Dihalomethanes

Table 1: ^{35}Cl NQCCs (MHz) in CH_2XCl, where X = F, Cl, Br, I.

X =	F[a]	^{35}Cl[b]	^{79}Br[c]	I[d]
χ_{aa}	–52.570(26)	–41.7418(11)	–33.64(70)	30.9451(31)
χ_{bb}	13.469(20)	1.8004(12)	–5.79(41)	–9.1413(37)
χ_{cc}	39.059(18)	39.9414(12)	39.43(81)	40.0881(49)
$\lvert\chi_{ab}\rvert$	43.7(23)	50.93(23)	53.7(52)	55.600(51)
χ_{xx}	35.20(186)	35.41(21)	35.76(505)[e]	36.614(52)
χ_{yy}	39.059(18)	39.9414(12)	39.43(81)	40.0881(49)
χ_{zz}	–74.30(187)	–75.35(21)	–75.19(505)[e]	–76.703(52)
η	0.0519	0.060(3)	0.04880	0.0457

[a] S.Blanco, A.Lesarri, J.C.López, J.L.Alonso, and A.Guarnier, J. Mol. Spectrosc. 174,397 (1995).
[b] Z.Kisiel, J.Kosarzewski, and L.Pszczólkowski, Acta Physica Polonica A, 92,507(1997).
[c] Y.Niide and I.Ohkoshi, J. Mol. Spectrosc. 136,17(1989).
[d] S.Bailleux, H.Ozeki, S.Sakai, T.Okabayashi, P.Kania, and D.Duflot, J. Mol. Spectrosc. 270,51(2011).
[e] The uncertainty in this component, not given in original paper, was calculated here using Kisiel's QDIAG program.

Table 2: ^{79}Br NQCCs (MHz) in CH_2XBr, where X = F, Cl, Br, I.

X =	F[a]	^{35}Cl[b]	^{79}Br[c]	I[d]
χ_{aa}	443.531(24)	383.33(59)	335.21(42)	304.3803(11)
χ_{bb}	–144.980(34)	–75.80(37)	–24.93(24)	4.3527(12)
χ_{cc}	–298.551(34)	–307.53(69)	–310.28(48)	–308.7331(17)
$\lvert\chi_{ab}\rvert$	278.63(54)	372.4(13)	402.12(79)	418.0130(52)
χ_{xx}	–255.97(38)	–283.70	–285.46	–289.7495(49)
χ_{yy}	–298.551(34)	–307.53	–310.28	–308.7331(17)
χ_{zz}	554.52(38)	591.23	595.74	598.4825(49)
η	0.07679(17)	0.04030	0.04166	0.0317

[a] A.Baldacci, P.Stoppa, A.Pietropolli Charmet, S.Giorgianni, G.Cazzoli, C.Puzzarini, and R. Wugt Larson, J. Phys. Chem. A, 111,7090(2007).
[b] Y.Niide and I.Ohkoshi, J.Mol.Spectrosc. 136,17(1989).
[c] Y.Niide, H.Tanaka, and I.Ohkoshi, J. Mol. Spectrosc. 139,11(1990).
[d] S.Bailleux, D.Duflot, K.Taniguchi, S.Sakai, H.Ozeki, T.Okabayashi, and W.C.Bailey, J. Phys. Chem. A, 118,11744(2014).

Table 3: ^{127}I NQCCs (MHz) in CH_2XI, where X = F, Cl, Br, I.

