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FORCE FIELD STUDIES OF SOME XY_4 TETRAHEDRAL TYPE HYDRIDES

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Molecular force field studies of some XY_4 tetrahedral type hydrides, have been carried out using the Parametric Representation method. With the use of additional data like isotopic frequencies for various isotopes, Coriolis coupling constants and D_J values, and through the methods of Redington and Aljibury and Sadao Isotani, the parametric angles ϕ's were determined. A critical study of all these methods, shows that the Coriolis coupling constants are highly sensitive compared to the other molecular constants. Also, the ϕ angles, obtained by the use of Coriolis coupling constants reproduce all the other molecular constants within reasonable accuracy. The best fit angles are: 34°33′ for SiH_4, 12°20′ for GeH_4 and 5° for SnH_4.

1. Introduction

Our ultimate goal in vibrational spectroscopic studies of molecular or ion complex systems, is to evaluate unique quadratic potential functions, which serve as a measure of the prevailing interatomic forces and their mutual interactions. In this context many attempts have been made which utilize experimental data like Coriolis coupling constants [1], isotopic frequencies [2] and mean amplitudes of vibration [3]. In cases where isotope and other experimental data are not available, certain methods [4–6] have been suggested. Of these methods, the method of Redington et al. [6] utilise the virial theorem approach and appears to be a reasonably good one in the case of simple molecular systems. In the present paper, an attempt to study the force fields of some XY_4 type molecules has been made utilizing all the available experimental constants [7–12] and the approximation of Redington and Aljibury and Sadao Isotani.

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2. Theoretical considerations

The main difficulty in the inverse eigenvalue problem is the fixation of the "true" eigenvector matrix L, the transformation matrix between the symmetry and normal coordinates. The L matrix is given by the relation

$$L = L_0 A, \tag{1}$$

where L_0 is obtained directly from the inverse kinetic energy matrix G, through the relation

$$L_0 = V\tau^{1/2}, \tag{2}$$

where V and τ are the eigenvector and eigenvalue matrices of G and A is the angle parameter matrix and is of the form,

$$A = \begin{bmatrix} C_\phi & S_\phi \\ -S_\phi & C_\phi \end{bmatrix}, \tag{3}$$

where C and S stand for the cosine and sine values of the angle parameter ϕ. The whole inverse vibrational problem reduces to fixing the angle parameter ϕ.

In order to determine the true ϕ, various constraints on force fields and additional experimental data are utilized. The method of Redington and Aljibury [6] is based on the restoring force balance of the molecular system, whereas Isotani's method [5] uses the extremal conditions of the symmetrised force constants. Jordanov and Nikolova [2] used the isotopic frequencies as additional data whereas Ananthakrishnan and Aruldhas [1] made use of the Coriolis coupling constants. The experimental values of rotational distortion constants D_J can also be utilized for the fixation of ϕ. All these methods were applied for the determination of the angle parameter ϕ, for some XY_4 tetrahedral type molecules. The capability of each method, of reproducing all the molecular constants were also studied. The detailed description of the use of the above methods in Parametric Representation form, was given by Ramaswamy and Chandrasekaran [13] and Ramaswamy and Srinivasan [14].

3. Results and discussions

The spectral data and the structural parameters used in the present calculations were given in Table I. The solutions for ϕ, were determined through various methods mentioned above. For each solution of ϕ, all the molecular constants were calculated and reported in Tables II, III and IV for the molecules SiH_4, GeH_4 and SnH_4.

SiH_4

For SiH_4, a value of 32°45′ for ϕ, was obtained from the F_{stp} criterian of Redington, while a value of 36°45′ was obtained from Isotani's method. The Coriolis coupling constants ζ_3 and ζ_4, yield the identical values of 34°34′ for ϕ since the experimental ζ values obey the theoretical sum value of 0.5. The use of isotopic frequencies, ν_3^* of $^{29}SiH_4$ and $^{30}SiH_4$ gives rise to two values for ϕ, 37°52′ and 37°33′ respectively. The ν_3 band analysis was carried out under high resolution by Dang-Nhu et al. [10], and they reported a value

