Calculation of Nuclear Quadrupole Coupling Constants on Approximate Equilibrium Molecular Structures

VI. Ethylene

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March 2007

Calculation was made of N, Cl, and Br nuclear quadrupole coupling constants on r_{opt} (= MP2/aug-cc-pVTZ(G03) optimization), ~ r_e, and experimental structures of the following derivatives of ethylene:

1. Vinyl Chloride, CH_2=CHCl
2. Vinyl Bromide, CH_2=CHBr
3. Vinyl Cyanide, CH_2=CHC≡N
4. 1-Chloro-1-Cyanoethylene, CH_2=CClC≡N
5. 1,1-Difluorovinyl Chloride, CF_2=CHCl
6. 1-Chloro-1-Fluoroethylene, CH_2=CFCl
7. 1-Bromo-1-Fluoroethylene, CH_2=CFBr
8. *cis*-1-Chloro-2-Fluoroethylene, c-CHF=CHCl
9. *trans-1-Chloro-2-Fluoroethylene*, t-CHF=CHCl
10. *cis-1-Bromo-2-Fluoroethylene*, c-CHF=CHBr
11. *trans-1-Bromo-2-Fluoroethylene*, t-CHF=CHBr
12. *cis-1,2-Dichloroethylene*, c-CHCl=CHCl
13. 1,1-Dichloroethylene, CH_2=CCl_2
14. Trichloroethylene, CHCl=CCl_2

The results - structure parameters, rotational constants, and nuclear quadrupole coupling constants - are given below in Tables 1 - 14. Summary and discussion follows.

Table 1. Vinyl Chloride, CH_2=CHCl. Structure parameters (Å and degrees), rotational constants (MHz), and Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e	r_e [a]	expt. [b]
C=C	1.3296	1.3259	1.3262	
CCl	1.7283	1.7251	1.7263	
CH	1.0796	1.0796	1.0784	
CH_c	1.0794	1.0794	1.0795	
CH_t	1.0801	1.0801	1.0797	
CCCl	122.91	122.91	122.77	
CCH	123.63	123.63	123.86	
CCH_c	121.71	121.71	121.80	
CCH_t	119.02	119.02	119.29	
A	57 325.5	57 505.5		
B	6 029.4	6 054.5		
C	5 455.6	5 477.8		
χ_{aa} (^{35}Cl)	-57.30	-57.12	-57.09	-57.21(13)
χ_{bb}	26.42	26.36	26.30	25.47
χ_{cc}	30.88	30.76	30.79	31.74
$\lvert\chi_{ab}\rvert$	35.61	35.53	35.64	
RMS	0.74 (1.9 %)	0.76 (2.0 %)	0.73 (1.7 %)	

χ_{xx}	39.52	39.43	39.45	
χ_{yy}	30.88	30.76	30.79	
χ_{zz}	-70.40	-70.20	-70.24	
η	-0.123	-0.124	-0.123	
$\varphi_{z,a}$	28.19	20.20	20.26	
$\varphi_{a,CCl}$	19.94	19.92	19.97	
$\varphi_{z,CCl}$	0.25	0.28	0.29	
χ_{aa} (^{37}Cl)	-45.27	-45.13	-45.11	-45.13(11)
χ_{bb}	20.94	20.89	20.84	20.25
χ_{cc}	24.34	24.24	24.27	24.88
$\lvert\chi_{ab}\rvert$	27.93	27.87	27.95	
RMS	0.51 (1.7 %)	0.52 (1.7 %)	0.49 (1.6 %)	

[a] Ref. [1]. [b] Ref. [2]. Back to Top

Table 2. Vinyl Bromide, CH_2=CHBr. Structure parameters (Å and degrees), rotational constants (MHz), and Br nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e	r_e [a]	expt. [b]
C=C	1.3296	1.3259	1.3256(3)	
CBr	1.8750	1.8836	1.8835(2)	
CH	1.0794	1.0794	1.0780(1)	

