Supplemental Material to accompany

Nuclear Quadrupole Coupling in Chlorodifluoroacetylchloride: Theory and Experiment

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Table S1. C-C Bond Lengths (Å).

r_e^{emp} = 0.95547 x r_{opt} + 0.06568, where r_{opt} = MP2/aug-cc-pVTZ opt.

Molecule	r_e / r_m^p	r_{opt}	r_e^{emp}	$\lvert r_e - r_e^{emp} \rvert$	Ref.
NC-CP	1.3759	1.3718	1.3764	0.0005	1
HCC-CN	1.3764	1.3722	1.3768	0.0004	2
NC-CN	1.3839	1.3778	1.3821	0.0018	3
CH_2=CH(CN)	1.429	1.4290	1.4310	0.002	4
CH_2=C$(CN)_2$	1.437	1.4338	1.4357	0.001	5
CH_3CN	1.457	1.4570	1.4578	0.001	6
HCC-CH_3	1.458	1.4584	1.4592	0.001	7
$CH_2(CN)_2$	1.464	1.4628	1.4634	0.001	5
CH_2=CH(-CH_3)	1.4957	1.4952	1.4943	0.0014	8
CH_3-CH_2Cl	1.5096	1.5112	1.5096	0.0000	8
CH_3-CH_2-CH_3	1.5209	1.5236	1.5214	0.0006	8
CH_3CH_3	1.522	1.5238	1.5216	0.000_4	9
			AVG [a]	0.0009	
			RMS [a]	0.0011	

[a] AVG is average absolute difference, RMS is root mean square difference.

Table S2. C-F Bond Lengths (Å).

r_e^{emp} = 0.97993 x r_{opt} + 0.02084, where r_{opt} = MP2/aug-cc-pVTZ opt.

Molecule	r_e	r_{opt}	r_e^{emp}	$\lvert r_e - r_e^{emp} \rvert$	Ref.
FCO^+	1.2014	1.2054	1.2021	0.0007	10
FCN	1.26405	1.2683	1.2637	0.0003	11
HCCF	1.2765	1.2804	1.2755	0.0010	12
FCH	1.305	1.3095	1.3041	0.001	13
$O=CF_2$	1.311	1.3161	1.3105	0.000_5	14
O=CFCl	1.3232	1.3304	1.3245	0.0013	15
CHF_3	1.3284	1.3363	1.3303	0.0019	16
c-CHF=CHCl	1.331	1.3350	1.3290	0.002	17
CH_2F_2	1.3508	1.3591	1.3527	0.0019	18
CH_3F	1.382	1.3879	1.3809	0.001	19
			AVG [a]	0.0012	
			RMS [a]	0.0013	

[a] AVG is average absolute difference, RMS is root mean square difference.

Table S3. C-Cl Bond Lengths (Å).

r_e^{emp} = 0.99872 x r_{opt} – 0.00097, where r_{opt} = MP2/aug-cc-pVTZ opt.

Molecule	r_e / r_m^{ρ}	r_{opt}	r_e^{emp}	$\lvert r_e - r_e^{emp} \rvert$	Ref.
ClCN	1.6290	1.6314	1.6283	0.0007	20
HCCCl	1.6353	1.6386	1.6355	0.0002	21
S=CFCl	1.7133	1.7193	1.7161	0.0028	22
c-CHF=CHCl	1.715	1.7147	1.7115	0.003	17
O=CFCl	1.7209	1.7247	1.7215	0.0006	15
$CH_2=CCl_2$	1.721	1.7219	1.7187	0.002	23
$S=CCl_2$	1.722	1.7300	1.7268	0.005	24
$CH_2=CHCl$	1.7263	1.7283	1.7251	0.0012	25
$O=CCl_2$	1.7381	1.7425	1.7393	0.0012	26
$CHCl_3$	1.760	1.7630	1.7597	0.000_3	27
CH_2Cl_2	1.7636	1.7674	1.7641	0.0005	28

O=CHCl	1.7650	1.7678	1.7646	0.0004	29
CH_3Cl	1.7760	1.7798	1.7766	0.0006	30
CH_3-CH_2Cl	1.7888	1.7916	1.7883	0.0005	8
			AVG [a]	0.0014	
			RMS [a]	0.0019	

[a] AVG is average absolute difference, RMS is root mean square difference.

Table S4. C=O Bond Lengths (Å).

r_e^{emp} = 1.06234 x r_{opt} – 0.08240, where r_{opt} = MP2/aug-cc-pVTZ opt.

Molecule	r_e	r_{opt}	r_e^{emp}	$\lvert r_e - r_e^{emp} \rvert$	Ref.
HCO+	1.105581	1.1193	1.1067	0.0011	31
CO	1.128323	1.1389	1.1275	0.0008	32
OCS	1.1572	1.1688	1.1592	0.0020	33
CO_2	1.1601	1.1702	1.1608	0.0007	34
$H_2C=C=O$	1.161	1.1681	1.1585	0.002_5	35
O=CFCl	1.1730	1.1813	1.1725	0.0005	15
$O=CF_2$	1.170	1.1778	1.1689	0.001	14
$O=CCl_2$	1.1756	1.1850	1.1765	0.0009	26
O=CHCl	1.1820	1.1900	1.1818	0.0002	29
HC(=O)OH	1.201	1.2053	1.1980	0.003	36
$O=CH_2$	1.2031	1.2131	1.2064	0.0033	37
			AVG [a]	0.0015	
			RMS [a]	0.0018	

[a] AVG is average absolute difference, RMS is root mean square difference.

