Semi-Experimental Equilibrium Structure Determinations by Employing B3LYP/SNSD Anharmonic Force Fields: Validation and Application to Semirigid Organic Molecules Supporting Informations

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Since asymmetric tops have only non-degenerate vibrational normal modes (hereafter indicated with m and n), the explicit form of $\Delta B^{\beta}_{\text{vib}}$ is,

$$\Delta B^{\beta}_{\text{vib}} = -\frac{1}{2}\sum_{m} \alpha^{\beta}_{m} \tag{1}$$

where the vibration-rotation interaction constants α^{β}_{m} are given by,

$$\begin{aligned} \alpha^{\beta}_{m} = -\frac{2(B^{\beta}_{e})^{2}}{\omega_m}\Bigg\{ \sum_{\gamma=x,y,z} \frac{3(a^{\beta\gamma}_{m})^{2}}{4I^{\beta}_{e}} + \sum_{n\neq m} \frac{(\zeta^{\beta}_{mn})^{2}}{2\omega_n}\left[\frac{(\omega_m-\omega_n)^2}{\omega_m+\omega_n} + \frac{(\omega_m+\omega_n)^2}{\omega_m-\omega_n}\right] \\ + \pi\left(\frac{c}{h}\right)^{1/2}\sum_{n}\phi_{mmn}\frac{a^{\beta\beta}_{n}\omega_m}{\omega_n^{3/2}}\Bigg\} \end{aligned} \tag{2}$$

In the above equation, $a^{\beta\gamma}_{m}$ are the inertial derivatives, $\zeta^{\beta}_{mn} = -\zeta^{\beta}_{nm}$ the Coriolis coupling constants, ω_m the harmonic frequencies and ϕ_{mmn} the cubic force constants in dimensionless normal coordinates. The first contribution in the right-hand side is then a corrective term related to the moment of inertia, the second is due to Coriolis interactions, and the last one is an anharmonic contribution. The Coriolis term has been explicitly written in its expanded form to point out that all possible Coriolis resonance terms appearing in the left-hand side of eq. 2 cancel once the summation of eq. 1 is performed, because the contribution of the terms having the difference $\omega_m - \omega_n$ as denominator in α^{β}_{m} and the same contribution in α^{β}_{n} are equal but in opposite sign.[1,2]

Symmetric tops have non-degenerate as well as doubly-degenerate (hereafter indicated with s and t) normal modes. For these systems,

$$\Delta B^{\beta}_{\text{vib}} = -\frac{1}{2}\sum_{m} \alpha^{\beta}_{m} - \sum_{s} \alpha^{\beta}_{s} \tag{3}$$

Superimposing the principal symmetry axis of the molecule with z, α_m^z and α_n^z are given by,

$$\alpha_m^z = -\frac{2(B_e^z)^2}{\omega_m}\left\{\frac{3(a_m^{zz})^2}{4I_e^z} + \sum_n \frac{(\zeta_{mn}^z)^2}{2\omega_n}\left[\frac{(\omega_m-\omega_n)^2}{\omega_m+\omega_n} + \frac{(\omega_m+\omega_n)^2}{\omega_m-\omega_n}\right] \right.$$
$$\left. + \pi\left(\frac{c}{h}\right)^{1/2}\sum_n \phi_{mmn}\frac{a_n^{zz}\omega_m}{\omega_n^{3/2}}\right\} \tag{4}$$
$$\alpha_s^z = -\frac{2(B_e^z)^2}{\omega_s}\left\{\frac{3(a_{s_1}^{xz})^2}{4I_e^x} + \sum_t \frac{(\zeta_{s_1t_2}^z)^2}{2\omega_t}\left[\frac{(\omega_s-\omega_t)^2}{\omega_s+\omega_t} + \frac{(\omega_s+\omega_t)^2}{\omega_m-\omega_n}\right] \right.$$
$$\left. + \pi\left(\frac{c}{h}\right)^{1/2}\sum_m \phi_{ms_1s_1}\frac{a_m^{zz}\omega_s}{\omega_m^{3/2}}\right\} \tag{5}$$