CH_c	1.0797	1.0797	1.0794(1)	
CH_t	1.0809	1.0809	1.0804(3)	
CCBr	122.90	122.90	122.62(1)	
CCH	123.63	123.63	124.34(3)	
CCH_c	121.92	121.92	122.03(2)	
CCH_t	119.13	119.13	119.28(4)	
A	54 886.4	54 950.8		
B	4 191.5	4 170.8		
C	3 894.1	3 876.6		
χ_{aa} (^{79}Br)	469.96	473.76	471.74	470.98(9)
χ_{bb}	-220.57	-221.83	-220.74	-216.97
χ_{cc}	-249.39	-251.93	-251.00	-254.01(10)
$\lvert\chi_{ab}\rvert$	244.48	244.39	244.68	246.14(564)
RMS	3.43 (1.09 %)	3.45 (1.10 %)	2.82 (0.90 %)	
χ_{xx}	-298.36	-299.11	-298.48	-295.97(328)
χ_{yy}	-249.39	-251.93	-251.00	-254.01(10)
χ_{zz}	547.75	551.04	549.47	549.97(328)
η	-0.0894	-0.0856	-0.0864	-0.0763
$\varphi_{z,a}$	17.65	17.55	17.62	17.78
$\varphi_{a,CCl}$	17.41	17.29		
$\varphi_{z,CCl}$	0.24	0.26		

χ_{aa} (^{81}Br)	392.78	395.96	394.27	393.58(7)
χ_{bb}	-184.43	-185.48	-184.57	-181.36
χ_{cc}	-208.36	-210.48	-209.70	-212.22
$\lvert\chi_{ab}\rvert$	204.05l	203.97	204.21	204.17(506)
RMS	2.88 (1.10 %)	2.92 (1.11 %)	2.39 (0.91 %)	

[a] Ref. [3]. [b] Ref. [4]. Back to Top

Table 3. Vinyl Cyanide, CH_2=CHC≡N. Structure parameters (Å and degrees), rotational constants (MHz), and ^{14}N nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e	near-r_e [a]	expt. [b]
C=C	1.3380	1.3342	1.337	
C-C	1.4290	1.4310	1.432	
C≡N	1.1731	1.1577	1.157	
CH	1.0813	1.0813	1.082	
CH_c	1.0804	1.0804	1.081	
CH_t	1.0798	1.0798	1.080	
C=C-C	122.17	122.17	122.1	
C-C≡N [c]	179.09	179.09	179.1	
CCH	121.29	121.29	121.4	
CCH_c	121.20	121.20	121.5	
CCH_t	120.30	120.30	120.3	

A	49 883.3	50 142.8		
B	4 948.6	4 985.9		
C	4 502.0	4 535.0		
χ_{aa} (^{14}N)	-3.653	-3.797	-3.799	-3.78913(40)
χ_{bb}	1.629	1.691	1.690	1.68607(43)
χ_{cc}	2.024	2.106	2.109	2.10306(49)
$\lvert\chi_{ab}\rvert$	1.664	1.728	1.736	
RMS	0.096 (3.8 %)	0.006 (0.23 %)	0.007 (0.29 %)	
χ_{xx}	2.110	2.190	2.193	
χ_{yy}	2.024	2.106	2.109	
χ_{zz}	-4.134	-4.296	-4.302	
η	-0.021	-0.019	-0.019	
$\varphi_{z,a}$	16.10	16.10	16.15	
$\varphi_{a,CN}$	15.43	15.46	15.52	
$\varphi_{z,CN}$	0.67	0.64	0.63	

[a] Ref. [5]. [b] Ref. [6]. [c] N tilts toward H, away from H_c. Back to Top

Table 4. 1-Chloro-1-Cyanoethylene, $CH_2=C^{35}ClC\equiv{}^{14}N$. Structure parameters (Å and degrees), rotational constants (MHz), and ^{35}Cl and ^{14}N nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	$\sim r_e$		expt. [a]
C=C	1.3359	1.3321		
CCl	1.7288	1.7256		
C-C	1.4286	1.4307		
C≡N	1.1736	1.1580		
CH_c [b]	1.0791	1.0791		
CH_t [b]	1.0800	1.0800		
C=CCl	122.48	122.48		
C=C-C	122.80	122.80		
C-C≡N [c]	179.74	179.74		
CCH_c	120.70	120.70		
CCH_t	119.34	119.34		
A	6953.4	6991.5		
B	3139.6	3158.5		
C	2163.0	2175.6		
χ_{aa} (^{35}Cl)	-31.66	-31.78		-31.8093(13)
χ_{bb}	-3.12	-2.82		-3.1730(16)
χ_{cc}	34.79	34.60		34.9823(16)
$\lvert\chi_{ab}\rvert$	57.76	57.53		57.173(12)