X =	F[a]	^{35}Cl[b]	^{79}Br[c]	I[d]
χ_{aa}	–1581.6142(27)	–1421.6753(25)	–1275.3137(13)	–1180.90(13)
χ_{bb}	584.1657(52)	392.3607(25)	236.3851(12)	144.238(70)
χ_{cc}	997.4485(52)	1029.3147(35)	1038.9286(18)	1036.662(70)
$\lvert\chi_{ab}\rvert$	857.209(70)	1177.095(24)	1296.1970(44)	1358.85(54)
χ_{xx}	882.383(44)	971.356(25)	981.0140(39)	993.45(49)
χ_{yy}	997.4485(52)	1029.3147(35)	1038.9286(18)	1036.662(70)
χ_{zz}	–1879.832(44)	–2000.670(25)	–2019.9426(39)	–2030.11(45)
η	0.06121(2)	0.0290	0.0287	0.02129(24)

[a] C.Puzzarini, G.Cazzoli, J.C.López, J.L.Alonso, A.Baldacci, A.Baldan, S.Stopkowicz, L.Cheng, and J.Gauss, J. Chem. Phys. 134,174312(2011); G.Cazzoli, A.Baldacci, A.Baldan, and C.Puzzarini, Mol. Phys. 109,2245(2011).

[b] S.Bailleux, H.Ozeki, S.Sakai, T.Okabayashi, P.Kania, and D.Duflot, J. Mol. Spectrosc. 270,51 (2011).

[c] S.Bailleux, D.Duflot, K.Taniguchi, S.Sakai, H.Ozeki, T.Okabayashi, and W.C.Bailey, J. Phys. Chem. A, 118,11744(2014).

[d] Z.Kisiel, L.Pszczólkowski, W.Caminati, and P.G.Favero, J. Chem. Phys. 105,1778(1996); J. Mol. Spectrosc. 189,283(1998).

DISCUSSION

Going from X = F to Cl to Br to I,
changes in $|\chi_{zz}|$(Cl) are +1.4 %, –0.2 %, and +2.0 %,
changes in $|\chi_{zz}|$(Br) are +6.6 %, +0.8 %, and +0.5 %
changes in $|\chi_{zz}|$(I) are +6.4 %, +1.0 %, and +0.5 %.

Any pattern that may exist here is obscured by the data for Cl. We note the rather large uncertainties in $|\chi_{ab}|$ for CH_2FCl and especially CH_2BrCl which, in turn, produce large uncertainties in $|\chi_{zz}|$. For CH_2FCl, *ab initio* calculation on an r_e^{SE} structure (1) of the inertial axes NQCC tensors yields diagonal components in good agreement with experimental values - and for CH_2BrCl, on an r_o structure (2), fair agreement - 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

CH_2BrCl	Expt.	Calc.
χ_{aa}	–33.64(70)	–35.69
χ_{bb}	–5.79(41)	–4.89
χ_{cc}	39.43(81)	40.58
$\|\chi_{ab}\|$	53.7(52)	54.25

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 54.25(290) MHz for CH_2BrCl, where the assumed uncertainties are, for each molecule, 2× the root mean square difference between calculated and experimental diagonal components. These results are shown below in Table 4, alongside the original diagonalizations (Table 1).

Table 4: ^{35}Cl NQCC tensors (MHz) in CH_2FCl and CH_2BrCl

		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)
CH_2BrCl	χ_{aa}	–33.64(70)	–33.64(70)
	χ_{bb}	–5.79(41)	–5.79(41)
	χ_{cc}	39.43(81)	39.43(81)
	$\lvert\chi_{ab}\rvert$	53.7(52)	54.25(290)
	χ_{xx}	35.76(505)	36.29(283)
	χ_{yy}	39.43(81)	39.43(81)
	χ_{zz}	–75.19(505)	–75.72(285)
	η	0.0488(681)	0.0414(389)

And now, going from X = F to Cl to Br to I,
changes in $|\chi_{zz}|$(Cl) are +5.7 %, +0.5 %, and +1.3 %,
changes in $|\chi_{zz}|$(Br) are +6.6 %, +0.8 %, and +0.5 %,
changes in $|\chi_{zz}|$(I) are +6.4 %, +1.0 %, and +0.5 %.

This is better.

REFERENCES

(1) N.Vogt, J.Demaison, and H.D.Rudolf, Mol. Phys. 112,2873(2014).
(2) Y.Niide and I.Ohkoshi, J.Mol.Spectrosc. 136,17(1989).