Calculation of Cl Nuclear Quadrupole Coupling Constants

on Approximate Equilibrium Molecular Structures

I. F, Cl - Methanes

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November 2006[1]

Abstract

Calculations were made of Cl nuclear quadrupole coupling constants on approximate equilibrium molecular structures of F, Cl substituted methanes derived by MP2/aug-cc-pVTZ(G03) optimization with empirically corrected bond lengths. The molecules are

Methyl Chloride, CH_3Cl	Chlorofluoromethane, CH_2FCl
Chlorodifluoromethane, CHF_2Cl	Chlorotrifluoromethane, CF_3Cl
Dichloromethane, CH_2Cl_2	Dichlorofluoromethane, $CHFCl_2$
Dichlorodifluoromethane, CF_2Cl_2	Trichloromethane (Chloroform), $CHCl_3$
Trichlorofluoromethane, $CFCl_3$	Carbon Tetrachloride, CCl_4

Excellent agreement between calculated and experimental coupling constants is obtained; which agreement validates, at least in part, the derived structures.

Introduction

The nuclear quadrupole coupling constant tensor is the spectroscopic measurement of the energy of interaction of the electric quadrupole moment of the nucleus of an atom with the gradient of the molecular electric field at the site of the nucleus.

Quantum chemistry calculation of the electric field gradient (efg) tensor permits calculation of the nuclear quadrupole coupling constant (nqcc) tensor, the latter being directly proportional to the former. Techniques for this have been developed for a number of quadrupolar nuclei [1].

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[1] Modified, November 2007. Updated experimental nqcc's for dichlorofluoromethane [21].

The accuracy of calculated nqcc's is, of course, sensitive to molecular structure. For calculation of near equilibrium structures, Demaison et al. [2 - 9] have shown in a series of publications that errors in quantum chemistry calculation of bond lengths at the MP2 level of theory are largely systematic and can be empirically corrected and that, with sufficiently large bases, accurate interatomic angles may be obtained *ab initio*.

Thus, we investigate here the efficacy of MP2/aug-cc-pVTZ(G03) optimization, with and without empirically corrected bond lengths, of the molecular structures of the following molecules for calculation of the Cl nqcc tensors.

Methyl Chloride, CH_3Cl	Chlorofluoromethane, CH_2FCl
Chlorodifluoromethane, CHF_2Cl	Chlorotrifluoromethane, CF_3Cl
Dichloromethane, CH_2Cl_2	Dichlorofluoromethane, $CHFCl_2$
Dichlorodifluoromethane, CF_2Cl_2	Trichloromethane (Chloroform), $CHCl_3$
Trichlorofluoromethane, $CFCl_3$	Carbon Tetrachloride, CCl_4

Carbon tetrachloride, which is not amenable to microwave studies, is included for completeness.

All calculations were made on a Mac G5 from Apple Inc. using the G03M quantum chemistry package of Gaussian Inc. [10]. This package contains Dunning bases that have been modified somewhat for computational efficiency. That these bases are not the originals is denoted here by the appendage G03.

Molecular Structures

The structures of these several molecules were derived as described in some detail in Ref. [1]. Briefly, the structures were optimized at the MP2/aug-cc-pVTZ(G03) level of theory, the CF and CCl optimized r_{opt} bond lengths then corrected via the following equations:

CF $\sim r_e\,(\text{Å}) = 0.97993 \times r_{opt} + 0.02084$, RSD = 0.0014 Å,

CCl $\sim r_e\,(\text{Å}) = 0.99872 \times r_{opt} - 0.00097$, RSD = 0.0022 Å.

RSD is the standard deviation of the residuals which may be taken as an estimate of the uncertainty in the corrected bond length, $\sim r_e$.

Nuclear Quadrupole Coupling Constants

The components of the nqcc tensor χ are related to those of the efg tensor q by

$$\chi_{ij} = (eQ/h)\ q_{ij}$$

where e is the fundamental electric charge, Q is the electric quadrupole moment of the nucleus, and h is Planck's constant. Subscripts ij refer to coordinate axes. Experimental nqcc's are measured in the principal axes system of the molecular inertia tensor. These axes are associated with the rotational constants A, B, and C; and are labeled a, b, and c. Principal axes of the nqcc tensor are here labeled x, y, and z.

