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Normal Coordinate Analysis and Evaluation of Molecular Constants of Chlorodifluoro Methane and its Isotopes

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The potential energy constants of chlorodifluoro-methane and its isotopes have been evaluated on the basis of GVFF using the very recently assigned vibrational frequencies. The other molecular constants such as mean square amplitudes of vibration, generalized mean square amplitudes of vibration, shrinkage constants, Coriolis coupling coefficients and the centrifugal distortion constants have also been computed for the first time. The findings are presented and discussed in brief.

INTRODUCTION

Laser induced reactions of $CHClF_2$ for the purpose of selective isotopic enrichment, constitute an area of current interest. A careful study was undertaken by Magil *et al.*[1] to obtain a self consistent set of vibrational data on the title molecule. But the molecular force constants have not been determined by them. Frequency data available for five isotopes in gas phase[1] have been used to arrive at reasonable force field with all possible interaction constants. Using these force constants all other molecular constants have also been computed for the first time. Chlorodifluoro methane is a twisted type of molecule having C_s point group symmetry. The internal coordinates, molecular configuration and the Cartesian coordinate axes are shown in Figure 1.

Methods of Calculation

The potential energy constants derived from general valence force field (GVFF) are evaluated by Wilson's FG matrix formalism[2]. Cyvin's W-matrix method[3] is followed for solving the determinantal equation $|F\ G - E\lambda| = O$. This method, employing W and T matrices, introduces several npn-vanishing off-diagonal elements in F which enables us to calculate many interaction constants.

A refined force field is obtained by adjusting the force constants to give the best frequency fit based on least square method.

A symmetrized mean square amplitude matrix Σ is determined by L

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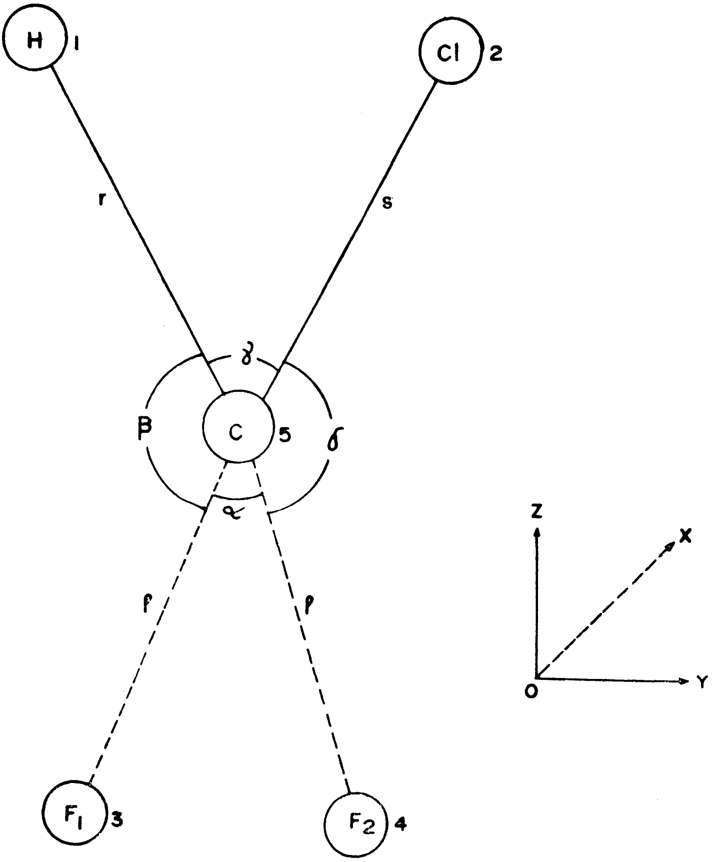

Fig. 1 The internal coordinates, numbering of atoms and the orientation of the Cartesian coordinate axes of $CHClF_2$

matrix method of Cyvin[4]. The elements of Σ matrix are used to calculate the mean square amplitude quantities (σ). The relation between Σ matrix elements and σ quantities is structurally similar to that of F matrix with f quantities.

The generalized mean square amplitudes of vibration in parallel and perpendicular directions are computed using the symmetrized mean square amplitude matrix, Σ following the method of Morino and Hirota[5]. The shrinkage constants are also calculated using perpendicular mean square amplitudes by the method suggested by Morino *et al.*[6]

Applying Jahn's rule[7] the non-vanishing elements are found to be the type ζ^x from $a' \times a''$ coupling. These constants have been estimated using the relatlon $\zeta^\alpha = L^{-1}C^\alpha\tilde{L}^{-1}$, where L is the normal coordinate transformation matrix and C^α ($\alpha = x, y, z$) is the skew symmetric matrix introduced

