chemists recently (Thirugnanasambandam & Mohan, 1974; Mohan 1977, 1979, 1980; Mohan & Ravikumar, 1980; and Thirugnanasambandam & Karunanidhi, 1976). The kinetic constants relating to molecules have been studied at length and these constants seem to provide interesting results concerning molecular dynamics. Such kinetic constants have been advantageously utilised in solving the secular equations governing potential constants. It was also demonstrated that these kinetic constants not only bring reasonable sets of potential energy constants but also the other molecular constants such as compliance constants, mean amplitudes of vibration, vibrational coupling constants and rotational distortion constants. The present investigation has been undertaken to obtain a reasonable set of potential constants for two molecules by kinetic constants method for the first time. The present sets of kinetic constants and potential constants are utilised to evaluate compliance constants, vibrational mean amplitudes, Coriolis coupling constants and rotational distortion constants of mono-and-tri-deutero-germane molecules. The calculated values of mean amplitudes and rotational distortion constants have been shown to stand in good comparison with the values found in the literature, thus establishing the merits of the new procedure. The essential features of the new procedure, involving kinetic constants, may be briefly mentioned. First, a comprehensive set of symmetry coordinates applicable to the general nontetrahedral structure and involving exterior interbond angles (Thirugnanasambandam & Mohan, 1974) has been framed for the molecular type under study. Secondly, redundant symmetry coordinates have been set up and redundancy constraints have been developed (Thirugnanasambandam & Karunanidhi, 1976; and Ford

& Orville, 1967) to identify the twelve independent force constants which characterise this structure. Thirdly, kinetic constants have been worked out and they have been utilised to link the concerned F-matrix elements in easily solving the secular equations. Thus, it may be seen that the new procedure adopted here is basically the traditional Wilson's FG matrix method (Wilson *et al.*, 1955) applied in a rigorous manner coupled with a new method for solving the secular equation on the basis of kinetic constants which appears to play a vital role in molecular dynamics.

THEORETICAL CONSIDERATIONS

Symmetry Coordinates

The structure, nomenclature of the parameters and the orientation of the Principal axes of the molecular type are shown in Fig. 1.

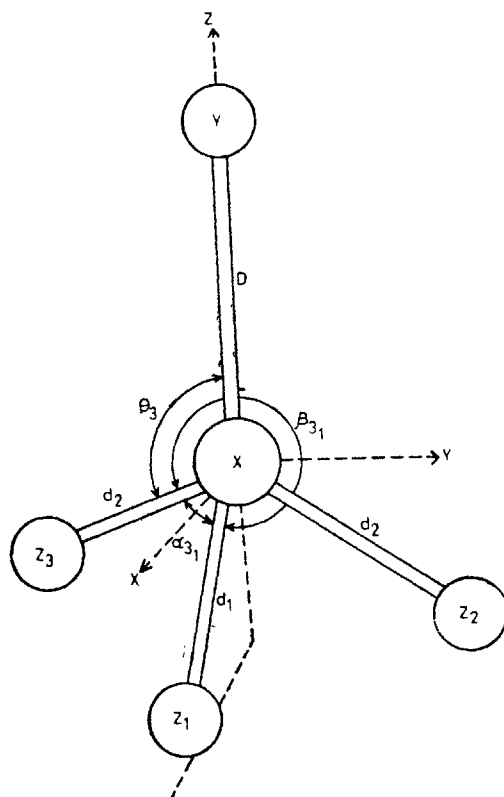


FIG. 1.

The following are the most general orthonormalised set of symmetry coordinates (6) :

A₁ Species :

$$S_1 = \Delta D,$$

$$S_2 = 3^{-1/2} (\Delta d_1 + \Delta d_2 + \Delta d_3),$$

$$S_3 = nd^{1/2} [Rd(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} - \Delta\beta_{12} - \Delta\beta_{23} - \Delta\beta_{31}) \\ - D(\Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3 - \Delta\phi_1 - \Delta\phi_2 - \Delta\phi_3)],$$

$$S_n = nd^{1/2} [Rd(\Delta\alpha_{12}) + \Delta\alpha_{23} + \Delta\alpha_{31} + \Delta\beta_{12} + \Delta\beta_{23} \\ + \Delta\beta_{31}) - D(\Delta\theta_1 + \Delta\theta_2 - \Delta\theta_3 + \Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3)] \equiv 0,$$

$$Sr_2 = ndD^{1/2} [(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} - \Delta\beta_{12} - \Delta\beta_{23} - \Delta\beta_{31}) \\ + R(\Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3 - \Delta\phi_1 - \Delta\phi_2 - \Delta\phi_3)] \equiv 0$$

and

$$Sr_3 = ndD^{1/2} [(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} + \Delta\beta_{12} + \Delta\beta_{23} + \Delta\beta_{31}) \\ + R(\Delta\theta_1 + \Delta\theta_2 + \Delta\theta_3 + \Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3)] \equiv 0.$$