while $\alpha_m^x = \alpha_m^y$ and $\alpha_s^x = \alpha_s^y$ by,

$$\alpha_m^x = -\frac{2(B_e^x)^2}{\omega_m}\left\{\frac{3\left[(a_m^{xx})^2 + (a_m^{xy})^2\right]}{4I_e^x} + \sum_s \frac{\left[(\zeta_{ms_1}^y)^2 + (\zeta_{ms_1}^x)^2\right]}{2\omega_s}\left[\frac{(\omega_m-\omega_s)^2}{\omega_m+\omega_s} + \frac{(\omega_m+\omega_s)^2}{\omega_m-\omega_n}\right] \right.$$
$$\left. + \pi\left(\frac{c}{h}\right)^{1/2}\sum_n \phi_{mmn}\frac{a_n^{xx}\omega_m}{\omega_n^{3/2}}\right\} \tag{6}$$
$$\alpha_s^x = -\frac{2(B_e^x)^2}{\omega_s}\left\{\frac{3(a_{s_1}^{xz})^2}{8I_e^z} + \frac{3(a_{s_1}^{xx})^2}{4I_e^x} + \frac{1}{2}\sum_m \frac{\left[(\zeta_{ms_1}^y)^2 + (\zeta_{ms_1}^x)^2\right]}{2\omega_m}\left[\frac{(\omega_s-\omega_m)^2}{\omega_s+\omega_m} + \frac{(\omega_s+\omega_m)^2}{\omega_s-\omega_m}\right] \right.$$
$$+ \sum_t \frac{\left[(\zeta_{s_1t_1}^y)^2 + (\zeta_{s_1t_1}^x)^2\right]}{2\omega_t}\left[\frac{(\omega_s-\omega_t)^2}{\omega_s+\omega_t} + \frac{(\omega_s+\omega_t)^2}{\omega_s-\omega_t}\right]$$
$$\left. + \pi\left(\frac{c}{h}\right)^{1/2}\sum_m \phi_{ms_1s_1}\frac{a_m^{xx}\omega_s}{\omega_m^{3/2}}\right\} \tag{7}$$

where the symmetry relations between the molecular parameters $a_i^{\beta\gamma}$ and ζ_{ij}^{β} (with i and j non- or doubly-degenerate) are used to derive the previous expressions (see refs. 3,4).

For linear molecules, only α_m^x and α_s^x (eqs. 6 and 7) do not vanish in equation 3.

In the following, $(B_0^\beta)^{\text{EXP}}$, $\Delta B_{\text{vib}}^\beta$ and $\Delta B_{\text{el}}^\beta$ results for all the molecules studied in the paper are shown in Tables 1-5. The comparison between the r_0 and r_e^{SE} geometries estimated using $\Delta B_{\text{vib}}^\beta$ from CCSD(T), MP2, B3LYP/SNSD and B3LYP/AVTZ cubic force fields is reported in Table 6. Finally, the statistical distributions of the deviations and the plots of the CCSD(T) r_e^{SE} versus the MP2 and B3LYP ones are shown in Figures 1 and 2, respectively.

Table 1: $(B_0^\beta)^{\mathrm{EXP}}$, $\Delta B^\beta_{\mathrm{vib}}$ and $\Delta B^\beta_{\mathrm{el}}$ ($g^{\beta\beta}$ at the B3LYP/AVTZ level) for all molecules belonging to the GeomCC set. All data are in MHz.