(Note: The G03M code calculates the efg tensor in a coordinate system other than the inertia system. A fortran program used here for transformation of the efg tensor from G03M axes to a,b,c and x,y,z principal axes is available in Ref. [1].)

Calibration of the B1LYP/TZV(3df,2p) model for calculation of the chlorine nqcc's [1] yields

$$\chi_{ij}\ (^{35}\mathrm{Cl}) = (-19.185\ \mathrm{MHz/a.u.})\ q_{ij},\quad \mathrm{RSD} = 0.49\ \mathrm{MHz},$$

$$\chi_{ij}\ (^{37}\mathrm{Cl}) = (-15.120\ \mathrm{MHz/a.u.})\ q_{ij},\quad \mathrm{RSD} = 0.44\ \mathrm{MHz},$$

where q_{ij} are the calculated efg's. The numerical factors contain the constants e, Q, and h, and unit conversions. For ^{35}Cl, Q = -81.65(80) mb, and for ^{37}Cl, Q = -64.35(64) mb [11]. The RMS differences may be taken as estimates of the uncertainty in the calculated nqcc's.

Results

The results of this investigation - structure parameters and nuclear quadrupole coupling constants - are collected below in Tables 1 - 10.

In Tables 1 - 10; r_{opt}, ~ r_e, and experimental structure parameters are compared. Coupling constants calculated on each structure are compared with experimental nqcc's. RMS is the root mean square difference between calculated and experimental diagonal nqcc's (percent of average experimental nqcc). $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$ and φ (degrees) is the angle between its subscripted parameters.

Table 1. Methyl Chloride, CH_3Cl. Structure parameters (Å and degrees). Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	$\sim r_e$	r_e [a]	Expt. [b]
CH	1.0839	1.0839	1.0854	
CCl	1.7798	1.7766	1.7760	
HCH	110.53	110.53	110.35	
χ_{zz} (^{35}Cl)	-74.92	-74.79	-74.86	-74.7514(11)
χ_{zz} (^{37}Cl)	-59.04	-58.94	-59.00	-58.9166(34)

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

Table 2. Chlorofluoromethane, CH_2FCl. Structure parameters (Å and degrees). Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	$\sim r_e$	r_o [a]	Expt. [a]
CH	1.0845	1.0845	1.09	
CCl	1.7672	1.7640	1.7621	
CF	1.3657	1.3592	1.370	
ClCH	107.96	107.96	109.4	
ClCF	110.11	110.11	110.1	
HCH	112.80	112.80	110.4	

χ_{aa} (^{35}Cl)	-53.03	-52.81	-53.01	-52.570(26)
χ_{bb}	13.63	13.58	13.39	13.469(20)
χ_{cc}	39.40	39.22	39.62	39.059(18)
$\lvert\chi_{ab}\rvert$	39.96	39.81	40.71	43.7(23)
RMS	0.34 (1.0 %)	0.18 (0.5 %)	0.42 (1.2 %)	
χ_{xx}	32.33	32.22	32.72	35.20(186)
χ_{yy}	39.40	39.22	39.62	39.059(18)
χ_{zz}	-71.73	-71.44	-72.34	-74.30(187)
η	0.0986	0.0980	0.095	0.0519
$\varphi_{z,a}$	25.08	25.09	25.40	26(3)
$\varphi_{a,CCl}$	24.69	24.62	24.8	24.8
$\varphi_{z,CCl}$	0.39	0.47	0.6	
χ_{aa} (^{37}Cl)	-41.96	-41.79	-41.96	-41.566(32)
χ_{bb}	10.91	10.88	10.73	10.774(27)
χ_{cc}	31.05	30.91	31.22	30.788(27)
$\lvert\chi_{ab}\rvert$	31.34	31.23	31.94	
RMS	0.29 (1.0 %)	0.16 (0.6 %)	0.34 (1.2 %)	