TABLE I

Vibrational frequencies (cm^{-1}), bond distances (Å), Coriolis coupling constants and rotational distortion constants (cm^{-1}) for some XY_4 type molecules

SiH_4	GeH_4	SnH_4
$\nu_1 = 2185.7$	$\nu_1 = 2110.6$	$\nu_1 = 1907.8$
$\nu_2 = 972.1$ [8]	$\nu_2 = 930.6$ [9]	$\nu_2 = 753.18$ [15]
$\nu_3 = 2189.08$	$\nu_3 = 2111.46$	$\nu_3 = 1905.32$
$\nu_4 = 913.28$	$\nu_4 = 820.0$	$\nu_4 = 681.04$
$d = 1.14806$ [8]	$d = 1.5251$ [9]	$d = 1.7108$ [15]
$\zeta_3 = 0.008$	$\zeta_3 = -0.049$	$\zeta_3 = -0.062$ [15]
$\zeta_4 = 0.492$	$\zeta_4 = 0.549$	$\zeta_4 = 0.562$
$D_J = 3.82\times10^{-5}$ [10]	$D_J = (3.3\pm0.6)\,10^{-5}$ [12]	
$D_J = (3.48\pm0.54)\,10^{-5}$ [11]	$D_J = (3.8\pm0.9)\,10^{-5}$ [9]	
$^{28}SiH_4\ \nu_3 = 2189.16$	$^{70}GeH_4\ \nu_3^* = 2112.25$	
$^{29}SiH_4\ \nu_3^* = 2187.63$ [7]	$^{72}GeH_4\ \nu_3 = 2111.78$ [7]	
$^{30}SiH_4\ \nu_3^* = 2186.19$	$^{74}GeH_4\ \nu_3^* = 2111.45$	
	$^{76}GeH_4\ \nu_3^* = 2111.05$	

TABLE II

The angle parameter ϕ, symmetrised force constants (mdyn/Å), Coriolis coupling constants, mean vibrational amplitudes (Å), rotational distortion constants (cm^{-1}) and isotopic frequencies (cm^{-1}) for f_2 species of SiH_4, calculated by different methods

Using / Parameters	Redington's method	Isotani's method	ζ_{33} and ζ_{44}	ν_3^* ($^{29}SiH_4$)	ν_3^* ($^{30}SiH_4$)	$D_J = 3.82\times10^{-5}$	$D_J = 3.48\times10^{-5}$
ϕ	32°45′	36°45′	34°34′	37°52′	37°33′	29°2′	40°12′
F_{33}	2.7100	2.7235	2.7235	2.7258	2.7263	2.6866	2.7183
F_{34}	0.0128	0.1214	0.0621	0.1517	0.1431	−0.0879	0.2143
F_{44}	0.2269	0.2314	0.2277	0.2350	0.2340	0.2336	0.2440
ζ_{33}	0.053	−0.046	0.008	−0.072	−0.065	0.149	−0.126
ζ_{44}	0.447	0.545	0.492	0.572	0.565	0.351	0.626
σ_{X-Y}	0.0890	0.0892	0.0890	0.0893	0.0893	0.0892	0.0897
$\sigma_{Y\ldots Y}$	0.1496	0.1472	0.1485	0.1464	0.1466	0.1519	0.1452
$D_J\ 10^5$	3.702	3.580	3.646	3.547	3.556	3.82	3.48
$D_{JK}10^5$	2.267	2.572	2.408	2.655	2.631	1.972	2.822
ν_3^* ($^{29}SiH_4$)	2187.239	2187.547	2187.381	2187.63	2187.609	2186.942	2187.799
ν_3^* ($^{30}SiH_4$)	2185.5	2186.1	2185.779	2186.259	2186.19	2184.917	2186.587

of $D_J = 3.82\times10^{-5}$ cm^{-1} and this corresponds to a solution of $\phi = 29°2'$. The R branch of the pure rotational spectrum of SiH_4 in the ground vibronic state has been studied by Rosenberg and Ozier [11] and they reported a value of $D_J = (3.48\pm0.54)10^{-5}$ cm^{-1}. Use of this data gives two values of ϕ, viz., $\phi_1 = 40°12'$ for $D_J = 3.48\times10^{-5}$ cm^{-1} and

$\phi_2 = 22°50'$ for $D_J = (3.48 \pm 0.54) \times 10^{-5}$ cm^{-1}. The value $D_J = (3.48 - 0.54) \times 10^{-5}$ cm^{-1} yield an imaginary solution and hence is discarded.