E Species :

$$S_{4a} = 6^{-1/2} (2\Delta d_1 - \Delta d_2 - \Delta d_3),$$

$$S_{4b} = 2^{-1/2} (\Delta d_2 - \Delta d_3),$$

$$S_{5a} = 12^{-1/2} \epsilon (2\Delta\theta_1 - \Delta\theta_2 - \Delta\theta_3 - 2\Delta\phi_1 + \Delta\phi_2 + \Delta\phi_3),$$

$$S_{5b} = 2^{-1} \epsilon (\Delta\theta_2 - \Delta\theta_3 - \Delta\phi_2 + \Delta\phi_3),$$

$$S_{6a} = 12^{-1/2} d (2\Delta\alpha_{23} - \Delta\alpha_{31} - \Delta\alpha_{12} - 2\Delta\beta_{23} + \Delta\beta_{31} + \Delta\beta_{12}).$$

$$S_{6b} = 2^{-1} d (\Delta\alpha_{31} - \Delta\alpha_{12} - \Delta\beta_{31} + \Delta\beta_{12}),$$

$$Sr_{4a} = 12^{-1/2} \epsilon (2\Delta\theta_1 - \Delta\theta_2 - \Delta\theta_3 + 2\Delta\phi_1 - \Delta\phi_2 - \Delta\phi_3) \equiv 0,$$

$$Sr_{4b} = 2^{-1} \epsilon (\Delta\theta_2 - \Delta\theta_3 + \Delta\phi_2 - \Delta\phi_3) \equiv 0,$$

$$Sr_{5a} = 12^{-1/2} d (2\Delta\alpha_{23} - \Delta\alpha_{31} - \Delta\alpha_{12} + 2\Delta\beta_{23} - \Delta\beta_{31} - \Delta\beta_{12}) \equiv 0,$$

and

$$Sr_{5b} = 2^{-1} d (\Delta\alpha_{31} - \Delta\alpha_{12} + \Delta\beta_{31} - \Delta\beta_{12}) \equiv 0,$$

where $\epsilon^2 = Dd$, $R^2 = \left(4 - \text{Sec}^2 \frac{\alpha}{2}\right)$ and $n = [6(D + R^2d)]^{-1/2}$.

Redundancy Relations and Reduced F-matrix

There are five redundant symmetry coordinates, three in the *A₁* Species and two in the *E* Species. These redundant coordinates are found to give rise to twenty four redundancy constraints among the potential constants. These constraints are useful to distinguish between the twelve independent potential constants and the remaining twenty four non-independent potential constants. Making use of the respective constraint equations the *F*-matrix elements are reduced as follows :

A_1 Species :

$$F_{11} = f_D,$$

$$F_{22} = f_d + 2f_{da},$$

$$F_{33} = A/3n^2d,$$

$$F_{12} = 3^{1/2} f_{Da},$$

$$F_{13} = 3D_{\alpha}/nRd^{1/2}$$

and

$$F_{23} = B/(3d)^{1/2} n.$$

E Species :

$$F_{44} = f_d - f_{da},$$

$$F_{55} = 3f_{\theta} - A/\rho^2,$$

$$F_{66} = 2(f_{\alpha} - f_{\alpha\alpha}),$$

$$F_{45} = -2^{1/2}(3f'_{d\theta} + B/\rho),$$

and

$$F_{46} = 2^{1/2}(f'_{d\alpha} - f''_{d\alpha})$$

$$F_{56} = 3f'_{\alpha\theta} + RA/\rho,$$

where $A = (f_{\alpha} + 2f_{\alpha\alpha})/R^2$, $B = (f'_{d\alpha} + 2f''_{d\alpha})/R$ and $\rho^2 = d/D$.

The number of primes relating to the interaction constants indicates the number of common bonds in the case of an interaction between an angle and its own reflex angle whereas it denotes the number of common atoms in all other cases.