RMS	0.14 (0.68 %)	0.30 (1.3 %)		
χ_{xx}	42.10	42.02		41.447(12)
χ_{yy}	34.79	34.60		34.982(2)
χ_{zz}	-76.89	-76.63		-76.430(12)
η	-0.0951	-0.0968		-0.0846(2)
$\varphi_{z,a}$	38.06	37.94		37.970(2)
$\varphi_{a,CCl}$	38.98	38.87		
$\varphi_{z,CCl}$	0.92	0.94		
χ_{aa} (^{14}N)	-2.964	-3.069		-3.0609(19)
χ_{bb}	1.031	1.044		1.0228(20)
χ_{cc}	1.933	2.025		2.0380(20)
$\lvert\chi_{ab}\rvert$	2.533	2.638		2.611(12)
RMS	0.082 (4.0 %)	0.015 (0.73 %)		
χ_{xx}	2.258	2.332		2.296(10)
χ_{yy}	1.933	2.025		2.038(2)
χ_{zz}	-4.192	-4.357		-4.336(10)
η	-0.078	-0.070		-0.060(2)
$\varphi_{z,a}$	25.87	26.03		25.99(7)
$\varphi_{a,CN}$	26.56	26.67		
$\varphi_{z,CN}$	0.69	0.64		

[a] Ref. [7]. [b] H_c and H_t are with respect to Cl. [c] N tilts toward Cl. Back to Top

Table 5. 1,1-Difluorovinyl Chloride, CF_2=CHCl. Structure parameters (Å and degrees), rotational constants (MHz), and ^{35}Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e	r_o [a]	expt. [b]
C=C	1.3273	1.3236	1.30	
CCl	1.7137	1.7105	1.726	
CH	1.0754	1.0754	1.08	
CF_c	1.3114	1.3059	1.32	
CF_t	1.3182	1.3126	1.32	
C=CCl	121.61	121.61	122.3	
C=CH	120.16	120.16	123.8	
$C=CF_c$	125.67	125.67	125	
$C=CF_t$	123.20	123.20	125	
A	10 708.6	10 789.8		
B	2 292.5	2 304.9		
C	1 888.2	1 899.2		
χ_{aa} (^{35}Cl)	-55.06	-54.83	-57.46	-55.05(10)
χ_{bb}	18.55	18.43	20.83	18.29(8)
χ_{cc}	36.51	36.40	36.63	36.76(10)
$\lvert\chi_{ab}\rvert$	47.01	46.85	46.01	46.3(40)

RMS	0.20 (0.56 %)	0.25 (0.69 %)	2.02 (5.5 %)	
χ_{xx}	41.45	41.27	42.10	40.64
χ_{yy}	36.51	36.40	36.63	36.76
χ_{zz}	-77.96	-77.68	-78.72	-77.40
η	-0.063	-0.063	-0.015	-0.050
$\varphi_{z,a}$	25.97	25.99	24.8	25.8(11)
$\varphi_{a,CCl}$	26.65	26.64	26.2	
$\varphi_{z,CCl}$	0.68	0.65	1.4	

[a] Ref. [8]. [b] Ref. [9]. Back to Top

Table 6. 1-Chloro-1-Fluoroethylene, CH_2=CFCl. Structure parameters (Å and degrees), rotational constants (MHz), and Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e		expt. [a]
C=C	1.3260	1.3223		
CCl	1.7132	1.7100		
CF	1.3323	1.3264		
CH_c	1.0755	1.0755		
CH_t	1.0780	1.0780		
CCCl	125.58	125.58		
CCF	122.58	122.58		
CCH_c	119.74	119.74		

CCH_t	119.18	119.18		
A	10 677.6	10 753.5		
B	5 101.6	5 124.3		
C	3 452.2	3 470.5		
χ_{aa} (^{35}Cl)	-73.06	-72.72		-72.92(4)
χ_{bb}	39.31	39.19		38.63(3)
χ_{cc}	33.75	33.53		34.30(4)
$\lvert\chi_{ab}\rvert$	6.32	6.26		
RMS	0.51 (1.0 %)	0.56 (1.2 %)		
χ_{xx}	39.67	39.54		
χ_{yy}	33.75	33.53		
χ_{zz}	-73.42	-73.07		
η	-0.080	-0.082		
$\varphi_{z,a}$	3.21	3.19		
$\varphi_{a,CCl}$	3.20	3.13		
$\varphi_{z,CCl}$	0.01	0.06		
χ_{aa} (^{37}Cl)	-57.58	-57.30		-57.52(5)
χ_{bb}	30.97	30.88		30.50(4)
χ_{cc}	26.60	26.42		27.02(4)
$\lvert\chi_{ab}\rvert$	5.08	5.04		

RMS	0.37 (0.95 %)	0.43 (1.1 %)		