		$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B^\beta_{\mathrm{vib}}$				$\Delta B^\beta_{\mathrm{el}}$
			CCSD(T)	MP2	B3LYP/SNSD	B3LYP/AVTZ	
HCN							
parent	B	44315.974970(156)[a]	192.820[×,x]	216.204[×]	183.749	187.075	−2.452
$H^{13}CN$	B	43170.126736(39)[b]	187.917	210.504	178.732	181.850	−2.380
$HC^{15}N$	B	43027.647798(36)[c]	185.125	207.595	176.315	179.470	−2.259
$H^{13}C^{15}N$	B	41863.94519(33)[d]	180.139	201.817	171.238	174.188	−2.187
DCN	B	36207.462159(126)[e]	122.553	138.607	119.771	122.876	−1.737
$D^{13}CN$	B	35587.645800(182)[e]	121.174	136.828	118.125	121.102	−1.709
$DC^{15}N$	B	35169.798344(30)[c]	117.484	132.928	114.758	117.721	−1.601
$D^{13}C^{15}N$	B	34531.299725(184)[e]	116.015	131.053	113.032	115.864	−1.572
HNC							
parent	B	45331.9864(24)[f]	157.108[×,x]	163.633[×]	149.462	149.314	−2.780
$HN^{13}C$	B	43545.6202(363)[f]	150.145	155.972	142.684	142.714	−2.501
$H^{15}NC$	B	44433.0475(429)[f]	159.403	165.016	151.442	151.775	−2.718
$H^{15}N^{13}C$	B	42629.642(40)[g]	152.170	157.114	144.417	144.910	−2.442
DNC	B	38152.9988(16)[h]	53.825	66.396	53.809	48.978	−2.064
$DN^{13}C$	B	36684.003(25)[i]	51.211	62.954	51.074	46.562	−1.862
$D^{15}NC$	B	37643.521(30)[i]	58.330	70.074	57.885	53.533	−2.039
$D^{15}N^{13}C$	B	36155.521(25)[i]	55.511	66.442	54.961	50.915	−1.835
$HNCCN^+$							
parent	B	4438.01064(45)[j]	−2.638[≍,y]	−0.199[×]	2.622	−1.532	0.005
$DNCCN^+$	B	4158.32201(49)[k]	−3.668	−1.472	1.048	−2.657	0.002
$H^{15}NCCN^+$	B	4320.49155(30)[j]	−2.461	−0.095	2.639	−1.524	0.003
$HN^{13}CCN^+$	B	4422.4404(13)[j]	−2.623	−0.203	2.578	−1.524	0.005
$HNC^{13}CN^+$	B	4417.16553(67)[j]	−2.339	0.007	2.745	−1.290	0.006
$HNCC^{15}N^+$	B	4305.02207(61)[j]	−2.688	−0.308	2.444	−1.600	0.007
HCCCCH							
parent	B	4389.3019(39)[l]	1.838[×,l]	2.098[÷,l]	8.072	2.314	0.009
DCCCCD	B	3809.2433(66)[l]	−0.237	−0.207	5.023	0.416	0.007
$H^{13}C^{13}C^{13}C^{13}CH$	B	4098.8959(36)[l]	1.890	2.145	7.502	2.281	0.008
$H^{13}C^{13}CCCH$	B	4243.7325(111)[l]	1.871	2.130	7.786	2.297	0.008
$H^{13}CCCCH$	B	4258.5465(105)[l]	1.829	2.112	7.843	2.282	0.008
$HC^{13}CCCH$	B	4371.6291(45)[l]	1.879	2.113	8.009	2.335	0.009
$H^{13}C^{13}C^{13}CCH$	B	4224.7392(99)[l]	1.905	2.138	7.722	2.317	0.008
$H^{13}C^{13}CC^{13}CH$	B	4115.0556(42)[l]	1.855	2.133	7.559	2.265	0.008
HCCCCD	B	4084.45342(7)[l]	0.688	0.815	6.407	1.265	0.008
$H^{13}CCCCD$	B	3964.11797(17)[l]	0.718	0.871	6.237	1.272	0.007
$HC^{13}CCCD$	B	4066.49893(16)[l]	0.725	0.830	6.352	1.284	0.008
$HCC^{13}CCD$	B	4071.64202(16)[l]	0.743	0.851	6.372	1.300	0.008
$HCCC^{13}CD$	B	3977.69016(15)[l]	0.718	0.870	6.260	1.274	0.007
HCO^+							
parent	B	44594.42895(27)[m]	238.681[×]	246.416[×]	239.497	235.471	−0.389
DCO^+	B	36019.76763(41)[n]	170.258	174.500	172.964	171.349	−0.378
$H^{13}CO^+$	B	43377.3019(17)[n]	229.246	236.816	229.757	225.726	−0.432
$HC^{18}O^+$	B	42581.26[o]	223.327	230.663	224.024	220.150	−0.239
HCCH							
parent	B	35274.9651(3)[p]	170.835[+,w]	179.738[÷]	150.563	163.194	0.947
$HC^{13}CH$	B	34429.9877(3)[q]	167.885	176.694	147.907	159.850	0.902
$H^{13}C^{13}CH$	B	33564.00473(300)[r]	164.781	173.488	145.123	156.376	0.858
DCCH	B	29725.24501(82)[s]	112.445	117.909	99.440	110.793	0.671
DCCD	B	25418.629(6)[t]	73.839	77.090	65.415	75.790	0.489
$D^{13}CCH$	B	29237.8864(27)[s]	111.925	117.399	98.966	109.827	0.649
$DC^{13}CH$	B	28995.7361(19)[s]	110.395	115.811	97.568	108.355	0.639
$D^{13}C^{13}CH$	B	28490.20067(1799)[u]	109.769	115.191	97.003	107.295	0.617
$D^{13}C^{13}CD$	B	24519.19191(1499)[v]	72.944	76.228	64.589	74.124	0.456
$D^{13}CCD$	B	24976.406(24)[w]	73.424	76.692	65.031	74.989	0.473