Kinetic Constants

The elements of the kinetic energy matrix have been obtained using Wilson's method (Wilson *et al.*, 1955) for the non-degenerate and degenerate vibrations and they are utilised to arrive kinetic constants. The general expressions for kinetic constants are given below :

A_1 Species :

$$K_D = m_y(m_x + 3m_z) M^{-1},$$

$$K_d + 2k_{da} = m_x(m_x + m_y + 4S^2m_z) M^{-1},$$

$$K_{\alpha} + 2K_{\alpha\alpha} = 9n^4R^2d^2m_z(m_x + m_y + 3C_{\theta}^2m_z) M^{-1},$$

$$K_{Da} = -C_{\theta} m_y m_z M^{-1},$$

$$K_{D\alpha} = -12^{1/2} n^2 R d S m_y m_z M^{-1},$$

$$K'_{d\alpha} + 2K''_{d\alpha} = -6(3^{1/2} n^2 R d) S C_{\theta} m_z^2 M^{-1},$$

$$K_c - K_{dd} = D^2 m_z (4\rho^4 S^4 m_z^2 + m_x m_y + \rho^4 (1 + 2C^2) (m_x + m_y) m_z \\ + (1 + 2C^2 - 6\rho^2 C_{\theta}) m_y m_z) (I_x M)^{-1},$$

$$3K_{\theta} - \frac{(k_{\alpha} + 2K_{\alpha\alpha})}{R^2} = D d m_y m_z [(1 + 2C^2) m_x + 6S^2 m_z] (3I_x M)^{-1},$$

$$2(K_{\alpha} - K_{\alpha\alpha}) = D^2 C^2 m_z (6\rho^4 S^2 m_z^2 + 2m_x m_y + 3\rho^4 m_x m_z \\ + 3(1 + \rho^4 - 2\rho^2 C^2) m_y m_z) (3I_x M)^{-1},$$

$$3K'_{d\theta} + \frac{(K'_{d\alpha} + 2K''_{d\alpha})}{\rho R} = -3^{-1/2} D \epsilon S m_y m_z^2 [\rho^2 (1 + 2C^2) - 3C_{\theta}] (I_x M)^{-1},$$

$$K'_{d\alpha} - K''_{d\alpha} = D d C S m_z^2 [(C_{\theta} - 1/\rho^2) m_y - 2\rho^2 S^2 m_z] (I_x M)^{-1},$$

and

$$3K'_{\alpha\theta} + \frac{(K_{\alpha} + 2K_{\alpha\alpha})}{\rho R} = 3^{-1/2} D C_{\theta} m_y m_z (C_{\theta} m_x + 2\rho^2 S^2 m_z) (I_x M)^{-1}$$

Here $S = \sin \alpha/2$, $C = \cos \alpha/2$ and $C = \cos \theta$. m_i denotes the Mass of the atom i , M the Mass of the Molecule and I_x the Moment of inertia of the molecule about the X -axis. It should be mentioned that identical suffixes have been adopted for the kinetic constants as well as the force constants.

Method of Kinetic Constants

The determination of symmetry potential constant involved in the secular equation from the n_i vibrational frequencies alone has remained a mathematically unsolved problem so far. Therefore, any genuine attempt to evaluate all the symmetry force constants associated with a problem of order $n > 1$ should involve the incorporation of atleast $n_i(n_i - 1)/2$ additional data other than the n_i frequencies.

The method of Kinetic Constants seeks to relate the off diagonal elements to the diagonal elements of the F -matrix through the relation

$$\frac{F_{ij}}{F_{jj}} = \frac{K_{ij}}{K_{jj}} \quad (i < j; i, j = 1, 2, 3).$$

The kinetic constants have been employed here to solve the 3×3 vibrational problem associated with both the A_1 and the E type vibration of the axially symmetric XYZ_3 molecules.

Compliance Constants

The compliance constants may be determined for these two molecules by Decius (1963) Method.

Vibrational Mean Amplitudes

The Mean square amplitude matrix elements may be obtained using the normal coordinate transformation Matrix \mathbf{L} from the relation (cf. Cyvin, 1968)

$$\Sigma = \mathbf{L} \Delta \mathbf{L}'$$

and therefrom the valence mean square amplitudes and the mean amplitudes at 298.16 °K may be calculated.

Coriolis Coupling Constants

The Coriolis coupling constants which may be determined experimentally can, however, be evaluated from a reliable set of potential constants and the values can be used for detailed interpretation of vibrational spectra. The Coriolis Matrix elements C_{ij}^α ($\alpha = x, y, z$) may be obtained by the vector method of Meal and Polo (1956) and the Zeta Matrix elements may be evaluated from the relation

$$\zeta^\alpha = \mathbf{L}^{-1} \mathbf{C}^\alpha (\mathbf{L}^{-1})'$$

where \mathbf{L} is the normal coordinate transformation matrix.

