Force field for germylacetylene

By K. Ramaswamy and V. Balasubramanian

Department of Physics, Annamalai University, Annamalainagar

Approximate force field for germylacetylene was attempted using the kinematic methods suggested by Torkington (1949) and Herranz & Castano (1966). The former method was found to give a satisfactory force field for this molecule.

Introduction

The well known basic equations (Wilson, 1955) in molecular force field calculations are,

$$L \tilde{L} = G \qquad \qquad ...(1)$$

$$\tilde{L} FL = \Lambda \qquad \qquad ...(2)$$

and

$$GFL = L\Lambda \qquad \qquad ...(3)$$

where L is the transformation matrix between the set of symmetry coordinates and the normal coordinates, F and G refer to the potential and inverse kinetic energy matrices and Λ a diagonal matrix with the element $\Lambda_k = 4\pi^2\nu_k^2c^2$, where ν_k is the kth vibrational wavenumber and c is the velocity of light in cm sec^{-1}. It is seen from the above equations that the matrix L assumes importance in the determination of a unique set of force constants. The kinematic methods (Torkington 1949, Herranz & Castano 1966 and Biles 1966) are those which give the values of the L matrix elements consistent with the equations (1) to (3), purely from the geometry of the molecule without any assumptions regarding the force constants. In a previous paper (Ramaswamy & Balasubramanian 1969) approximate force fields for the germyl halides using the above kinematic methods were attempted and Torkington's method was found to give a better approximation to the correct force field for the two heavier molecules GeH_3Br and GeH_3I while the method suggested by Herranz & Castano gave a close approximation to the correct force field for the two lighter molecules GeH_3Cl and GeH_3F. This paper deals with the force field for germylacetylene by the first two methods.

Potential energy constants

In the method suggested by Torkington (1949) the product of the matrices G and F is triangular and the L matrix obtained as the eigen

vector of GF is also triangular. In the method suggested by Herranz & Castano (1966) the L matrix is defined as,

$$L = BM^{1/2} \tilde{B} \qquad \qquad ...(4)$$

where B is an orthogonal matrix which diagonalises G and M is a diagonal matrix with the reciprocals of the eigen values of G as its elements.

Germylacetylene belongs to the C_{3v} point group and its infrared spectrum was reported by Lovejoy & Baker (1967). Its microwave spectrum was given by Thomas & Laurie (1966). The structural data and the vibrational frequencies used in the calculations are given in table 1. The symmetry coordinates used are the same as those of Sathianandan & Margrave (1963). The values of important valence force constants obtained in the two methods are presented in table 2.

TABLE 1. OBSERVED FREQUENCIES IN WAVE NUMBERS AND STRUCTURAL
PARAMETERS FOR GeH_3CCH

Observed frequencies in cm^{-1} (Lovejoy & Baker, 1967)				Structural data (Thomas & Laurie, 1966)
a_1 species		e species		$d(Ge\text{-}H) = 1.521$ Å
ν_1	3313 5	ν_6	2117.2	$r_1(Ge\text{-}C) = 1.896$ Å
ν_2	2120.0	ν_7	886.0	$r_2(C\text{-}C) \equiv 1\,208$ Å
ν_3	2060.0	ν_8	673.0	$r_3(C\text{-}H) = 1\,056$ Å
ν_4	843.8	ν_9	643.8	$\angle(H\text{-}Ge\text{-}H) = 109° 54'$
ν_5	530 0	ν_{10}	216.4	$\beta(H\text{-}Ge\text{-}C) = 109° 2'$
				$\phi(Ge\text{-}C\text{-}C) = 180°$
				$\theta(C\text{-}C\text{-}H) = 180°$

MEAN AMPLITUDES

The various bonded mean amplitudes were calculated by the method of Cyvin (1959) and the nonbonded ones by the method of Ramaswamy et al (1962). The important mean amplitudes obtained in the first method are given in table 3.