[a] Ref. [10]. Back to Top

Table 7. 1-Bromo-1-Fluoroethylene, CH_2=CFBr. Structure parameters (Å and degrees), rotational constants (MHz), and Br nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter [a]	r_{opt}	~ r_e		expt. [b]
C=C	1.3262	1.3226		
CBr	1.8643	1.8730		
CF	1.3338	1.3279		
CH_c	1.0757	1,0757		
CH_t	1.0789	1.0789		
CCBr	125.35	125.35		
CCF	122.40	122.40		
CCH_c	119.84	119.84		
CCH_t	119.26	119.26		
A	10 676.5	10 752.2		
B	3 124.9	3 107.3		
C	2 417.4	2 410.6		
χ_{aa} (^{79}Br)	577.38	580.07		578.81(20)
χ_{bb}	-303.90	-304.76		-302.31

χ_{cc}	-273.48	-275.31		-276.50(11)
$\lvert\chi_{ab}\rvert$	53.35	53.40		54.3(15)
RMS	2.13 (0.55 %)	1.73 (0.45 %)		
χ_{xx}	-307.12	-307.97		-305.64(21)
χ_{yy}	-273.48	-275.31		-276.50(11)
χ_{zz}	580.60	583.28		582.15(27)
η	-0.0579	-0.0560		-0.0700(4)
$\varphi_{z,a}$	3.45	3.44		3.5(1)
$\varphi_{a,CBr}$				
$\varphi_{z,CBr}$				
χ_{aa} (^{81}Br)	482.37	484.62		483.22(19)
χ_{bb}	-253.89	-254.60		-252.29
χ_{cc}	-228.49	-230.02		-230.93(10)
$\lvert\chi_{ab}\rvert$	44.66	44.70		47.5(22)
RMS	1.75 (0.54 %)	1.65 (0.51 %)		

[a] H_c and H_t are with respect to Br. [b] Ref. [11]. Back to Top

Table 8. *cis*-1-Chloro-2-Fluoroethylene, c-CHF=CHCl. Structure parameters (Å and degrees), rotational constants (MHz), and Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e	r_e [a]	expt. [b]
C=C	1.3294	1.3257	1.325(1)	
C(1)Cl	1.7147	1.7115	1.715(2)	
C(2)F	1.3350	1.3290	1.331(1)	
C(1)H	1.0771	1.0771	1.077(1)	
C(2)H	1.0792	1.0792	1.079(1)	
CCCl	123.15	123.15	123.3(1)	
CCF	122.74	122.74	123.1(1)	
C(2)C(1)H	120.16	120.16	120.4(1)	
C(1)C(2)H	123.17	123.17	122.9(1)	
A	16 499.4	16 602.7		
B	3 733.6	3 752.4		
C	3 044.6	3 060.6		
χ_{aa} (^{35}Cl)	-22.58	-22.64	-23.07	-22.719(14)
χ_{bb}	-10.25	-10.07	-9.75	-10.600(13)
χ_{cc}	32.83	32.71	32.83	33.319(17)
$\lvert\chi_{ab}\rvert$	57.75	57.54	57.60	54.4770(86)
RMS	0.35 (1.6 %)	0.46 (2.1 %)	0.60 (2.7 %)	

χ_{xx}	41.66	41.53	41.57	41.136(13)
χ_{yy}	32.83	32.71	32.83	33.319(17)
χ_{zz}	-74.50	-74.24	-74.40	-74.455(13)
η	-0.1186	-0.1187	-0.1175	-0.10499(29)
$\varphi_{z,a}$	41.95	41.88	41.70	41.9909(47)
$\varphi_{a,CCl}$	42.56	42.49	42.4	
$\varphi_{z,CCl}$	0.61	0.60	0.7	
χ_{aa} (^{37}Cl)	-18.32	-18.37	-18.71	-18.488(63)
χ_{bb}	-7.55	-7.41	-7.16	-7.739(36)
χ_{cc}	25.88	25.78	25.87	26.227(36)
$\lvert\chi_{ab}\rvert$	45.46	45.29	45.33	45.403(86)
RMS	0.25 (1.4 %)	0.32 (1.9 %)	0.41 (2.4 %)	

[a] Ref. [12]. [b] Ref. [13]. Back to Top

Table 9. *trans*-1-Chloro-2-Fluoroethylene, t-CHF=CHCl. Structure parameters (Å and degrees), rotational constants (MHz), and Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e	r_e [a]	expt. [b]
C=C	1.3281	1.3245	1.324(2)	
C(1)Cl	1.7209	1.7177	1.720(2)	
C(2)F	1.3424	1.3363	1.338(1)	

