NOTE

Vibrational Analysis of the Raman Spectra of Trifluorohalomethanes

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The general valence force field (GVFF), has been used to rein-
vestigate the force constants for trifluorohalomethanes. Coriolis
coupling constants, centrifugal distortion constants, bond order and
bond polarizability derivatives are also computed. In addition to
this the relationship between stretching force constant and other
parameters are also worked out.

Davidson and Davies[1], using the latest, technique[2] have reported the complete Raman spectra of trifluorohalomethanes CF_3X (X = Cl, Br, I) for the first time, removing hitherto the ambiguity regarding the assignment of v_6 mode also. Various investigators[3-5] could not present the complete vibrational analysis of CF_3X, due to lack of full and reliable vibrational data. A literature survey also reveals that vibrational spectra so obtained are quite different from their spectra in other environments[3,4]. It was therefore considered worth while to reinvestigate the bond and molecular parameters such as force constants, Coriolis coupling constants, centrifugal distortion constants, bond order and bond polarizabilty derivatives.

CF_3X (X = Cl, Br, I) molecules belong to C_{3v} point group and give rise to six fundamental modes distributed as $\Gamma_{vib} = 3a_1 + 3e$, where symbols have their usual meaning. The normal co-ordinate analysis has been performed in Wilson's FG matrix framework[6] using GVFF model employing extended L-F approximation method[7].

Coriolis coupling constants, ζ, belonging to ExE coupling, have been calculated using Muller's method[8]. The centrifugal distortion constants D_J, D_{JK} and D_K have been evaluated by the method of Kivelson and Wilson[9].

Bond order N and bond polarizability derivatives, $\overline{\alpha}'$, have been computed by the methods proposed in literature[10,11] respectively.

The vibrational[1] and structural data[3] used here are compiled in Table-1. The computed force constants are summarised in Table-2. In order to examine the reliability of the methods followed, these force constants in turn are used to reproduce the fundamental wavenumbers which are also compared with the observed wavenumbers (Table-1). The difference Δv, in calculated and observed

wavenumbers, is $\Delta v = \pm 5$, which indicates the accuracy of the present computation.

TABLE-1

COMPARISON OF OBSERVED AND COMPUTED WAVE NUMBERS
$(10^2 \, m^{-1})$ OF CF_3X (X = Cl, Br, I)

Wavenumbers		CF_3Cl	CF_3Br	CF_3I
v_1	Obs.	1107	1069	1064
	Cal.	1112	1073	1062
v_2	Obs.	480	351	286
	Cal.	483.5	353.2	290
v_3	Obs.	782	761	741
	Cal.	786.9	763.3	744.4
v_4	Obs.	1217	1194	1178
	Cal.	1220	1199	1182.5
v_5	Obs.	563	549	539
	Cal.	565.1	553	541
v_6	Obs.	350	303	267
	Cal.	354.5	300.8	268.2

TABLE-2

GVFF FORCE CONSTANTS $(10^2 \, Nm^{-1})$ OF CF_3X (X = Cl, Br, I)

	CF_3Cl	CF_3Br	CF_3I
f_r	7.4215	7.1633	6.7753
	(6.75)	(6.46)	
f_{rr}	1.8790	1.8007	1.5326
f_R	3.0519	2.9803	2.3512
	(3.60)	(2.91)	
f_{Rr}	1.0757	0.9666	0.7574
f_α	1.2471	1.2483	0.9716
f_β	0.4157	0.3324	0.2856
$f_{R\alpha} - f_{R\beta}$	−0.4723	−0.4354	−0.3562
$f_{r\beta} - f'_{R\beta}$	0.5597	0.3815	0.1046
$f_{\alpha\alpha}$	0.0864	0.0441	0.0310
$f_{\beta\beta}$	0.0864	0.0440	0.0310

Values in parenthesis are from Ref. 3

In GVFF model for CF_3X (X = Cl, Br, I) species, bond stretching force constants f_r and f_R for C—F and C—X bonds respectively vary as: $f_{C—F}(CF_3Cl) > f_{C—F}(CF_3Br) > f_{C—F}(CF_3I)$ and $f_{C—Cl} > f_{C—Br} > f_{C—I}$. The decrease in electronegativity of X-atom accounts for this trend. This trend shows that electronegativity of X-atom has a definite influence on the C—F bond; as a result the C—F bond gets loosened with the corresponding decrease in frequency and

decrease in electonegativity of X-atom. The above sequence also explains the trend in strength of the bonds involved in the present investigation.

The other force constants: interaction constants f_{rr}, f_{Rr} angle bending f_{α}, f_{β}, bend-bend interaction $f_{\alpha\alpha}$ and $f_{\beta\beta}$ in Table 2 follow the same trend as f_r and f_R as expected[12]. It is also noted that $f_{\alpha\alpha} \approx f_{\beta\beta}$ and has negligible contribution.

The calculated results of ζ's of e-species (Table-3) are in agreement with the reported values in literature[3]. This further supports the method employed in the present investigation. These results will be very useful in the interpretation of vibration-rotation spectra of these molecules. The evaluated values of D_J, D_{JK} and D_K (Table-3) are also well comparable with the observed values[3]. These data will be of great use for interpretation of the microwave spectra of these molecules.

TABLE-3

e-SPECIES CORIOLIS COUPLING CONSTANTS (ζ's) AND CENTRIFUGAL
DISTORTION CONSTANTS (kHz) OF CF_3X (X = Cl, Br, I)

	CF_3Cl		CF_3Br		CF_3I	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
ζ_4	0.790	0.8021	0.800	0.812	0.800	0.819
ζ_5	−0.730	−0.7510	−0.789	−0.799	−0.780	−0.759
ζ_6	0.270	0.2890	—	0.295	0.100	0.280
D_J	0.590	0.6107	—	0.272	—	0.288
D_{JK}	2.060	2.1341	1.260	1.291	—	1.988
D_K	—	−1.2480	—	−0.247	—	−0.207

The computed values of N, $\overline{\alpha}'$ along with computed f_r are presented in Table-4. A study of correlation between various parameters show that $\overline{\alpha}'$ varies as : $\overline{\alpha}'_{C—Cl} < \overline{\alpha}'_{C—Br} < \overline{\alpha}'_{C—I}$. This trend is in accordance with bond length R but opposite to f_r and N as expected[12]. This trend can be explained on the fact that greater the $\overline{\alpha}'$, weaker is the bond. The $\overline{\alpha}'$ for the same bond are in the sequence: $\overline{\alpha}'_{C—F}$ (CF_3Cl) $\simeq$ $\overline{\alpha}'_{C—F}$(CF_3Br) $\simeq$ $\overline{\alpha}'_{C—F}$(CF_3I). This trend is in line with the fact that their respective C—F bonds have nearly the same bond length.

TABLE-4

CORRELATION BETWEEN f_r (10^2 Nm^{-1}), BOND ORDER N, BOND LENGTH
R (10^2 pm) AND BOND POLARIZABILITY DERIVATIVES $\overline{\alpha}'$ ($10^4 p^2 m^2$)

	Bond	f_r	N	R	$\overline{\alpha}'$
CF_3Cl	C-F	7.4215	1.0000	1.3248	0.7275
	C-Cl	3.0519	0.7357	1.7522	1.7685
CF_3Br	C-F	7.1633	1.0000	1.3264	0.7302
	C-Br	2.9803	0.6940	1.9229	2.1301
CF_3I	C-F	6.7753	1.0000	1.3298	0.7358
	C-I	2.3512	0.5846	2.1379	4.1318

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