TABLE 2. VALENCE FORCE CONSTANTS
IN MDYN FOR/$\mathring{A}$ GeH_3CCH

Valence force constant	Method I[a]	Method II[b]
f_{r_3}	6.1161*	6.2609
f_{r_2}	16.4557	24.1624
f_{r_1}	3.1112	7.4759
f_d	2.6276	2.6286
$f_{r_2 r_3}$	1.2742	2.5875
$f_{r_1 r_2}$	1.6183	11.4762
$f_{r_1 d}$	0.0135	0.0964
f_{dd}	0.0146	0.0156
$f_\alpha - f_{\alpha\alpha}$	0.1905	0.1957
$f_\beta - f_{\beta\beta}$	0.1951	0.2050
f_θ	0.1775	0.1939
f_ϕ	0.0739	0.0906
$f_{d\alpha}$	0.0059	0.0181
$f_{d\beta}$	0.0056	0.0264

[a]Method of 'Progressive rigidity' suggested by Torkington
[b]Method of 'characterestic set of valence coordinates' suggested by Herranz and Castano.
*As under table 3

TABLE 3. VIBRATIONAL MEAN AMPLITUDES OF
GeH_3CCH AT 298.16°K.

Pair	Mean amplitudes ($\mathring{A}$)	Mean amplitudes for similar types of bonds in different molecules.		
		Mean amplitudes ($\mathring{A}$)	Molecule	Reference
C-H	0.0740*	0.0743	C_2H_2	Bakken (1958)
C$\equiv$H	0.0366	0.0357	C_2H_2	Bakken (1958)
Ge-C	0.0484	—	—	—
Ge-H	0.0895	0.0895	GeH_4	Cyvin (1968)
H...H.	0.1540	0.1525	GeH_4	Cyvin (1968)
H...C	0.1318	—	—	—

*This number of significant figures is retained to secure internal consistency in the calculations.

4

ROTATIONAL DISTORTION CONSTANTS

The centrifugal stretching constants D_J, D_{JK} and D_K were calculated using the relations given by De Alti *et al* (1965). The values are presented in table 4.

TABLE 4. ROTATIONAL
DISTORTION CONSTANTS
IN KC/SEC. FOR GeH_3CCH

Quantity	Calculated	Observed
D_J	0.6565*	—
D_{JK}	26.6906	38
D_K	802.9760	—

CORIOLIS COUPLING CONSTANTS

The ζ^t values for the perpendicular modes of vibration were calculated using the relations given by Meal & Polo (1965). The values are presented along with the experimentally observed values. The ζ sum rule for this molecule is,

$$\sum_i \zeta_i = \frac{I_A}{2I_B} + 2 \qquad \qquad ...(5)$$

where, I_A and I_B are the principal components of the moment of inertia tensor.

TABLE 5. CORIOLIS COUPLING
CONSTANTS ζ FOR GERMYLACETYLENE

	Calculated	Observed
ζ_6	0.0183*	—0.052
ζ_7	—0.2043	—0.266
ζ_8	1.0000	—
ζ_9	0.2579	0.364
ζ_{10}	0.9503	—
$\sum_i \zeta_i$	2.0222	
$(I_A/2I_B)+2$	2.0222	

*As under table 3

DISCUSSION

The method of Torkington (1949) gives for the $C\equiv C$ stretching and C—H stretching force constant values of 16.4557 mdyn/Å and 6.1161 mdyn/Å while the method given by Herranz & Castano (1966) gives the values of 24.1624 mdyn/Å and 6.2609 mdyn/Å, respectively. The first set is comparable with the values of 15.80 mdyn/Å and 6.442 mdyn/Å obtained by Daykin *et al* (1962) for methylacetylene and 15.59 mdyn/Å and 5.87 mdyn/Å of Duncan (1964) for silylacetylene. For Ge-C bond stretching we obtain values of 3.1112 mdyn/$\overset{\circ}{A}$ and 7.4759 mdyn/$\overset{\circ}{A}$ in the two methods, respectively.The first value is closer to the value of 2.87 mdyn/$\overset{\circ}{A}$ obtained by Clark & Weber (1966) for methylgermane. The second method gives an abnormally high value of 11.4762 mdyn/$\overset{\circ}{A}$ for the interaction force constant $f_{r_1 r_3}$. The other bending, stretching and interaction force constants are of comparable magnitude in both the methods as seen from table 2. They are also consistent with the values obtained for germylhalides in our previous study. The second method gives quite large values for the various force constants of the linear skeleton Ge–$C\equiv C$–H, barring the C-H stretching. High values for interaction force constants were also obtained by Ramaswamy & Srinivasan (1967, 1969) for the linear molecules like cyanoacetylene, diacetylene and dicyanoacetylene. They attributed these high values to the high degree of conjugation, and electron transfer in those molecules. Here the linear skeleton Ge—$C\equiv C$–H is not a conjugated system and hence the second method is quite unsatisfactory in describing the force field for this molecule. So the other molecular constants were found using only the L matrix obtained in the first method.