C(1)H	1.0781	1.0781	1.078(1)	
C(2)H	1.0791	1.0791	1.079(1)	
CCCl	120.58	120.58	120.6(1)	
CCF	120.33	120.33	120.3(1)	
C(2)C(1)H	122.85	122.85	123.1(1)	
C(1)C(2)H	125.67	125.67	125.6(1)	
A	54 062.1	54 253.0		53 655.7296(13)
B	2 472.9	2 487.0		2 476.60705(40)
C	2 364.7	2 378.0		2 366.41041(45)
χ_{aa} (^{35}Cl)	-63.66	-63.41	-63.73	-63.586(58)
χ_{bb}	28.42	28.27	28.35	27.53(27)
χ_{cc}	35.24	35.13	35.37	36.05(27)
$\lvert\chi_{ab}\rvert$	34.12	34.08	34.01	
RMS	0.69 (1.6 %)	0.68 (1.6 %)	0.62 (1.5 %)	
χ_{xx}	39.68	39.55	39.55	
χ_{yy}	35.24	35.13	35.37	
χ_{zz}	-74.92	-74.69	-74.92	
η	-0.059	-0.059	-0.056	
$\varphi_{z,a}$	18.27	18.31	18.22	
$\varphi_{a,CCl}$	18.57	18.57	18.5	
$\varphi_{z,CCl}$	0.30	0.26	0.3	

χ_{aa} (^{37}Cl)	-50.22	-50.03	-50.29	-52.12(87)
χ_{bb}	22.45	22.34	22.40	22.97(34)
χ_{cc}	27.77	27.69	27.88	29.15(34)
$\lvert\chi_{ab}\rvert$	26.82	26.79	26.73	
RMS	1.38 (4.0 %)	1.52 (4.4 %)	1.33 (3.8 %)	

[a] Ref. [14]. [b] Ref. [15]. Back to Top

Table 10. *cis*-1-Bromo-2-Fluoroethylene, c-CHF=CHBr. Structure parameters (Å and degrees), rotational constants (MHz), and Br nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	$\sim r_e$		expt. [a]
C=C	1.3285	1.3248		
C(1)Br	1.8606	1.8694		
C(2)F	1.3348	1.3288		
C(1)H	1.0772	1.0772		
C(2)H	1.0801	1.0801		
CC(1)Br	123.16	123.16		
CC(2)F	122.92	122.92		
CC(1)H	120.01	120.01		
CC(2)H	123.34	123.34		
A	15 244.5	15 292.2		

B	2 492.3	2 486.6		
C	2 142.1	2 138.8		
χ_{aa} (^{79}Br)	275.63	281.94		278.044(9)
χ_{bb}	-10.21	-13.46		-9.364
χ_{cc}	-265.42	-268.47		-268.68(1)
$\lvert\chi_{ab}\rvert$	431.68	432.64		431.50(3)
RMS	2.39 (1.29 %)	3.27 (1.76 %)		
χ_{xx}	-322.02	-322.92		-320.45(3)
χ_{yy}	-265.42	-268.47		-268.68(1)
χ_{zz}	587.44	591.39		589.14(3)
η	-0.0963	-0.0920		-0.08788(7)
$\varphi_{z,a}$	35.84	35.58		35.791(2)
$\varphi_{a,CBr}$	36.58	36.32		
$\varphi_{z,CBr}$	0.74	0.74		
χ_{aa} (^{81}Br)	231.03	236.29		233.04(1)
χ_{bb}	-9.27	-11.98		-8.62
χ_{cc}	-221.76	-224.30		-224.42(1)
$\lvert\chi_{ab}\rvert$	360.41	361.20		360.27(4)
RMS	1.96 (1.26 %)	2.70 (1.74 %)		

[a] Ref. [11]. Back to Top

Table 11. *trans*-1-Bromo-2-Fluoroethylene, t-CHF=CHBr. Structure parameters (Å and degrees), rotational constants (MHz), and Br nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	$\sim r_e$		expt. [a]
C=C	1.3280	1.3243		
C(1)Br	1.8658	1.8745		
C(2)F	1.3424	1.3363		
C(1)H	1.0781	1.0781		
C(2)H	1.0794	1.0794		
CC(1)Br	120.48	120.48		
CC(2)F	120.50	120.50		
CC(1)H	122.74	122.74		
CC(2)H	125.78	125.78		
A	52 390.8	52 478.4		
B	1 671.1	1 669.0		
C	1 619.4	1 617.6		
χ_{aa} (^{79}Br)	512.75	516.44		514.499(12)
χ_{bb}	-228.72	-229.73		-227.489
χ_{cc}	-284.03	-286.70		-287.01(18)
$\lvert\chi_{ab}\rvert$	247.97	248.81		265.9(75)
RMS	2.12 (0.62 %)	1.72 (0.50 %)		