Graphical symbols denote: ÷ VTZ; ≍ VQZ; × CVQZ; + wCVQZ.
References: a) 5; b) 6; c) 7; d) 8; e) 9; f) 10; g) 11; h) 12; i) 11; j) 13; k) 14; l) 15; m) 16; n) 17; o) 18; p) 19; q) 20; r) 21; s) 22; t) 23; u) 24 v) 25; w) 26; x) 27; y) 28;

— Table 1 continued —

		$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B_{\mathrm{vib}}^\beta$				$\Delta B_{\mathrm{el}}^\beta$
			CCSD(T)	MP2	B3LYP/SNSD	B3LYP/AVTZ	
$\mathbf{SH_3^+}$							
parent	B	146737.6663(13)[a]	1705.760[+,s]	1644.107[×]	1585.370	1606.091	26.925
	C	126760.0(11)[b]	1597.050	1456.171	1653.279	1660.595	20.041
SH_2D^+	A	142553.4460(43)[c]	1386.990	1308.338	1312.657	1326.901	25.242
	B	98027.4348(78)[c]	1026.240	982.570	957.017	966.338	11.846
	C	90373.8729(55)[c]	1017.870	954.449	1035.093	1042.623	10.097
SHD_2^+	A	103327.92014(847)[a]	879.190	846.005	807.902	820.472	13.012
	B	89077.3239(106)[a]	774.280	692.884	741.288	744.089	9.785
	C	70472.74887(659)[a]	748.580	732.676	765.014	772.067	6.088
SD_3^+	B	76217.9527(37)[a]	635.550	611.564	595.455	602.604	6.993
	C	63616.(779)[d]	571.460	520.251	588.048	591.301	5.018
$^{34}SH_3^+$	B	146424.6233(13)[a]	1700.060	1638.759	1579.669	1600.326	26.868
	C	–	1596.020	1455.365	1652.076	1659.393	20.041
$^{34}SD_3^+$	B	75931.5594(40)[a]	632.050	608.322	592.210	599.342	6.963
	C	–	570.740	519.687	586.759	590.005	5.018
$\mathbf{NH_3}$							
parent	B	298192.92[e]	2245.988[×,t]	1837.590[×]	1946.876	1677.154	90.610
	C	186695.86[e]	3615.703	3593.360	3767.176	3756.216	50.414
ND_3	B	154175.90998(2650)[f]	940.608	804.558	831.942	760.239	23.459
	C	93672.22[f]	1323.056	1312.545	1372.659	1374.489	12.621
NT_3	B	105565.373(34)[g]	571.616	500.678	530.835	483.361	10.732
	C	–	742.993	736.050	774.138	772.083	5.628
$^{15}NH_3$	B	297464.913(24)[h]	2213.376	1803.049	1910.987	1640.133	90.361
	C	186707.64(75)[h]	3606.957	3585.147	3758.118	3747.158	50.414
$^{15}ND_3$	B	153603.1429(4047)[i]	923.832	786.813	850.847	740.773	23.368
	C	–	1317.613	1307.424	1378.339	1368.805	12.621
$\mathbf{H_2O}$							
parent	A	835839.10(13)[j]	−11637.727[×,t]	−12151.736[×]	−13248.461	−13659.537	287.304
	B	435347.353(27)[j]	2393.157	2181.981	2954.940	2586.336	168.147
	C	278139.826(57)[j]	7000.211	6903.581	6920.100	6872.206	97.723
D_2O	A	462278.942(78)[k]	−4650.028	−4847.012	−5309.003	−5485.655	79.876