Graphs are drawn connecting ζ_3, ζ_4, D_J, ν_3^* of $^{29}SiH_4$ and $^{30}SiH_4$ and ϕ angles in the range 0° to 90°, and these are represented in Fig. 1.

As seen from the Figure 1, the ϕ solutions namely 40°12′ and 22°50′, calculated from $D_J = (3.48 \pm 0.54)\ 10^{-5}$ cm^{-1} are far apart, since the experimental errors given

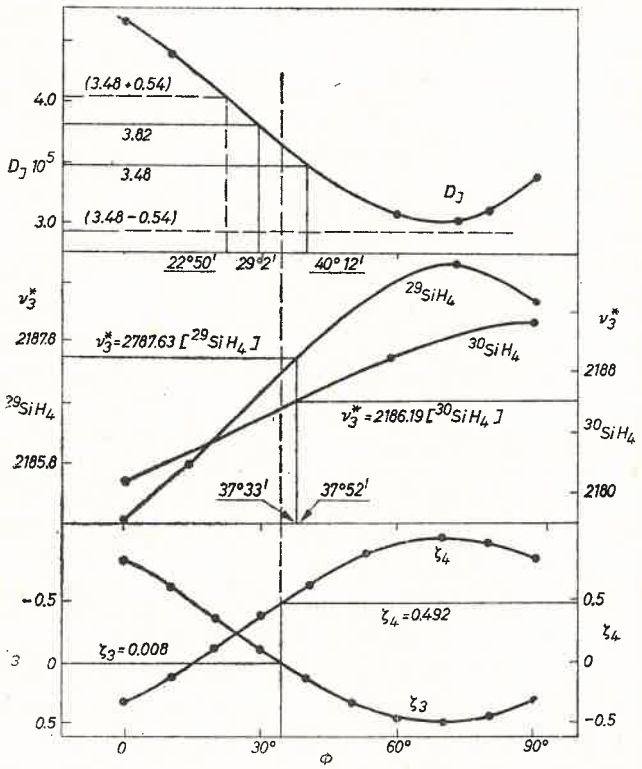

Fig. 1. Plot of ϕ versus ζ_3, ζ_4, ζ_3^* of $^{29}SiH_4$, $^{30}SiH_4$ and D_J values for the molecule SiH_4

by the authors in their measurements are very high. Use of $D_J = (3.48 - 0.54)\ 10^{-5}$ cm^{-1} yields an imaginary solution, since this value is smaller than the lowest value expected in the Parametric method, and this is indicated by a line below the D_J curve.

A solution of $\phi = 29°2'$, obtained for another experimental value ($D_J = 3.82 \times 10^{-5}$ cm^{-1}) is also shown in the graph. The calculated Coriolis coupling constants for these two angles, obtained from D_J's ($\zeta_3 = 0.149$, $\zeta_4 = 0.351$ for $\phi = 29°2'$ and $\zeta_3 = -0.126$, $\zeta_4 = 0.626$ for $\phi = 40°12'$) show large discrepancies, compared to the experimental values ($\zeta_3 = 0.008$ and $\zeta_4 = 0.492$). The stretch-bend interaction and bending force constants ($F_{34} = -0.0879$, $F_{44} = 0.2336$ mdyn/Å for 29°2′ and $F_{34} = 0.2143$, $F_{44} = 0.2440$ mdyn/Å for 40°12′) also deviate largely when compared to literature values.