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

Table 3. Chlorodifluoromethane, CHF_2Cl. Structure parameters (Å and degrees). Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	~ r_e	r_s [a]	Expt. [a,b]
CH	1.0845	1.0845	1.098	
CCl	1.7595	1.7563	1.742	
CF	1.3422	1.3361	1.346	
ClCH	109.55	109.55	110.8	
ClCF	109.65	109.65	110.5	
FCF	108.02	108.02	107.5	
χ_{aa} (^{35}Cl)	-65.62	-65.19	-65.91	-65.0239(65) [b]
χ_{bb}	35.64	35.45	35.56	35.467(14)
χ_{cc}	29.98	29.74	30.34	29.566(14)
$\lvert\chi_{ac}\rvert$	26.82	26.72	26.37	24.0(5)
RMS	0.43 (1.0 %)	0.14 (0.3 %)	0.68 (1.6 %)	
χ_{xx}	36.99	36.74	37.10	35.3(25)
χ_{yy}	35.64	35.45	35.56	35.467(14)
χ_{zz}	-72.63	-72.20	-72.66	-70.8(25)
η	-0.0186	-0.0179	0.021	0.0024(390)
$\varphi_{z,a}$	14.65	14.69	14.36	13.4(25)
$\varphi_{a,CCl}$	14.36	14.32	14.3	
$\varphi_{z,CCl}$	0.28	0.36	< 0.1	

χ_{aa} (^{37}Cl)	-51.76	-51.43	-51.99	-51.342(31) [a]
χ_{bb}	28.09	27.94	28.03	27.920
χ_{cc}	23.68	23.48	23.96	23.422
$\|\chi_{ac}\|$	21.05	20.98	20.70	
RMS	0.30 (0.9 %)	0.06 (0.2 %)	0.49 (1.4 %)	

[a] Ref. [15]. [b] Ref. [16]. Back to Top

Table 4. Trifluoromethyl Chloride, CF_3Cl. Structure parameters (Å and degrees). Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	~ r_e	r_{av} [a]	Expt. [b]
CF	1.3271	1.3213	1.3248	
CCl	1.7519	1.7486	1.7522	
FCF	108.57	108.57	108.57	
χ_{zz} (^{35}Cl)	-78.42	-77.86	-78.28	-77.902(30)
χ_{zz} (^{37}Cl)	-61.81	-61.37	-61.70	-61.496(166)

[a] Ref. [17]. [b] Ref. [18]. Back to Top

Table 5. Dichloromethane, $CH_2{}^{35}Cl_2$. Structure parameters (Å and degrees). Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	~ r_e	$r_m{}^{\rho}$ [a]	Expt. [b]
CCl	1.7674	1.7641	1.7636	
CH	1.0827	1.0827	1.0851	
ClCCl	112.21	112.21	112.25	
HCH	111.80	111.80	111.90	
χ_{aa} (^{35}Cl)	-42.32	-42.19	-42.24	-41.7418(11)
χ_{bb}	2.17	2.13	2.19	1.8004(12)
χ_{cc}	40.15	40.06	40.04	39.9414(12)
$\lvert\chi_{ab}\rvert$	51.24	51.16	51.12	50.93(23)
RMS	0.42 (1.5 %)	0.33 (1.2 %)	0.37 (1.3 %)	
χ_{xx}	35.78	35.72		35.41(21)
χ_{yy}	40.15	40.06		39.9414(12)
χ_{zz}	-75.94	-75.78		-75.35(21)
η	0.057	0.057		0.060(3)
$\varphi_{z,a}$	33.26	33.29		33.43(5)
$\varphi_{a,CCl}$	33.89	33.89		
$\varphi_{z,CCl}$	0.63	0.60		

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

The following three Tables - 6(a), 6(b), and 6(c) - are respectively $CHF^{35}Cl_2$, $CHF^{35}Cl^{37}Cl$, and $CHF^{37}Cl_2$. Structure parameters are repeated.