Rotational Distortion Constants

Cyvin *et al.* (1968) have reformulated the theory of Rotational distortion by introducing certain new elements $T_{\alpha\beta,s}$ instead of partial derivatives of inertia tensor components = $J_{\alpha\beta,s}$ of Kivelson and Wilson (1952). The quantities $t_{\alpha\beta\gamma\delta}$ have been obtained using Cyvin's relation and hence $\tau_{\alpha\beta\gamma\delta}$ values have been evaluated.

RESULTS AND DISCUSSION

Results relating to the two axially symmetric XYZ₃ type molecules, viz., *Mono-and-tri-deutero-germanes* are discussed here. The structural parameters and the harmonic frequencies used in the present investigation are taken from references (Wilkinson & Wilson, 1966; and Shimanouchi, 1972). The kinetic constants and the valence potential constants of the molecules are given in Tables I and II respectively. The kinetic constants exhibit the following characteristics :

(a) The angle-angle interaction constants $K_{\alpha\alpha}$ and $K'_{\alpha\theta}$ and the bond angle interaction constants $K_{D\alpha}$, $K'_{d\alpha}$ and $K'_{d\theta}$ are uniquely negative in both the cases studied here.

(b) The stretching constant K_D and the bending constant k_θ decreases with the increasing mass of the Y atom. It is highly interesting to note that the potential constants of these isotopic pairs of molecules practically remain the same. It is remarkable that five of the interaction constants are uniquely negative while the

TABLE I
Kinetic constants (10^{-23}g)

Molecule	k_D	k_{da}	$-k_{\alpha\alpha}$	$-k'_{d\alpha}$
	k_a	k_α	$-k'_{\alpha\theta}$	$+k''_{d\alpha}$
	k_{Da}	k_θ	$-k_{D\alpha}$	$-k'_{d\theta}$
GeHD ₃	0.1651	0.0020	0.0041	0.0016
	0.3251	0.0268	0.0081	0.0018
	0.0014	0.0200	0.0010	0.0014
GeDH ₃	0.3279	0.0005	0.0014	0.0004
	0.1651	0.0141	0.0074	0.0005
	0.0014	0.0199	0.0010	0.0007

TABLE II
Potential constants (10^5 dynes/cm)

Molecule	f_D	f_{da}	$-f_{\alpha\alpha}$	$-f'_{d\alpha}$
	f_a	f_α	$-f'_{\alpha\theta}$	$f''_{d\alpha}$
	f_{Da}	f_θ	$-f_{D\alpha}$	$-f'_{d\theta}$
GeHD ₃	2.6012	0.0031	0.0091	0.0032
	2.6332	0.0371	0.0124	0.0032
	0.0109	0.0381	0.0017	0.0038
GeDH ₃	2.6620	0.0082	0.0099	0.0016
	2.5971	0.0399	0.0144	0.0014
	0.0111	0.0318	0.0034	0.0012

other interaction constant f_{Da} , f_{da} and $f''_{d\alpha}$ are positive in both the molecules studied here. It is interesting to note that the corresponding kinetic constants are also negative in these cases. It may also be added that the general quadratic valence potential constants of mono-and-tri-deutero-germanes are available here for the first time.

The compliance constants for the molecules under study are also given in Table III. These constants are invariant to the choice of coordinates defining the force field and they may be used as a measure of the bond strengths and interactions instead of potential constants as pointed out by Decius (1963) and Jones (1971). It may also be noted that the compliance constants exhibit trends opposite to that of the force constants. Once again a very systematic set of values for the compliance constants of the mono-and-tri-deutero-germanes are available in the present work.

TABLE III
Compliance constants (A/m dynes)

Molecule	C_D	$-C_{dd}$	$-C_{\alpha\alpha}$	$-C'_{d\alpha}$
	C_d	C_α	$-C'_{\alpha\theta}$	$-C''_{d\alpha}$
	$-C_{Dd}$	C_θ	$C_{D\alpha}$	$C'_{d\theta}$
GeHD ₃	0.3844	0.0006	0.9383	0.0086
	0.3777	4.6832	0.5356	0.0074
	0.0012	4.5741	0.0043	0.0071
GeDH ₃	0.3752	0.0044	0.8434	0.0065
	0.3874	4.7674	0.3126	0.0050
	0.0018	5.2430	0.0122	0.0020

The valence mean square amplitudes and the vibrational mean amplitudes for both the bonded and the non-bonded distances at 298.16 °K are reported in Table IV and V respectively. The mean amplitudes of the bonded X — Y, X — Z and non-bonded Y...Z and Z...Z distances are in the expected range and they are bound to exhibit characteristic values. The values obtained in the present investigation agree quite well with Cyvin's (1968) values.