Considering the angles obtained through the isotopic shifts (37°52′ and 37°33′), the

force constants and mean amplitudes of vibrations (see Table II) calculated for these angles, are compared with those reported by Cleveland et al. [16], Shimanouchi et al. [17] and Cyvin [18] ($\sigma_{X-Y} = 0.0888$ and $\sigma_{Y\ldots Y} = 0.1500$ Å) respectively. Even though, these angles lie very close to those obtained by the use of the experimental ζ values, ($\phi = 34°34'$) (which is shown in the Figure), the calculated Coriolis coupling constant ζ_3 for these angles ($\zeta_3 = -0.072$ for 37°52′ and $\zeta_3 = -0.062$ for 37°33′) are found to be negative, whereas the observed Coriolis coupling constant ζ_3 ($\zeta_3 = 0.008$) is positive. Hence these solutions are also to be rejected.

The same situation is also observed for the ϕ solutions (32°45′ and 36°45′) obtained through Redington's method and Isotani's method. These solutions are very close to the angle obtained from ζ. But the calculated Coriolis coupling constants for the above angles (see Table II) are not in agreement with the experimental values. Hence, the two above angles are also to be ignored.

It is found that, even for a very small change in the angle ϕ, the Coriolis coupling constants vary considerably and the ζ constants, are highly sensitive to the ϕ angles. The variation of other molecular constants with the angle parameter ϕ, is not appreciable (which can be seen from Table II) and it is evident that these constants are not so sensitive as that of ζ constants to the angle parameters. Also a variation of $\pm 5'$ is obtained for the experimental error of ± 0.002 in constants, whereas a change of 19°22′ was obtained for the experimental error of 0.54×10^{-5} cm^{-1} in D_J values. Hence, the errors and uncertainities in the determination of ϕ, are high if data other than ζ constants are used. These facts lead one to conclude that the value of $\phi = 34°34'$, obtained by the use of ζ's, has to be taken as the best fit solution, for this molecule SiH_4.

The calculated D_J value ($= 3.646 \times 10^{-5}$ cm^{-1}) is in excellent agreement with the theoretically calculated value of D_J (3.6 ± 0.4) 10^{-5} cm^{-1} by Rosenberg and Ozier [11]. Also, this value lies within the error limits of the experimentally determined D_J value, namely $D_J = (3.48 \pm 0.54)$ 10^{-5} cm^{-1}. The calculated isotopic frequencies are also comparable with the experimental data [11]. The calculated mean amplitudes of vibration ($\sigma_{X-Y} = 0.089$, and $\sigma_{Y\ldots Y} = 0.1485$ Å) are in good agreement with the values of Cyvin [18]. The calculated force constants are in good agreement with the values of earlier workers and they are reported in Table V. It is found that the force constants reported by Cleveland et al. [16], Shimanouchi et al. [17], and Duncan and Mills [19] were obtained by the use of the ζ constants, namely $\zeta_3 = 0.046$ [21]. But the ζ values used for the present study are $\zeta_3 = 0.008$ and $\zeta_4 = 0.492$, were determined by the analysis of the infrared and gas Raman spectrum of SiH_4, under high resolution. Hence, the force field obtained through these ζ constants are more reasonable than the earlier ones. The observation that, the force constants are not as sensitive as the ζ constants to the parametric angle ϕ, may be attributed to the small variation found between the force constants of the present work and those of literature values [16, 17, 19, 20]. The force constant F_{34} is found to be positive, whereas Duncan and Mills [19] obtained negative values for F_{34}, for all XY_4 type hydrides and they explained this fact on the basis of "Hybrid-Orbital model". Our values of F_{34} obtained here though agrees in magnitude with those of Duncan and Mills, but not in sign.

GeH_4

For GeH_4, the variation of the isotopic frequencies ν_3^* of $^{70}GeH_4$, $^{74}GeH_4$ and $^{76}GeH_4$, Coriolis coupling constants and D_J values with the angle parameter ϕ, is shown in Fig. 2. The value of $D_J = (3.3 \pm 0.6)\ 10^{-5}\ cm^{-1}$, obtained by the analysis of the pure rotational spectrum of GeH_4 by Ozier and Rosenberg [12], yields two solutions for ϕ. They are: $\phi_1 = 13°10'$ for $D_J = 3.3 \times 10^{-5}\ cm^{-1}$ and $\phi_2 = -4°37'$ for $D_J = (3.3+0.6)\ 10^{-5}\ cm^{-1}$

