Fluorinated Halomethanes

Table 1: ^{35}Cl, ^{79}Br, ^{127}I NQCC tensors (MHz) in increasingly fluorinated methyl halides. (References are given below.)

X =		Cl	Br	I
CH_3X	χ_{zz}	–74.7514(11)	577.1300(18)	–1934.13022(39)
CH_2FX	χ_{aa}	–52.570(26)	443.531(24)	–1581.6142(27)
	χ_{bb}	13.469(20)	–144.980(34)	584.1657(52)
	χ_{cc}	39.059(18)	–298.551(34)	997.4485(52)
	$\lvert\chi_{ab}\rvert$	43.7(23)	278.63(54)	857.209(70)
	χ_{xx}	35.20(186)	–255.97(38)	882.383(44)
	χ_{yy}	39.059(18)	–298.551(34)	997.4485(52)
	χ_{zz}	–74.30(187)	554.52(38)	–1879.832(44)
	η	0.0519	0.07679(17)	0.06121(2)
CHF_2X	χ_{aa}	–65.0239(65)	521.257(9)	–1817.9153(33)
	χ_{bb}	35.467(14)	–279.804(40)	966.1092(32)
	χ_{cc}	29.566(14)	–241.453(40)	851.8060(32)
	$\lvert\chi_{ac}\rvert$	24.(5)	185.87(28)	520.2074(78)
	χ_{xx}	35.3(25)	–284.34(13)	949.5893(42)
	χ_{yy}	35.467(14)	–279.804(40)	966.1092(32)
	χ_{zz}	–70.8(25)	564.14(12)	–1915.6986(42)
	η	0.0024(390)	0.0080(2)	0.0086234(28)
CF_3X	χ_{zz}	–77.902(30)	618.2628(21)	–2144.9949(28)

Discussion

Going from CH_3X to CH_2FX to CHF_2X to CF_3X,

changes in $|\chi_{zz}|$(Cl) are –0.6 %, –4.7 %, and +10.0 %,
changes in $|\chi_{zz}|$(Br) are –3.9 %, +1.7 %, and +9.6 %,
changes in $|\chi_{zz}|$(I) are –2.8 %, +1.9 %, and +12.0 %.

Any pattern that may exist here is obscured by the data for Cl. Note the rather large uncertainties in $|\chi_{ab}|$ for CH_2FCl and $|\chi_{ac}|$ for CHF_2Cl which, in turn, produce large uncertainties in $|\chi_{zz}|$. For each of these molecules, *ab initio* calculation on ${r_e}^{SE}$ structures (N.Vogt, J.Demaison, and H.D.Rudolf, Mol. Phys. 112,2873(2014)) of the inertial axes NQCC tensors yield diagonal components in good agreement with experimental values, as shown below:

CH_2FCl	Expt.	Calc.
χ_{aa}	–52.570(26)	–52.77
χ_{bb}	13.469(20)	13.55
χ_{cc}	39.059(18)	39.22
$\|\chi_{ab}\|$	43.7(23)	39.86

CHF_2Cl	Expt.	Calc.
χ_{aa}	–65.0239(65)	–65.17
χ_{bb}	35.467(14)	35.46
χ_{cc}	29.566(14)	29.70
$\|\chi_{ac}\|$	24.(5)	26.77

There being no reason why the calculated off-diagonal components should be any less accurate then the diagonal, re-diagonalization was made with $|\chi_{ab}|$ = 39.86(30) MHz for CH_2FCl, and $|\chi_{ac}|$ = 26.77(22) MHz for CHF_2Cl, where the assumed uncertainties in these are, for each molecule, 2× the root mean square difference between calculated and experimental diagonal components. These results are shown below in Table 2, alongside the original diagonalizations (Table 1).

Table 2: ^{35}Cl NQCC tensors (MHz) in CH_2FCl and CHF_2Cl

		Diag	Re-Diag
CH_2FCl	χ_{aa}	–52.570(26)	–52.570(26)
	χ_{bb}	13.469(20)	13.469(20)
	χ_{cc}	39.059(18)	39.059(18)
	$\lvert\chi_{ab}\rvert$	43.7(23)	39.86(30)
	χ_{xx}	35.20(186)	32.21(23)
	χ_{yy}	39.059(18)	39.059(18)
	χ_{zz}	–74.30(187)	–71.31(23)
	η	0.0519	0.0960(3)
CHF_2Cl	χ_{aa}	–65.0239(65)	–65.0239(65)
	χ_{bb}	35.467(14)	35.467(14)
	χ_{cc}	29.566(14)	29.566(14)
	$\lvert\chi_{ac}\rvert$	24.(5)	26.77(22)
	χ_{xx}	35.3(25)	36.62(11)
	χ_{yy}	35.467(14)	35.467(14)
	χ_{zz}	–70.8(25)	–72.07(11)
	η	0.0024(390)	0.0160(15)

And now, going from CH_3X to CH_2FX to CHF_2X to CF_3X,
changes in $|\chi_{zz}|$(Cl) are –4.6 %, +1.1 %, and +8.1 %,
changes in $|\chi_{zz}|$(Br) are –3.9 %, +1.7 %, and +9.6 %,
changes in $|\chi_{zz}|$(I) are –2.8 %, +1.9 %, and +12.0 %.

This makes much more sense.

References

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