TABLE IV
Valence mean square amplitude of vibration at 298.16 K (10^{-3} \AA^2)

Molecule	σ_D	σ_{dd}	$\sigma_{\alpha\alpha}$	$\sigma'_{d\alpha}$	$\sigma_p(Y...Z)$
	σ_d	σ_α	$\sigma'_{\alpha\theta}$	$\sigma''_{d\alpha}$	
	σ_{Dd}	σ_θ	$\sigma_{D\alpha}$	$\sigma_{d\theta}$	
GeHD ₃	8.0153	0.0267	6.7751	0.1506	20.9116
	5.6091	30.8001	2.5721	0.1416	
	0.0381	34.9989	0.1017	0.1401	17.6102
GeDH ₃	5.6061	0.0282	8.9715	0.1001	21.2241
	8.0201	40.1212	1.5234	0.1016	
	0.0379	37.0211	0.1498	0.1009	23.8121

TABLE V
Mean amplitudes of vibration (\AA)

Molecule	$I_{D(x-y)}$	$I_{d(x-z)}$	$I_{p(y...z)}$	$I_{q(z...z)}$
GeHD ₃	0.0895	0.0749	0.1446	0.1327
	(0.0895)	(0.0756)	(0.1424)	(0.1309)
GeDH ₃	0.0749	0.0896	0.1457	0.1543
	(0.0756)	(0.0895)	(0.1424)	(0.1525)

*values in the parentheses refer Cyvin's (1968) values.

The important first order Coriolis coupling constants are those of the type $E \times E$ with respect to the Z axis. The second order Coriolis coupling constants are those of the type $A_1 \times E$ and $E \times E$ with respect to X axis and Y axis. All the coupling constants are given in Table VI. All the zeta constants obey the linear and quadratic sum rules derived by Boyd and Longuet-Higgins (1952) and Oka (1969) respectively. The high values of the constants ζ_{15} , ζ_{34} , ζ_{36} and ξ_{46} in both the molecules suggest that the coupling between the vibration concerned is more significant than others. As expected, the constant ζ_5 decreases rapidly with the increasing mass of the substituent Y atom. The rotational distortion constants of these molecules obtained in the present investigation are given in Table VII and they are in the expected range. The present values are in good agreement with Thyagarajan's (1962) work.

TABLE VI
Coriolis coupling constants

Molecule	ξ_4	$-\xi_{45}^z$	$-\xi_{14}$	$-\xi_{15}$	ξ_{16}	ξ_{45}
	ξ_5	ξ_{36}^z	ξ_{24}	ξ_{25}	$-\xi_{26}$	ξ_{46}
	$-\xi_6$	$-\xi_{56}^z$	ξ_{34}	ξ_{35}	ξ_{36}	ξ_{56}
GeHD ₃	0.0350	0.0238	0.0212	0.8678	0.1354	0.2433
	0.7537	0.9081	0.0173	0.3513	0.0624	0.2767
	0.1716	0.2569	0.7189	0.0176	0.6261	0.2360
GeDH ₃	0.0174	0.2194	0.0217	0.6768	0.0192	0.3105
	0.5587	0.8959	0.0090	0.5525	0.0079	0.3112
	0.2110	0.1934	0.7129	-0.1263	0.6277	0.3525

TABLE VII
Rotational distortion constants (MHZ)

Molecule	D_J	D_{JK}	D_K
GeHD ₃	0.44022	-0.30169	0.10421
	(0.440)	(-0.286)	
GeDH ₃	0.42881	1.60012	-1.21206
	(0.425)	(1.439)	

Values in the Parentheses refer to Thyagarajans's (1962) values.

CONCLUSION

The kinetic constants play a major role in molecular dynamics. A fresh attempt has been made to evaluate all the molecular constants of mono-and-tri-deutero-germanes of the XYZ₃ type molecules, using kinetic constants. The general harmonic potential

constants of these molecules are available for the first time. The values of other molecular constants, viz., compliance constants, vibrational mean amplitudes, Coriolis coupling constants and centrifugal distortion constants evaluated by the new procedure seem to be reasonable and a systematic set of molecular constants are available for the first time. Thus, it may be concluded that the recognition of kinetic constants lend an acceptable set of molecular constants in molecular vibration. There are to the authors' knowledge, no experimental data available for these molecules for comparative study.

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