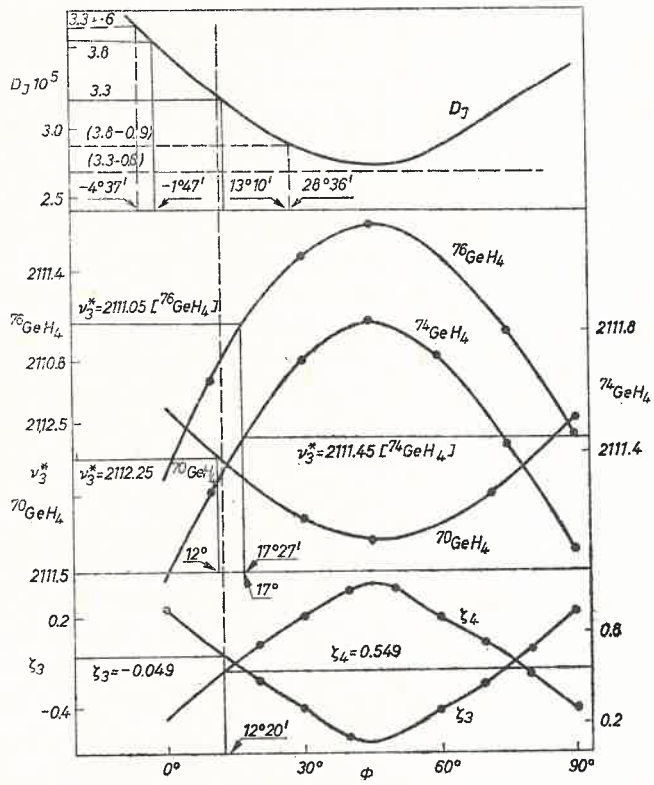

Fig. 2. Plot of ϕ versus ζ_3, ζ_4, ν_3^* of $^{70}GeH_4$, $^{74}GeH_4$, $^{76}GeH_4$ and D_J values for the molecule GeH_4

and these solutions are shown in the graph. Use of $D_J = (3.3-0.6)\ 10^{-5}\ cm^{-1}$ yields an imaginary solution for ϕ, since this D_J value is well below the lowest value expected by the Parametric method. This imaginary solution for ϕ is indicated by a line well below the D_J curve. The vibration-rotation structure of GeH_4 was studied by Kattenberg and Oskam [9] and they reported a value of $(3.8 \pm 0.9)\ 10^{-5}\ cm^{-1}$ for D_J. The corresponding ϕ values obtained are: $\phi_1 = -1°42'$ for $D_J = 3.8 \times 10^{-5}\ cm^{-1}$, $\phi_2 = 28°36'$ for $D_J = (3.8-0.9)\ 10^{-5}\ cm^{-1}$ and $\phi_3 = -47°42'$ for $D_J = (3.8+0.9)\ 10^{-5}\ cm^{-1}$. The use of isotopic frequencies ν_3^* of $^{70}GeH_4$, $^{74}GeH_4$ and $^{76}GeH_4$ yields solutions of 12°, 17° and 17°21′ respectively, while a value of $\phi = 12°20'$ is obtained by the use of Coriolis coupling ccnstans ζ_3 and ζ_4. These solutions are also graphically illustrated in Fig. 2. The methods of Redington and Isotani yield parametric angles 9°30′ and 11° respectively. For all these solutions, obtained through various methods, the force constants, Coriolis coupling

TABLE III

The angle parameter ϕ, symmetrised force constants (mdyn/Å), Coriolis coupling constants, mean vibrational amplitudes (Å), rotational distortion constants (cm^{-1}) and isotopic frequencies (cm^{-1}) for f_2 species of GeH_4, calculated by different methods