χ_{xx}	-304.00	-305.09		-313.3(37)
χ_{yy}	-284.03	-286.70		-287.01(18)
χ_{zz}	588.03	591.79		600.3(37)
η	-0.0340	-0.0311		-0.0880(1)
$\varphi_{z,a}$	16.89	16.84		17.9(3)
$\varphi_{a,CBr}$	17.21	17.14		
$\varphi_{z,CBr}$	0.32	0.29		
χ_{aa} (^{81}Br)	428.48	431.56		429.897(9)
χ_{bb}	-191.18	-192.03		-190.137
χ_{cc}	-237.30	-239.53		-239.76(18)
$\lvert\chi_{ab}\rvert$	207.03	207.74		223.7(71)
RMS	1.75 (0.61 %)	1.46 (0.51 %)		

[a] Ref. [11]. Back to Top

Table 12. *cis*-1,2-Dichloroethylene, c-CHCl=CHCl. Structure parameters (Å and degrees), rotational constants (MHz), and ^{35}Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	$\sim r_e$	r_s [a]	expt. [b]
C=C	1.3339	1.3301	1.319	
CCl	1.7126	1.7094	1.717	
CH	1.0792	1.0792	1.100	

CCCl	124.19	124.19	124.2	
CCH	120.43	120.43	123.2	
A	11 581.5	11 621.5		
B	2535.7	2 547.4		
C	2080.2	2089.4		
χ_{aa} (^{35}Cl)	4.84	4.89	4.08	4.51(6)
χ_{bb}	-35.52	-35.42	-34.80	-35.87(3)
χ_{cc}	30.68	30.53	30.72	31.36
$\lvert\chi_{ab}\rvert$	53.66	53.50	54.08	
RMS	0.48 (2.0 %)	0.59 (2.4 %)	0.76 (3.2 %)	
χ_{xx}	41.99	41.91	42.11	
χ_{yy}	30.68	30.53	30.72	
χ_{zz}	-72.67	-72.44	-72.83	
η	-0.156	-0.157	-0.156	
$\varphi_{z,a}$	55.31	55.32	54.88	
$\varphi_{a,CCl}$	55.81	55.81	55.81	
$\varphi_{z,CCl}$	0.50	0.49	0.93	

[a] Ref. [16]. [b] Ref. [16,17]. Back to Top

Table 13. 1,1-Dichloroethylene, $CH_2=CCl_2$. Structure parameters (Å and degrees), rotational constants (MHz), and ^{35}Cl nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e	r_e [a]	expt. [b]
C=C	1.3314	1.3278	1.324(5)	
CCl	1.7219	1.7187	1.721(3)	
CH	1.0783	1.0783	1.079(12)	
ClCCl	114.46	114.46	114.0(3)	
HCH	120.29	120.29	120.5(8)	
A	7482.3	7516.1		
B	3406.1	3418.8		
C	2340.6	2349.9		
χ_{aa} (^{35}Cl)	-42.83	-42.68	-42.12	-42.44147(67)
χ_{bb}	8.70	8.70	8.09	7.86221(81)
χ_{cc}	34.14	33.98	34.03	34.57925(80)
$\lvert\chi_{ab}\rvert$	52.26	52.12	52.50	52.0933(85)
RMS	0.59 (2.1 %)	0.61 (2.2 %)	0.39 (1.4 %)	
χ_{xx}	41.20	41.12	41.18	40.5578(77)
χ_{yy}	34.14	33.98	34.03	34.57925(80)
χ_{zz}	-75.33	-75.10	-75.21	-75.1371(77)

η	-0.094	-0.095	-0.095	-0.07957(10)
$\varphi_{z,a}$	31.89	31.88	32.2	32.114(2)
$\varphi_{a,CCl}$	32.77	32.77	33.0	
$\varphi_{z,CCl}$	0.89	0.89	0.8	

[a] Ref. [18]. [b] Ref. [19]. Back to Top

Table 14(a). Trichloroethylene, CHCl(1)=CCl_2. Structure parameters (Å and degrees), rotational constants (MHz), and ^{35}Cl(1) nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in that same column.