Table 6(a). Dichlorofluoromethane, $CHF^{35}Cl_2$. Structure parameters (Å and degrees). Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	~ r_e	r_o-like [a]	Expt. [a]
CCl	1.7605	1.7573	1.764(2)	
CF	1.3505	1.3442	1.335(5)	
CH	1.0834	1.0834	[1.09]	
HCF	109.50	109.50	[110.0]	
FCCl	109.28	109.28	109.6(2)	
ClCCl	111.33	111.33	111.0(2)	
χ_{aa} (^{35}Cl)	-41.35	-41.23	-40.97	-40.8921(19)
χ_{bb}	11.39	11.43	10.85	11.4127(30)
χ_{cc}	29.96	29.80	30.11	29.4794(30)
$\lvert\chi_{ab}\rvert$ [b]	45.28	45.06	45.57	44.63(43)
$\lvert\chi_{ac}\rvert$	26.29	26.23	25.73	26.18(96)
$\lvert\chi_{bc}\rvert$	13.89	13.85	13.83	13.63(51)
RMS	0.38 (1.4 %)	0.27 (1.0 %)	0.49 (1.8 %)	
χ_{xx}	36.75	36.63	36.74	36.19(92)
χ_{yy}	38.99	38.81	38.80	38.6(12)

χ_{zz}	-75.74	-75.44	-75.54	-74.81(91)
η	0.030	0.029	0.027	0.032(28)
$\varphi_{z,CCl}$	1.09	1.13	1.09	

[a] Ref. [21]. Values in square brackets are assumed. [b] The product $\chi_{ab}\ \chi_{ac}\ \chi_{bc}$ is negative.

Table 6(b). Dichlorofluoromethane, $CHF^{35}Cl^{37}Cl$. Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	~ r_e	r_o-like [a]	Expt. [a]
CCl	1.7605	1.7573	1.764(2)	
CF	1.3505	1.3442	1.335(5)	
CH	1.0834	1.0834	[1.09]	
HCF	109.50	109.50	[110.0]	
FCCl	109.28	109.28	109.6(2)	
ClCCl	111.33	111.33	111.0(2)	
χ_{aa} (^{35}Cl)	-39.74	-39.63	-39.36	-39.3009(67)
χ_{bb}	9.81	9.87	9.27	9.849(15)
χ_{cc}	29.93	29.76	30.08	29.452(15)
$\lvert\chi_{ab}\rvert$ [b]	46.16	45.94	46.43	
$\lvert\chi_{ac}\rvert$	26.09	26.02	25.52	
$\lvert\chi_{bc}\rvert$	14.36	14.32	14.29	
RMS	0.38 (1.4 %)	0.26 (1.0 %)	0.49 (1.9 %)	

χ_{aa} (^{37}Cl)	-33.84	-33.72	-33.56	-33.4548(78)
χ_{bb}	10.16	10.18	9.77	10.165(15)
χ_{cc}	23.68	23.54	23.79	23.290(15)
$\lvert\chi_{ab}\rvert$ [b]	34.99	34.82	35.97	
$\lvert\chi_{ac}\rvert$	20.81	20.76	18.99	
$\lvert\chi_{bc}\rvert$	10.54	10.52	10.53	
RMS	0.32 (1.4 %)	0.21 (0.9 %)	0.37 (1.7 %)	

[a] Ref. [21]. Values in square brackets are assumed. [b] The product $\chi_{ab}\ \chi_{ac}\ \chi_{bc}$ is negative.

Table 6(c). Dichlorofluoromethane, CHF^{37}Cl$_2$. Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column. RMS is the root mean square difference between calculated and experimental diagonal nqcc's (percent of average experimental nqcc).

Parameter	r_{opt}	~ r_e	r_o-like [a]	Expt. [a]
CCl	1.7605	1.7573	1.764(2)	
CF	1.3505	1.3442	1.335(5)	
CH	1.0834	1.0834	[1.09]	
HCF	109.50	109.50	[110.0]	
FCCl	109.28	109.28	109.6(2)	
ClCCl	111.33	111.33	111.0(2)	
χ_{aa} (^{37}Cl)	-32.59	-32.49	-32.29	-32.2262(20)