Using / Parameters	Redington's method	Isotani's method	ζ_{33} and ζ_{44}	ν_3^* ($^{70}GeH_4$)	ν_3^* ($^{74}GeH_4$)	ν_3^* ($^{76}GeH_4$)	$D_J = 3.3\times10^{-5}$	$D_J = 3.8\times10^{-5}$
ϕ	9°30′	11°	12°20′	12°	17°	17°27′	13°10′	−1°42′
F_{33}	2.6006	2.6022	2.6010	2.6015	2.5803	2.5766	2.5991	2.5442
F_{34}	0.0104	0.0448	0.0808	0.0648	0.1985	0.2108	0.1032	−0.2031
F_{44}	0.1928	0.1932	0.1953	0.1938	0.2090	0.2113	0.1970	0.2133
ζ_{33}	0.020	−0.016	−0.049	−0.034	−0.150	−0.160	−0.069	0.310
ζ_{44}	0.480	0.517	0.549	0.534	0.650	0.660	0.569	0.190
σ_{X-Y}	0.0896	0.0896	0.0897	0.0897	0.0905	0.0906	0.0898	0.0907
$\sigma_{Y\ldots Y}$	0.1547	0.1536	0.1527	0.1532	0.1498	0.1495	0.1521	0.1603
$D_J\,10^5$	3.418	3.370	3.326	3.346	3.193	3.179	3.3	3.8
$D_{JK}\,10^5$	1.930	2.050	2.159	2.109	2.492	2.526	2.224	0.974
$\nu_3^*(^{70}GeH_4)$	2112.316	2112.272	2112.239	2112.25	2112.12	2112.119	2112.213	2112.60
$\nu_3^*(^{74}GeH_4)$	2111.253	2111.290	2111.331	2111.32	2111.45	2111.456	2111.35	2111.02
$\nu_3^*(^{76}GeH_4)$	2110.677	2110.749	2110.817	2110.8	2111.031	211.05	2110.86	2110.13

constants mean amplitudes of vibration and D_J constants were calculated and reported in Table III.

A critical survey of Table III reveals that, there is no considerable variation among the force constants, mean amplitudes of vibration an rotational distortion constants calculated for all the ϕ angles. They were also in comparison with the reported values of Cleveland et al. [16], Cyvin [18] and Ozier and Rosenberg [12] respectively. So, these molecular constants are insensitive to the angle parameter ϕ.

Considering the experimentally observed isotopic shifts [7] ($\Delta\nu_3 = 0.47\ \text{cm}^{-1}$ for $^{72-70}GeH_4$, $0.33\ \text{cm}^{-1}$ for $^{72-74}GeH_4$ and $0.73\ \text{cm}^{-1}$ for $^{72-76}GeH_4$) they are very small and they cannot be taken as reliable parameters for the fixation of ϕ. Hence the only sensitive available data is Coriolis coupling constants and the solution $\phi = 12°20'$, obtained by the use of the above constants, has to be taken as the best fit solution for this molecule GeH_4.

It is also seen from Figure 2 that, the angle parameters calculated using D_J values and isotopic frequencies are close to the angle obtained from ζ constants. But, it is seen from the Table that the calculated ζ constants for all these angles are not in agreement with the experimental ζ values and hence all these angles obtained, by the use of experimental data other than ζ's, are to be rejected.

The rotational-distortion constant, $D_J = 3.326 \times 10^{-5}\ \text{cm}^{-1}$, calculated for the ζ angle is in good agreement with the experimental value of $D_J = 3.3 \times 10^{-5}\ \text{cm}^{-1}$, determined by Ozier and Rosenberg [12]. The isotopic frequencies are also reproduced within reasonable accuracy. The calculated mean amplitudes of vibration ($\sigma_{X-Y} = 0.0897$ and $\sigma_{Y-Y} = 0.1527$ Å) are in good agreement with the reported values of Cyvin [18] ($\sigma_{X-Y} = 0.0895$ and $\sigma_{Y\ldots Y} = 0.1525$ Å). The force constants calculated for this angle ($F_{33} = 2.6010$, $F_{34} = 0.0808$ and $F_{44} = 0.1953$ mdyn/Å) are in good agreement with the values of Cleveland et al., ($F_{33} = 2.6034$, $F_{34} = 0.0009$ and $F_{44} = 0.1922$ mdyn/Å) and Duncan and Mills [19] $F_{33} = 2.807$, $F_{34} = -0.083$ and $F_{44} = 0.2077$ mdyn/Å).