Parameter	r_{opt}	~ r_e	r_o [a]	expt. [b]
C=C	1.3387	1.3348	[1.337]	
CCl(1)	1.7092	1.7060	1.714(3)	
CH	1.0784	1.0784	[1.08]	
CCl_c [b]	1.7077	1.7045	1.712(4)	
CCl_t	1.7199	1.7167	1.720(5)	
CCCl(1)	123.14	123.14	122.5(8)	
CCH	120.53	120.53	[120.6]	
$CCCl_t$	120.08	120.08	120.1(4)	
Cl_tCCl_c	116.00	116.00	115.5	
A	3939.6	3955.5		
B	1532.5	1539.1		
C	1103.3	1108.0		

χ_{aa} (^{35}Cl(1))	-62.61	-62.41	-62.20	-62.5626(61)
χ_{bb}	30.60	30.56	29.85	29.9647(50)
χ_{cc}	32.00	31.85	32.34	32.5957(50)
$\lvert\chi_{ab}\rvert$	35.06	34.96	36.19	32.12(15)
RMS	0.50 (1.2 %)	0.56 (1.3 %)	0.26 (0.6 %)	
χ_{xx}	42.32	42.24	42.37	41.784(92)
χ_{yy}	32.00	31.85	32.34	32.5979(50)
χ_{zz}	-74.32	-74.09	-74.72	-74.382(93)
η	-0.139	-0.140	-0.134	-0.1235(13)
$\varphi_{z,a}$	18.48	18.47	19.09	18.60(6)
$\varphi_{a,CCl}$	19.22	19.19	19.62	
$\varphi_{z,CCl}$	0.74	0.72	0.53	

[a] Ref. [20]. Values in brackets are assumed. Cl_c and Cl_t are with respect to Cl(1).
[b] Ref. [19].

Table 14(b). Trichloroethylene, CHCl(1)=CCl_2. $^{35}Cl_c$ nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the indicated molecular structure.

Parameter	r_{opt}	~ r_e	r_o [a]	expt. [b]
χ_{aa} ($^{35}Cl_c$)	42.45	42.37	42.81	41.9247(25)
χ_{bb}	-75.89	-75.63	-76.39	-75.9033(22)
χ_{cc}	33.44	33.26	33.58	33.9786(22)

$\lvert\chi_{ab}\rvert$	7.76	7.78	6.86	7.06(14)
RMS	0.43 (0.9 %)	0.51 (1.0 %)	0.63 (1.2 %)	
χ_{xx}	42.95	42.88	43.20	42.346(17)
χ_{yy}	33.44	33.26	33.58	33.9786(22)
χ_{zz}	-76.39	-76.14	-76.78	-76.325(17)
η	-0.124	-0.126	-0.125	-0.1096(23)
$\varphi_{z,a}$	93.73	93.75	86.71	86.58(7)
$\varphi_{a,CCl}$	93.72	93.75	86.52	
$\varphi_{z,CCl}$	0.01	0.00	0.19	

[a] Ref. [20]. [b] Ref. [19].

Table 14(c). Trichloroethylene, CHCl(1)=CCl_2. $^{35}Cl_t$ nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the indicated molecular structure.

Parameter	r_{opt}	~ r_e	r_o [a]	expt. [b]
χ_{aa} ($^{35}Cl_t$)	-59.64	-59.48	-60.04	-59.8537(67)
χ_{bb}	23.29	23.28	23.75	23.2307(57)
χ_{cc}	36.35	36.20	36.28	36.6230(57)
$\lvert\chi_{ab}\rvert$	41.79	41.64	41.30	40.94(14)
RMS	0.20 (0.5 %)	0.32 (0.8 %)	0.38 (0.9 %)	

χ_{xx}	40.69	40.61	40.69	40.01(10)
χ_{yy}	36.35	36.20	36.28	36.6230(57)
χ_{zz}	-77.04	-76.81	-76.97	-76.63(10)
η	-0.056	-0.057	-0.057	-0.0442(13)
$\varphi_{z,a}$	22.61	22.59	22.30	22.29(5)
$\varphi_{a,CCl}$	22.27	22.24	22.02	
$\varphi_{z,CCl}$	0.34	0.34	0.28	

[a] Ref. [20]. [b] Ref. [19]. Back to Top

Discussion and Summary

Comparisons of the ~ r_e structures with the r_e structures of CH_2=CHCl, CH_2=CHBr, CH_2=CHCN, c-CHF=CHCl, and CH_2=CCl_2 respectively are made in Tables 1 - 3, 8, and 12. Agreement between the structures is quite good. Some of the larger differences are, in CH_2=CHBr, the C=CBr and C=CH angles (0.28° and 0.71° respectively); in CH_2=CHCN, the C=C bond length (0.002_8 Å); in c-CHF=CHCl, the CCl bond length (0.003_5 Å); and in CH_2=CCl_2, the ClCCl angle (0.46°).