	B	218038.287(39)[k]	884.781	804.510	1088.739	958.245	42.098
	C	145258.00(16)[k]	2626.202	2589.701	2603.646	2580.867	25.320
HDO	A	701931.7(1.0)[l]	−6671.371	−7083.608	−7600.158	−7991.621	228.288
	B	272911.84(51)[l]	958.371	861.393	1162.723	1017.395	60.678
	C	192055.458(78)[l]	3938.679	3887.864	3898.842	3865.562	45.326
T_2O	A	338810.896[m]	−2826.385	−2941.732	−3235.558	−3350.322	39.132
	B	145665.397[m]	505.850	459.235	619.826	548.599	18.771
	C	100259.401[m]	1503.280	1481.978	1494.363	1478.926	11.627
HTO	A	677844.8(25.5)[n]	−4923.930	−5330.406	−5649.833	−6026.424	227.349
	B	198198.2(6.6)[n]	623.286	570.997	722.405	638.158	30.065
	C	150466.4(6.0)[n]	2672.542	2641.495	2647.479	2620.944	27.190
DTO	A	410174.145(78)[o]	−3524.376	−3689.230	−4027.234	−4190.619	64.542
	B	172101.952(45)[o]	592.986	537.112	725.312	640.603	25.428
	C	119127.850(45)[o]	1939.611	1912.995	1925.604	1906.691	16.703
$H_2^{17}O$	A	830279.4(12.6)[p]	−11549.089	−12060.527	−13145.687	−13551.744	285.448
	B	435349.0(6.3)[p]	2387.361	2177.142	2948.788	2579.601	168.147
	C	277506.8(6.3)[p]	6973.435	6877.163	6892.311	6845.426	97.498
$H_2^{18}O$	A	825365.8(10.2)[p]	−11470.657	−11979.814	−13054.774	−13456.411	283.767
	B	435353.5(5.1)[p]	2382.285	2172.917	2942.262	2573.689	168.147
	C	276948.9(5.1)[p]	6949.542	6853.585	6867.525	6821.534	97.312
$D_2^{18}O$	A	451891.5230(16)[q]	−4531.672	−4725.356	−5170.987	−5340.430	78.111
	B	218045.22743(78)[q]	875.925	796.853	1078.706	948.226	42.098
	C	144201.63828(51)[q]	2594.947	2558.982	2570.991	2549.495	25.142
$HD^{18}O$	A	692844.04[e]	−6499.788	−6908.274	−7400.971	−7786.627	226.281
	B	271457.501[e]	925.627	830.414	1123.999	981.595	60.013
	C	190812.982[e]	3891.397	3841.295	3850.145	3818.327	44.948
$D_2^{17}O$	A	456768.140(13)[r]	−4587.233	−4782.470	−5325.755	−5408.569	78.951
	B	218041.937(11)[r]	880.053	800.416	1083.389	952.902	42.098
	C	144701.861(14)[r]	2609.743	2573.528	2586.443	2564.343	25.230
$HD^{17}O$	A	697096.423(35)[r]	−6580.485	−6990.738	−7494.629	−7882.987	227.251
	B	272216.963(38)[r]	941.106	845.065	1142.308	998.518	60.330
	C	191336.440(37)[r]	3913.711	3863.276	3873.121	3840.615	45.122

Graphical symbols denote: × CVQZ; + wCVQZ.

References: a) 29; b) 30; c) 31; d) 32; e) JPL catalog 33, see also 34; f) 35; g) 36; h) 37; i) 38. j) 39; k) 40; l) 41; m) 42; n) 43; o) 44; p) 45; q) 46; r) 47; s) 48; t) 27.