It was pointed out by Duncan and Mills that the force constants of Cleveland et al., are fitted to incorrect ζ values [22] ($\zeta_3 = 0.024$ and $\zeta_4 = 0.476$), and the ζ values used by them are $\zeta_3 = -0.042$ and $\zeta_4 = 0.542$. The ζ constants used, in the present calculations are $\zeta_3 = -0.049 \pm 0.002$ and $\zeta_4 = 0.549 \pm 0.002$, were obtained by the analysis of the vibration-rotational spectrum of GeH_4 through infrared and Laser Raman methods, under high resolutions. These values are in comparison with those of Duncan and Mills.

SnH_4

For SnH_4, the force constants, Coriolis coupling constants, mean amplitudes of vibration and rotational distortion constants were calculated, for each solution for ϕ, obtained through Redington's method, Isotani's method and by the use of Coriolis coupling constants, and are reported in Table IV.

The discussions given for GeH_4 is also applicable for SnH_4 and the angle $\phi = 5°$ obtained by the use of Coriolis coupling constants are taken to be the best fit solution for SnH_4.

The force constants, calculated using the best fit angle solutions ϕ are reported in Table V, along with literature values for all three molecules.

TABLE IV

The angle parameter ϕ, symmetrised force constants (mdyn/Å), Coriolis coupling constants, mean vibrational amplitudes (Å) and rotational distortion constants (cm^{-1}), for f_2 species od SnH_4, calculated by different methods

Parameter \ Using	Redington's method	Isotani's method	ζ_{33} and ζ_{44}
ϕ	2°	2°51′	5°
F_{33}	2.1323	2.1328	2.1302
F_{34}	0.0033	0.0227	0.0858
F_{44}	0.1348	0.1350	0.1373
ζ_{33}	0.011	−0.010	−0.062
ζ_{44}	0.489	0.510	0.562
σ_{X-Y}	0.0941	0.0941	0.0943
$\sigma_{Y\ldots Y}$	0.1689	0.1679	0.1661
$D_J\ 10^5$	2.366	2.345	2.294
$D_{JK}\ 10^5$	1.666	1.717	1.846

TABLE V

Force constants (mdyn/Å), calculated using the best fit angle parameters for some XY_4 tetrahedral type molecules

Molecule	Force constants	Present work	Cleveland et al. [16]	Shimanouchi et al. [15]	Duncan and Mills [19]	Ranganathan [20]
SiH_4	F_{11}	2.8374	2.8397	2.8385	2.840	2.7990
	F_{22}	0.1871	0.1880	0.1881	0.188	0.1846
	F_{33}	2.7235	2.7214	2.7237	2.742	2.7927
	F_{34}	0.0621	0.0206	0.0345	−0.023	−0.1534
	F_{44}	0.2271	0.2272	0.2273	0.231	0.2411
GeH_4	F_{11}	2.6244	2.6333	—	2.658	2.3323
	F_{22}	0.1715	0.1715	—	0.173	0.1365
	F_{33}	2.6010	2.6034	—	2.631	2.5968
	F_{34}	0.0808	0.0009	—	−0.077	0.0992
	F_{44}	0.1953	0.1922	—	0.196	0.1962
SnH_4	F_{11}	2.1617				
	F_{22}	0.1123				
	F_{33}	2.1302				
	F_{34}	0.0858				
	F_{44}	0.1373				

The following conclusions are drawn from the present work on XY_4 hydrides:

(1) The ζ constants are highly sensitive to the angle parameters, and these data if available alone can be successfully utilised to obtain a reasonably unambiguous good force field.

(2) All the other molecular constants are not that sensitive as ζ constants.

(3) Though the ϕ solutions, obtained through Redington and Isotani's method are close to the angle obtained using ζ constants, they are not capable of reproducing the Coriolis coupling constants and these methods cannot be used as such for the fixation of the parametric angle. However, these methods may be of use as a starting point for the unique evaluation of force constants which can be further refined to fit other molecular constants.

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