TABLE 1

OBSERVED AND CALCULATED WAVE NUMBERS (cm^{-1}) OF CHLORODIFLUOROMETHANE AND ITS ISOTOPES

Species	Assignment	$CHClF_2$		$CH^{37}ClF_2$		$^{13}CHClF_2$		$^{13}CH^{37}ClF_2$		$CDClF_2$		$CD^{37}ClF_2$		Potential Energy Distribution % X_{ij}
		Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	
a′	ν_1	3021	3021	3021	3021	3010	3012	3010	3012	2261	2228	2261	2228	99 S_1, 1 S_6
	ν_2	1312	1315	1312	1315	1306	1313	1306	1312	1103	1077	1103	1076	68 S_2, 27 S_6
	ν_3	1107	1107	1107	1107	1080	1079	1080	1078	1013	1022	1013	1021	50 S_3, 23 S_4
	ν_4	814	815	818	814	792	800	795	799	750	762	753	762	46 S_4, 16 S_5, 9 S_6
	ν_5	596	596	597	593	592	596	593	592	592	590	593	586	57 S_5, 21 S_6
	ν_6	413	413	417	410	413	406	418	404	411	410	416	408	Lo S_4, 9S_5, 41 S_6
	ν_7	1352	1354	1352	1354	1348	1352	1348	1352	1161	1167	1161	1167	65 S_7, 23 S_9
a″	ν_8	1127	1127	1127	1127	1101	1099	1101	1099	971	949	971	949	9 S_7, 68 S_8
	ν_9	366	366	366	364	363	364	363	362	363	365	363	363	30 S_7, 68 S_9

by Meal and Polo[8]. The centrifugal distortion constants are computed with the aid of the relation given by Kivelson and Wilson[9] and Cyvin[10]. Since the molecule is an asymmetric rotor, the centrifugal distortion constants are expressed as Δ_J, Δ_K, Δ_{JK}, δ_J and δ_K, following the method given by James[11].

RESULTS AND DISCUSSION

The observed and calculated frequencies are in close agreement with each other and the symmetry coordinates are seen to give maximum contribution of the potential energy. They are presented in Table 1.

The values of the three principal stretching force constants (Table 2) agree with corresponding values from earlier investigation[12]. High nega-

TABLE 2

VALENCE FORCE CONSTANTS OF $CHClF_2$ (mdyn $\mathring{A}^{-1}$)

Sl. No.	Description	$CHClF_2$	Sl. No.	Description	$CHClF_2$
1.	f_r	4.95200 (5.03000)	18.	$f_{s\nu}$	0.75637
2.	f_s	3.36500 (3.60850)	19.	$f_{s\alpha}$	−0.29833
3.	f_ρ	6.11700 (5.95000)	20.	$f_{s\beta}$	0.39644
4.	$f_{\rho\rho}$	0.28900	21.	$f_{s\partial}$	1.02761
5.	f_ν	0.60096	22.	$f_{\rho\nu}$	−0.26949
6.	f_α	1.37770	23.	$f_{\rho\alpha}$	0.05501
7.	f_β	0.77454	24.	$f_{\rho\beta}$	0.20249
8.	f_∂	1.10510	25.	$f'_{\rho\beta}$	−0.40139
9.	$f_{\beta\beta}$	0.22254	26.	$f_{\rho\partial}$	0.05519
10.	$f_{\partial\partial}$	0.45710	27.	$f'_{\rho\partial}$	−0.24746
11.	f_{rs}	0.20200	28.	$f_{\alpha\nu}$	−0.02084
12.	$f_{r\rho}$	0.35285	29.	$f_{\beta\nu}$	−0.23286
13.	$f_{r\alpha}$	0.02583	30.	$f_{\partial\nu}$	−0.70186
14.	$f_{r\nu}$	−0.15590	31.	$f_{\alpha\beta}$	0.12411
15.	$f_{r\beta}$	0.28309	32.	$f_{\alpha\partial}$	−0.00120
16.	$f_{r\partial}$	0.09430	33.	$f_{\beta\partial}$	−0.30696
17.	$f_{s\rho}$	0.53316	34.	$f_{\beta\partial}'$	−0.13996

Values given in brackets are from Ref. (12).

tive values of interaction constants involving a bond stretching coordinate will mean high localization of electrons near this bond[13]. The high positive values of f_s and $f_{s\delta}$ will therefore indicate that the electrons are highly delocalized near this bond.

From the mean square amplitudes computed at 300 K, it is observed that higher the force constants, smaller are the mean square amplitudes. The generalized mean square amplitudes of vibration for various bonded and non-bonded distances in parallel and perpendicular directions are computed at 300 K. There is good agreement between the values of the present work and the results compiled by Cyvin[3] and the comparison is given in Table 3.

TABLE 3

THE GENERALIZED MEAN SQUARE AMPLITUDES OF VIBRATION

Designation	Present value Å	Values in Ref. (3) Å
C–H	0.079	0.078
C–Cl	0.066	0.054
C–F	0.047	0.044
C–D	0.068	0.066

TABLE 4

CENTRIFUGAL DISTORTION CONSTANTS (MHz) OF $CHClF_2$ AND $CDClF_2$

Designation	$CHClF_2$	$CDClF_2$
Δ_J	1.588	1.503
Δ_K	−2.723	−2.597
Δ_{JK}	3.540	3.239
R_5	0.150	0.143
R_6	0.108	0.099
δ_J	0.127	0.085
δ_K	32.505	2.303

The calculated Coriolis coupling coefficients are found to obey the following ζ-square sum rules;

$$\sum_{i=1}^{6} (\zeta)^2_{jj} = 1 \quad \text{for } j = 7 \text{ and } 8$$

$$\sum_{i=1}^{6} (\zeta)^2_{ij} = 0.5 \text{ for } j = 9$$

$$\sum_{i=1}^{9} (\zeta)^2_{ij} = 0.5 \text{ for 1, 2 and 5 on both Z and Y components.}$$

The centrifugal distortion constants are shown in Table 4. The distortion constants are smaller for heavier isotopes. The coefficient Δ_J is positive. This indicates that the centrifugal forces about any given axis will always tend to increase the moment of inertia about the axis, which in turn reduces the centrifugal distortion constants.

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