— Table 1 continued —

		$(B_0^\beta)^{\rm EXP}$	$-\Delta B^\beta_{\rm vib}$				$\Delta B^\beta_{\rm el}$
			CCSD(T)	MP2	B3LYP/SNSD	B3LYP/AVTZ	
H_2CO							
parent	A	281970.5578(61)[a]	3244.224$^{\times,l}$	3043.405$^{\times}$	3173.034	3240.083	−463.336
	B	38833.98715(31)[a]	157.644	159.592	137.820	134.499	−4.925
	C	34004.24349(31)[a]	301.781	299.219	287.228	287.126	−1.960
$H_2^{13}C^{17}O$	A	281987.3(1.9)[b]	3226.263	3024.681	3156.650	3223.091	−463.336
	B	36776.790(25)[b]	142.725	144.903	123.956	120.835	−4.417
	C	32412.920(19)[b]	275.305	273.278	261.399	261.196	−1.779
$H_2^{13}C^{18}O$	A	281984.997(930)[c]	3230.273	3028.216	3160.925	3227.458	−463.336
	B	35859.2557(100)[c]	138.059	140.237	119.802	116.772	−4.174
	C	31697.86825(960)[c]	265.321	263.451	251.723	251.482	−1.681
$D_2^{13}CO$	A	141668.408(26)[d]	1211.840	1143.848	1180.418	1206.173	−116.015
	B	31733.2045(60)[d]	126.738	125.650	115.164	112.998	−3.376
	C	25822.3933(56)[d]	229.380	225.683	221.519	222.070	−1.191
$H_2^{13}CO$	A	281993.0397(31)[e]	3221.810	3020.759	3151.901	3218.240	−463.336
	B	37809.106966(213)[e]	148.034	150.208	128.686	125.464	−4.698
	C	33215.941417(207)[e]	286.674	284.465	272.422	272.266	−1.892
$HC_2^{17}O$	A	281965.0(3.0)[b]	3248.615	3047.275	3177.715	3244.865	−463.336
	B	37812.287(45)[b]	152.256	154.218	133.004	129.786	−4.638
	C	33214.523(31)[b]	290.351	287.977	276.138	275.989	−1.845
$D_2C^{18}O$	A	141648.(3)[f]	1230.665	1162.195	1198.750	1225.016	−116.015
	B	30595.86(2)[f]	124.589	123.450	113.520	111.448	−3.082
	C	25063.12(2)[f]	221.583	217.986	213.966	214.456	−1.083
$H_2C^{18}O$	A	281961.215(82)[g]	3252.568	3050.762	3181.927	3249.166	−463.336
	B	36902.27551(36)[g]	147.517	149.487	128.771	125.644	−4.392
	C	32513.40589(36)[g]	280.307	278.096	266.398	266.208	−1.747
D_2CO	A	141653.5494(16)[h]	1226.746	1158.784	1185.945	1220.731	−116.002
	B	32283.56403(30)[h]	132.806	131.456	120.738	118.839	−3.474
	C	26185.31517(28)[h]	237.387	233.448	228.873	229.983	−1.213
HDCO	A	198118.3259(38)[i]	1820.221	1710.387	1772.827	1804.742	−226.645
	B	34910.53734(64)[i]	145.873	145.663	130.827	128.378	−4.052
	C	29561.46242(58)[i]	265.871	262.420	255.091	255.359	−1.515
H_2CCCH_2							
parent	A	144249.78(33)[j]	1380.298$^{\div}$	1313.863$^{\div}$	1415.205	1314.517	−37.793
	B	8882.0971(33)[j]	35.513	36.380	28.823	33.514	−0.078
D_2CCCD_2	A	72408(9).[j]	483.625	461.851	499.829	456.325	−9.461
	B	6959.77(45)[j]	25.835	26.309	22.152	25.066	−0.048
D_2CCCH_2	A	96431.96(27)[j]	720.684	686.294	741.147	686.480	−16.816
	B	7955.11[j]	27.444	26.048	20.511	24.171	−0.062
	C	7737.14[j]	32.716	31.421	26.266	29.694	−0.059
CH_2ClF							
parent	A	41811.2198(98)[k]	414.891^{‡,m}	402.774$^{\div}$	416.292	418.301	−1.062
	B	5715.97941(42)[k]	28.677	27.828	27.160	26.882	−0.064
	C	5194.89167(14)[k]	33.263	32.455	32.075	31.949	−0.079
$^{13}CH_2ClF$	A	40495.4041(49)[k]	391.488	380.392	393.303	395.217	−1.018
	B	5696.81221(64)[k]	27.928	27.095	26.398	26.129	−0.064
	C	5158.06281(60)[k]	32.602	31.816	31.419	31.303	−0.078
	A	41738.9232(29)[k]	414.537	402.464	415.974	417.946	−1.061
$CH_2{}^{37}ClF$	B	5580.79460(38)[k]	27.847	27.026	26.360	26.090	−0.061
	C	5081.90667(35)[k]	32.281	31.498	31.110	30.985	−0.075