By way of summary, the RMS differences between calculated and experimental nqcc's for ^{35}Cl, ^{79}Br, and ^{14}N are collected below in Tables 15(a) - 15(c).

In the case of ^{35}Cl, for calculation on the ~ r_e structures, the RMS differences range from 0.25 MHz in CF_2=CHCl to 0.76 MHz in CH_2=CHCl. (These should be compared with the RSD of calibration of the model for calculation of the nqcc's, namely 0.49 MHz.) In CH_2=CCl_2, the difference in the ClCCl angle of 0.46° between the ~ r_e and r_e structures has a notable effect on the calculated nqcc's; for calculation on the ~ r_e structure, RMS = 0.61 MHz, whereas for calculation on the r_e structure, RMS = 0.39 MHz. (This inaccuracy in optimization of the ClCCl angle makes suspect the results in CHCl=CCl_2.)

Curiously, the RMS differences for Cl for calculation on the r_{opt} structures are generally less than those calculated on the ~ r_e structures. We note that the r_{opt} C=C, CCl, and CF bonds are all somewhat longer than the ~ r_e bonds.

For ^{79}Br, for calculation on the ~ r_e structures, the RMS differences for CH_2=CFBr and t-CHF=CHBr are respectively 1.73 and 1.72 MHz (compare with RSD = 1.58 MHz); and in CH_2=CHBr and c-CHF=CHBr respectively 3.45 and 3.27 MHz. The RMS difference

for calculation on the r_{opt} structure is notably better only for c-CHF=CHBr, namely 2.39 MHz.

For ^{14}N, for calculation on the ~ r_e structures, the RMS differences for CH_2=CHC≡N and CH_2=CClC≡N are respectively 0.006 and 0.015 MHz (compare with RSD = 0.030 MHz). RMS differences for calculation on the r_{opt} structures are much larger, the C≡N bond length must be corrected. (Thus, for ^{35}Cl in this CH_2=CClC≡N, the excellent RMS difference of 0.14 MHz is accidental.)

In summary, for ^{35}Cl, the RMS differences are comparable to the RSD (estimated uncertainty in the model for calculation of the nqcc's). For ^{79}Br, the RMS differences are comparable to the RSD for CH_2=CFBr and t-CHF=CHBr, but about 2×RSD for CH_2=CHBr and c-CHF=CHBr. And for ^{14}N, the RMS differences are significantly less than the RSD.

Table 15(a). RMS differences (MHz) between calculated and experimental ^{35}Cl diagonal inertia axes nqcc's for calculation on the r_{opt}, ~ r_e, and experimental structures.

Molecule	r_{opt}	~ r_e	experimental structure	
CH_2=CHCl	0.74	0.76	r_e	0.73
CH_2=CClC≡N	0.14 [a]	0.30	---	
CF_2=CHCl	0.20	0.25	r_o	2.02
CH_2=CFCl	0.51	0.56	---	
c-CHF=CHCl	0.35	0.46	r_e	0.60
t-CHFCHCl	0.69	0.68	r_e	0.62
c-CHCl=CHCl	0.48	0.59	r_s	0.76
CH_2=CCl_2	0.59	0.61	r_e	0.39
CHCl(1)=CCl_2, Cl(1)	0.50	0.56	partial r_o	0.26
Cl_c	0.43	0.51		0.63
Cl_t	0.20	0.32		0.38

[a] This is an accidental good result on a structure that is not realistic because of a C≡N bond that is clearly too long (see Table 15(c)).

Table 15(b). RMS differences (MHz) between calculated and experimental ^{79}Br diagonal inertia axes nqcc's for calculation on the r_{opt}, ~ r_e, and on the semi-experimental r_e structure of vinyl bromide.

Molecule	r_{opt}	~ r_e	experimental structure	
CH_2=CHBr	3.43	3.45	semi-expt r_e	2.82
CH_2=CFBr	2.13	1.73	---	
c-CHF=CHBr	2.39	3.27	---	
t-CHF=CHBr	2.12	1.72	---	

Table 15(c). RMS differences (MHz) between calculated and experimental ^{14}N diagonal inertia axes nqcc's for calculation on the r_{opt}, ~ r_e, and on the experimental r_e structure of vinyl cyanide.

Molecule	r_{opt}	~ r_e	experimental structure	
CH_2=CHC≡N	0.096	0.006	near-r_e	0.007
CH_2=CClC≡N	0.082	0.015	---	

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