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Force Constant Trends in the 1-Fluoro, 2-Haloethanes

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INTRODUCTION

Although the vibrational spectra and conformational behavior of 1,2-dihaloethanes (halo=Cl,Br or I) has been investigated and there are many reports also on the alkyl fluorides [1,2,3], it is interesting to report that there has been very little study to date on the mixed 1-fluoro,2-haloethanes. The infrared and Raman spectra of this series was reported by Bermani and Jonathan [4]. Their study, however, was concerned primarily with rotational isomerism, and the assignments of the vibrations were only tentative, particularly in the CH_2 bending region. In this communication, we report the results of normal coordinate calculations on these compounds in the gauche and trans molecular configurations, employing the overlay method [5]. The goal of this study is to determine trends in force constants among the members of this series which might be useful in interpretation of the vibrational spectra of other related compounds.

EXPERIMENTAL

The calculations were performed on an IBM 360/50 computer utilizing programs developed by Schachtschneider [6,7]. Due to the absence of experimental values, the standard molecular parameters were used (C-H = 1.12 Å, C-C = 1.54Å, C-F = 1.38Å, C-Cl = 1.78Å, C-Br = 1.93Å, C-I = 2.13Å and a valence angle of $109^{o}28'$). The dihedral angle between the C-F and C-X bonds was assumed to be 60^{o} and 180^{o} for the gauche and trans conformers. The initial force constant values were transferred from FCH_2CH_2OH[8], $CH_2XC{\equiv}N$ (X = Cl, Br or I) [9]. CH_3CH_2F[10], CH_3CH_2Cl[11], CH_3CH_2I[12] or estimated. After several manual adjustments using the P.E.D. and JZ matrices as guides, the least-squares force constant refinement procedure finally yielded an average error of 4.5 cm [13].

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RESULTS and DISCUSSION

As a result of these calculations, a reassignment of several of the bending modes has been made. In the previous work [4], the two CH_2 wagging vibrations were both assigned to higher frequency than the corresponding twisting modes, in accordance with the commonly observed results on 1,2-disubstituted ethanes. In contrast, it was found here that these frequencies appear to alternate in the sequence wag>twist>wag>twist. This trend, which was observed for both rotamers in all members of the series, is unusual, but not unique. The same sequence has been reported for 1,2-dichloroethane in the trans conformation [14].

The observed [4] and calculated frequencies of the C-C and C-F stretching modes are compared in Table I. It is perhaps somewhat surprising to find that the C-F stretching vibrations in this series lie far higher in frequency than in the parent compound ethyl fluoride (880 cm^{-1}) [3] and in other acyclic fluorinated hydrocarbons [15]. The C-F stretch shows a downward trend from Cl to I, which is similar to the behavior observed by Tuazon et al. [15] when C-F bonds become attached to increasingly heavier frameworks [16, 17]. The mixing between the C-C and C-F stretching modes (as indicated by the P.E.D.) is much less significant than that observed in the alkyl fluorides [1,2].

TABLE I

Observed and calculated C-C and C-F stretching frequencies (cm^{-1}) for gauche (G) and trans (T) conformers of 1-fluoro,2-haloethanes.

Compound	Obsd.	Calcd.	P.E.D. (%)[a]
$\mathrm{ClCH_2CH_2F}$ (G)	1075	1075	C-C (49)
	1030	1028	C-F (62), C-C (19)
$\mathrm{BrCH_2CH_2F}$ (G)	1067	1080	C-C (50)
	1004	1000	C-F (69), C-C (23)
$\mathrm{ICH_2CH_2F}$ (G)	1060	1059	C-C (58)
	980	984	C-F (76), C-C (27)
$\mathrm{ClCH_2CH_2F}$ (T)		1149	C-C (70)
	1092	1091	C-F (72)
$\mathrm{BrCH_2CH_2F}$ (T)		1144	C-C (69)
	1070	1069	C-F (78), C-C (13)
$\mathrm{ICH_2CH_2F}$ (T)		1140	C-C (68)
	1063	1061	C-F (73)

[a] Contributions less than 10% excluded.

An examination of the force field for these molecules reveals several points of interest. As observed in Table II, a number of trends involving halogen size and conformation were observed: (1) The bending force constant, $H_{\Theta(x)}$, decreases in going from Cl to I, and is generally greater for the gauche conformers. (2) The force constant $H_{\delta(x)}$ (H-C-X bend) has similar values for both rotamers and decreases uniformly from Cl to I. (3) The force constant $H_{r\ (x)}$ (C-C stretch, C-C-X bend interaction) increases from Cl to I and is of opposite sign for the two conformers.

TABLE II

The $H_{\delta(x)}$, $H_{\Theta(x)}$ and $Fr_{\delta(x)}$ force constants for 1-fluoro,2-haloethanes.

Force[a] Constant	Coordinate(s) involved	Cl(G)	Br(G)	I(G)	Cl(T)	Br(T)	I(T)
$H_{\delta(x)}$	C-C-X	1.040	1.030	0.710	0.830	0.800	0.741
$H_{\Theta(x)}$	H-C-X	0.718	0.676	0.620	0.739	0.701	0.584
$F_{r\delta(x)}$	C-C, C-C-X	-0.145	-0.478	-0.684	0.190	0.200	0.299

[a] Bending constants in units of mdyn Å rad^{-2} and stretch-bend interaction constants in units of mdyn rad^{-1}.

TABLE III

Observed and calculated frequencies (cm^{-1}) and potential energy distribution for C-C-X bending ($H_{\delta(x)}$) and torsional (H_{τ}) modes.

Compound	Obsd.	Calcd.	P.E.D. (%)
$ClCH_2CH_2F$ (G)	290	286	$H_{\delta(x)}$(41), H_{τ}(29)
	142	145	H_{τ}(59), $H_{\delta(x)}$(16)
$BrCH_2CH_2F$ (G)	264	263	$H_{\delta(x)}$(39), H_{τ}(35)
	126	126	H_{τ}(52), $H_{\delta(x)}$(22)
ICH_2CH_2F (G)	224	232	H_{τ}(47), $H_{\delta(x)}$(44)
	116	109	$H_{\delta(x)}$(44), H_{τ}(39)

[a] Contributions less than 10% are excluded.

Another point resulting from this study is that the C-C-X bending ($H_{\delta(x)}$) and torsion (H_{τ}) modes are highly coupled in the gauche conformation (but not in the trans). The mixing increases from Cl to I and becomes overwhelming for the gauche iodo conformer, and shown in Table III.

It is hoped that the results obtained here in the 1-fluoro,2-haloethanes may be of aid in future vibrational investigations on similar molecules. In particular, we are interested in studying the 2-haloethylmethyl ethers. Due to the near mass coincidence between oxygen and fluorine and their similar electronegativities, it is felt that some of the above observed trends may be found in this series.

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