χ_{bb}	8.94	8.97	8.52	8.9588(33)
χ_{cc}	23.65	23.52	23.77	23.2674(33)
$\|\chi_{ab}\|$ [b]	35.72	35.55	35.95	35.36(41)
$\|\chi_{ac}\|$	20.66	20.61	20.22	19.3(12)
$\|\chi_{bc}\|$	10.92	10.89	10.87	10.51(70)
RMS	0.30 (1.4 %)	0.21 (1.0 %)	0.39 (1.8 %)	

[a] Ref. [21]. Values in square brackets are assumed. [b] The product $\chi_{ab}\ \chi_{ac}\ \chi_{bc}$ is negative. Back to Top

Table 7. Dichloromethane, $CF_2{}^{35}Cl_2$. Structure parameters (Å and degrees). Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	~ r_e	r_s [a]	Expt. [b]
CCl	1.7561	1.7528	1.744	
CF	1.3342	1.3283	1.347	
ClCCl	111.59	111.59	112.6	
FCF	107.76	107.76	106.2	
χ_{aa} (^{35}Cl)	-43.94	-43.83	-45.08	-43.688(33)
χ_{bb}	4.78	4.87	6.11	4.6905
χ_{cc}	39.16	38.96	38.98	38.9975
$\|\chi_{ab}\|$	54.57	54.21	54.09	52.7(46)
RMS	0.18 (0.6 %)	0.13 (0.4 %)	1.15 (3.9 %)	

χ_{xx}	40.18	39.95	40.35	38.5 [c]
χ_{yy}	39.16	38.96	38.98	38.9975
χ_{zz}	-79.34	-78.91	-79.32	-77.5
η	-0.013	-0.012	-0.017	-0.006
$\varphi_{z,a}$	32.97	32.91	32.34	32.67
$\varphi_{a,CCl}$	34.20	34.20	33.7	
$\varphi_{z,CCl}$	1.23	1.29	1.4	

[a] Ref. [22]. [b] Ref. [23]. [c] Calculated here from experimental data. Back to Top

In Tables 8 and 9 below, χ_{uu} is the component of the nqcc tensor along the threefold symmetry axis; χ_{vv} and χ_{ww} are the components along the v- and w- axes for the Cl atom in the uv-plane.

Table 8. Trichloromethane (Chloroform), $CH^{35}Cl_3$. Structure parameters (Å and degrees). Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	$\sim r_e$	r_e [a]	Expt. [b]
CCl	1.7630	1.7597	1.760	
CH	1.0820	1.0820	1.080	
ClCCl	110.88	110.88	110.68	
HCCl	108.02	108.02	108.23	
χ_{uu} (^{35}Cl)	29.15	29.04	28.62	28.6436(4)
χ_{vv}	-68.45	-68.27	-67.89	-67.8309(5)
χ_{ww}	39.30	39.23	39.27	39.1872(5)

$\lvert\chi_{uv}\rvert$	33.77	33.73	34.29	34.137(32)
RMS	0.47 (1.0 %)	0.34 (0.8 %)	0.06 (0.1 %)	
χ_{xx}	39.69	39.59	39.57	39.501(18)
χ_{yy}	39.30	39.23	39.27	39.1872(5)
χ_{zz}	-78.99	-78.82	-78.84	-78.688(18)
η	-0.0050	-0.0046	-0.0038	-0.0040(2)
$\varphi_{z,u}$	72.66	72.63	72.30	72.357(13)
$\varphi_{u,CCl}$	71.98	71.98	71.77	71.77(2) [c]
$\varphi_{z,CCl}$	0.68	0.65	0.53	0.59(2) [c]

[a] Ref. [2]. [b] Ref. [24]. [c] r_e structure. Back to Top

Table 9. Trichlorofluoromethane, $CF^{35}Cl_3$. Structure parameters (Å and degrees). Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	$\sim r_e$	avg. r_o [a]	Expt. [b]
CCl	1.7608	1.7576	1.757	
CF	1.3430	1.3369	1.346	
ClCCl	110.47	110.47	110.35	
FCCl	108.45	108.45		
χ_{uu} (^{35}Cl)	29.20	29.17	28.76	28.98(4)
χ_{vv}	-70.59	-70.40	-70.16	-70.28 [c]