Table S5. ^{35}Cl Nuclear Quadrupole Coupling Constants, χ_{ij} (MHz). χ_{ij} = (-19.185 MHz/a.u.) q_{ij}, where q_{ij} (a.u.) = B1LYP/TZV(3df,2p). Where two references are given, the first is for the molecular structure, the second is for the experimental χ_{ij}.

Molecule	i j	Expt. X_{ij}	Calc. q_{ij}	Calc. X_{ij}	| E- C |	Ref.
HCl	aa	-67.60916(30)	3.5466	-68.04	0.43	38
FCl	aa	-145.87182(3)	7.6328	-146.43	0.56	39, 40
Cl_2	aa	-111.7902(38)	5.8628	-112.48	0.69	32, 41
BrCl	aa	-102.378(1)	5.3866	-103.34	0.96	42, 43
BCl	aa	-16.737(11)	0.8669	-16.63	0.11	44, 45
ClCN	aa	-83.27519(40)	4.3144	-82.77	0.50	20, 46
ClCP	aa	-71.75(18)	3.7253	-71.47	0.28	47, 48
ClBS	aa	-42.54(1)	2.2168	-42.53	0.01	49, 50
HOCl	aa	-121.958(8)	6.3757	-122.32	0.36	51, 52
	bb	59.519(10)	-3.1187	59.83	0.31	
	cc	62.439(10)	-3.2569	62.48	0.04	
Cl_2O	aa	-71.45	3.7507	-71.96	0.51	53, 54
	bb	6.86	-0.3661	7.02	0.16	
	cc	64.59	-3.3846	64.93	0.34	
ClO_2	aa	-52.086(102)	2.7368	-52.50	0.42	55, 56
	bb	2.808(66)	-0.1398	2.68	0.12	
	cc	49.278(66)	-2.5969	49.82	0.54	
HCCCl	aa	-79.7358(19)	4.1490	-79.60	0.14	21, 57
O=CHCl	aa	-51.10(4)	2.6498	-50.84	0.26	29
	bb	30.04	-1.6253	31.18	1.14	
	cc	21.06(6)	-1.0245	19.65	1.40	
O=CFCl	aa	-73.0277(8)	3.7632	-72.20	0.83	58
	bb	44.7074	-2.3602	45.28	0.57	
	cc	28.3204	-1.4030	26.92	1.40	
$O=C^{35}Cl^{37}Cl$	aa	-36.009(36)	1.8555	-35.60	0.41	26, 59
	bb	8.705(39)	-0.4940	9.48	0.77	
	cc	27.304(16)	-1.3614	26.12	1.18	
ClF_3	aa	-82.0281(90)	4.2434	-81.41	0.62	60
	bb	-65.3590(101)	3.4052	-65.33	0.03	
	cc	147.3871(86)	-7.6486	146.74	0.65	
$FClO_2$	aa	-34.90065(43)	1.8305	-35.12	0.22	61, 62
	bb	-17.10863(53)	0.9124	-17.50	0.40	

	cc	52.00928(39)	-2.7430	52.62	0.61	
CH_3Cl	aa	-74.7514(11)	3.9019	-74.86	0.11	63, 64
CH_2Cl_2	aa	-41.7418(11)	2.1828	-41.88	0.13	65, 66
	bb	1.8004(12)	-0.0944	1.81	0.01	
	cc	39.9414(12)	-2.0883	40.06	0.12	
$CHCl_3$	aa	-67.8309(5)	3.5387	-67.89	0.06	27, 67
	bb	39.1872(5)	-2.0468	39.27	0.08	
	cc	28.6436(4)	-1.4920	28.62	0.02	
SiH_3Cl	aa	-39.689(5)	2.0864	-40.03	0.34	68
SiH_2Cl_2	aa	-20.4150	1.0784	-20.69	0.27	69, 70
	bb	-0.3095(19)	0.0135	-0.26	0.05	
	cc	20.7245(19)	-1.0920	20.95	0.22	
GeH_3Cl	aa	-46.9500(26)	2.4405	-46.82	0.13	71, 72
c-CHF=CHCl	aa	-22.719(14)	1.2027	-23.07	0.36	17, 73
	bb	-10.600(13)	0.5084	-9.75	0.84	
	cc	33.319(17)	-1.7112	32.83	0.49	
$CH_2=CCl_2$	aa	-42.48(10)	2.1953	-42.18	0.36	23, 74
	bb	8.12(18)	-0.4215	8.09	0.03	
	cc	34.36(15)	-1.7738	34.03	0.33	
CH_3CH_2Cl	aa	-49.29(9)	2.5902	-49.69	0.40	8, 75
	bb	13.65	-0.7239	13.89	0.24	
	cc	35.64	-1.8663	35.80	0.16	
				AVG [a]	0.33	
				RMS [a]	0.46	

[a] AVG is average absolute difference, RMS is root mean square difference.

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