From table 3 it is seen that the mean amplitudes of vibration for the bonds C—H(0.0740/$\overset{\circ}{A}$) and $C\equiv C$ (0.0366$\overset{\circ}{A}$) are comparable with the values of 0.0743$\overset{\circ}{A}$ and 0.0357$\overset{\circ}{A}$ obtained by Bakken (1958) for C_2H_4. The bonded Ge-H (0.0895A) and the nonbonded H···H(0.1540$\overset{\circ}{A}$) mean amplitudes are also comparable to the values of (0.0895$\overset{\circ}{A}$) and (0.1525$\overset{\circ}{A}$) for GeH_4 obtained by Cyvin (1968). These values are also consistent with the values obtained for germylhalides in our earlier study.

The value of the centrifugal stretching constant D_{JK} (26.6906 kc/sec) is low compared to the value of 38 kc/sec obtained by Thomas & Laurie (1966) from microwave studies of germylacetylene. The difference might be due to the approximate description of the normal modes.

Lovejoy & Baker (1967) from the analysis of perpendicular band contours of the infrared spectrum of germylacetylene reported the values of ζ_6, ζ_7 and ζ_9. From the sum rule, $\zeta_8 + \zeta_{10}$ was calculated to be 1.975,

Further, they predicted ζ_8 and ζ_{10} to be approximately equal and slightly less than one. In similar molecules like silylacetylene (Reeves $et\ al$ 1964) and methylacetylene (Thomas & Thompson 1968) the sum of the above two corresponding ζ elements is 1.89. For methylacetylene the two ζ's have the values of 1 and 0.89 respectively. The values ζ_8 (1) and ζ_{10} (0.95) of the present study are close to those predicted by Lovejoy & Baker (1967). The value of ζ_6 (0.0183) and ζ_7 (-0.2043) are consistent with the values obtained for similar motions in the germylhalides. As for the germylhalides, here also the individual ζ values differ from the observed values. The ζ sum rule is thus verified.

CONCLUSION

Of the two kinematic methods the above study shows the method of 'Progressive regidity' suggested by Torkington as the most satisfactory in describing the force field for this molecule. However, as shown by the values of the ζ elements and the centrifugal stretching constant, the solution to the force field is only an approximate one. This may be due to the approximate L matrix which is derived entirely from the geometry of the molecule.

ACKNOWLEDGEMENT

REFERENCES

Bakken J. 1958 *Acta Chem. Scand.*, **12**, 594.

Biles F. 1966 *Acta. Chim. Acad. Sci. Hung.*, **47**, 53.

Cyvin S. J. 1959 *Acta. Chem. Scand.*, **13**, 2135.

1968 *Molecular vibrations and Mean square amplitudes, Universitet for laget, Oslo.*

Clark A. & Alfons Weber. 1966 *J. Chem. Phys.*, **45**, 1759.

Daykin P. N., Sundaram, S. & Cleveland F. F. 1962, *J. Chem. Phys.*, **37**, 1087.

Duncan J. L. 1964 *Spectrochim. Acta*, **20**, 1807.

Gian Carlo De Alti Vinicio Galasso & Giacomo Costa 1965 *Spectrochim Acta* **21**, 649.

Herranz J. & Castano F. 1966 *Spectrochim. Acta*, **22**, 1965.

Lovejoy, R. W. & Baker D. R. 1967 *J. Chem. Phys.*, **46**, 658.

Meal J. H. & Polo S. R. 1956 *J. Chem. Phys.*, **24**, 1119.

Ramaswamy K. & Balasubramanian V. *Ind. J. Phys.* (In press)

Ramaswamy K. Sathianandan K. & Cleveland F. F. 1962 *J. Mol. Spectry.*, **9**, 107.

Ramaswamy K. & Srinivasan K. 1967 *Aust. J. Chem.*, **21**, 575.

                   1969 *Aust. J. Chem.*, **22**, 1123

Sathianandan K. & Margrave J. L. 1963 *J. Mol. Spectry.*, **10**, 442.

Thomas E. C. & Laurie W. 1966 *J. Chem. Phys.*, **44** 2602

Thomas R. K. & Thompson H. W. 1968 *Spectrochim. Acta*, **24**A, 1337.

Torkington P. 1949 *J. Chem. Phys.*, **17**, 1026.

Wilson E. B. Jr., Decius J. C. & Cross P. C. 1955 *Molecular Vibrations*, McGraw Hill,

                                              New York.