χ_{ww}	41.39	41.22	41.40	41.30 [c]
$\|\chi_{uv}\|$	34.18	33.95	34.58	
RMS	0.23 (0.5 %)	0.14 (0.3 %)	0.15 (0.3 %)	
χ_{xx}	39.78	39.64	39.63	
χ_{yy}	41.39	41.22	41.38	
χ_{zz}	-81.18	-80.87	-81.01	
η	0.020	0.020	0.022	
$\varphi_{z,u}$	72.79	72.85	72.52	
$\varphi_{u,CCl}$	71.55	71.55	71.42	
$\varphi_{z,CCl}$	1.24	1.30	1.10	

[a] Average of two quite different r_o structures [25, 26]. See Ref. [1]. [b] Ref. [27].
[c] Calculated here from χ_{uu} and $\eta_Q = (\chi_{vv} - \chi_{ww})/\chi_{uu}$ = -3.85(20) MHz [27]. Back to Top

Table 10. Carbon Tetrachloride, CCl_4. Structure parameters (Å and degrees). Chlorine nuclear quadrupole coupling constants (MHz). Coupling constants in a given column were calculated on the molecular structure given in the same column.

Parameter	r_{opt}	~ r_e		
CCl	1.7666	1.7634		
χ_{zz} (^{35}Cl)	-83.66	-83.46		
χ_{zz} (^{37}Cl)	-65.93	-65.78		

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Discussion

Comparison of ~ r_e and r_e molecular structure parameters of CH_3Cl and $CHCl_3$ are made in Tables 1 and 8, and comparison of ~ r_e and r_m^ρ parameters of CH_2Cl_2 in Table 5. For these, the average CCl difference is 0.0003 Å while the largest difference is 0.0006 Å in CH_3Cl; the average CH difference is 0.002 Å, the largest difference, 0.0024 Å in CH_2Cl_2. For the angles, HCH and ClCCl, the average difference is 0.13°, the largest difference is 0.21° for HCCl in $CHCl_3$. The ~ r_e structures of these molecules approximate the equilibrium structures. This, along with the results of calculations of the nqcc's, leads us to believe that the ~ r_e structures of the other molecules in this series also approximate equilibrium structures.

For CH_2Cl_2, in addition to the r_m^ρ structure, two r_e structures have been reported [28, 29]. These three structures are somewhat different (See Ref. [1]). Whereas the ~ r_e structure is in better agreement with the r_m^ρ structure, nqcc's calculated on the r_e structures are in better agreement with the experimental nqcc's (See Ref. [1]). The former argues in favor of the r_m^ρ structure as the more accurate equilibrium structure, while the latter argues in favor of the r_e structures.

Excellent agreement between calculated and experimental coupling constants is obtained on the ~ r_e structures of these substituted methanes. The average RMS difference between calculated and experimental ^{35}Cl diagonal inertia axes nqcc's is 0.18 MHz; the largest differences are 0.33 and 0.34 MHz for CH_2Cl_2 and $CHCl_3$ respectively. These all lie well within the estimated uncertainty in the calculated nqcc's of 0.49 MHz.

In $CHCl_3$, it is perhaps instructive to note the differences between nqcc's calculated on the ~ r_e and r_e structures. Let us note first that the calculated values of χ_{ww}, χ_{xx}, χ_{yy}, and χ_{zz} are essentially the same for both structures, and in good agreement with the experimental values (Table 8). As the CCl bond lengths are the same in both structures, the relatively large differences between χ_{uu} and χ_{vv} calculated on ~ r_e compared with those calculated on r_e - respectively, 0.42 and 0.38 MHz - are due to the 0.21° angular difference in the two structures between CCl and the u- and v- axes.

As a final observation, we note the structural changes with increasing fluorine substitution - namely, a pronounced shortening of both CCl and CF bond lengths. Going from CH_3Cl to CH_2FCl to CHF_2Cl to CF_3Cl, CCl decreases from 1.7766 to 1.7640 to 1.7563 to 1.7486 Å. Going from CH_2FCl to CHF_2Cl to CF_3Cl, CF decreases from 1.3592 to 1.3361 to 1.3213 Å. And lastly, in CF_4, which completes this sequence, ~ r_e is 1.3154 Å.

References

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