Graphical symbols denote: ÷ VTZ; ‡ CVTZ; × CVQZ.
References: a) 49; b) 50; c) 51; d) 52; e) 53; f) 54; g) 55; h) 56; i) 57; j) 58; k) 59; l) 27; m) 60.

— Table 1 continued —

		$(B_0^\beta)^{\rm EXP}$	$-\Delta B^\beta_{\rm vib}$				$\Delta B^\beta_{\rm el}$
			CCSD(T)	MP2	B3LYP/SNSD	B3LYP/AVTZ	
***cis*-CHFCHCl**							
parent	A	16405.679(1)^a	136.035$^{\div,d}$	133.919$^{\div,d}$	136.069	135.617$^{\div}$	−0.780
	B	3756.4416(3)^a	4.914	4.415	4.166	4.351	−0.049
	C	3052.9045(4)^a	11.424	11.072	10.839	10.990	−0.014
$CDF{=}CD^{35}Cl$	A	13966.6164(26)^b	93.061	91.270	92.690	92.273	−0.571
	B	3637.68368(54)^b	8.686	8.259	8.081	8.409	−0.046
	C	2882.77342(54)^b	12.552	12.259	12.086	12.327	−0.013
$CDF{=}CH^{35}Cl$	A	15578.01990(96)^b	118.692	116.649	117.887	117.925	−0.707
	B	3643.16983(58)^b	6.580	6.125	6.092	6.172	−0.046
	C	2949.29478(58)^b	11.771	11.453	11.346	11.446	−0.013
$CHF{=}CD^{35}Cl$	A	14617.4062(19)^b	104.997	103.177	104.623	104.561	−0.622
	B	3750.17170(39)^b	7.112	6.639	6.506	6.665	−0.049
	C	2980.94306(25)^b	12.265	11.940	11.784	11.930	−0.013
$CHF{=}CH^{37}Cl$	A	16346.606(1)^a	135.608	133.529	135.710	135.243	−0.774
	B	3662.6914(4)^a	4.722	4.232	3.977	4.159	−0.046
	C	2988.7084(5)^a	11.009	10.663	10.427	10.575	−0.013
$CDF{=}CD^{37}Cl$	A	13918.2633(42)^b	92.810	91.046	92.451	92.033	−0.567
	B	3546.26244(67)^b	8.384	7.966	7.787	8.116	−0.043
	C	2823.06213(37)^b	12.146	11.858	11.684	11.926	−0.012
$CDF{=}CH^{37}Cl$	A	15532.03690(50)^b	118.431	116.418	117.594	117.619	−0.702
	B	3550.80487(46)^b	6.339	5.893	5.878	5.951	−0.043
	C	2886.87142(65)^b	11.360	11.048	10.952	11.047	−0.012
$CHF{=}CD^{37}Cl$	A	14556.6913(13)^b	104.606	102.820	104.213	104.141	−0.616
	B	3657.50861(30)^b	6.856	6.392	6.277	6.433	−0.046
	C	2919.64735(25)^b	11.854	11.535	11.389	11.532	−0.013
$CHF{=}^{13}CH^{35}Cl$	A	15971.8028(83)^b	131.404	129.338	131.224	130.680	−0.742
	B	3756.55171(130)^b	4.696	4.205	4.027	4.226	−0.049
	C	3037.56076(64)^b	11.319	10.974	10.784	10.938	−0.014
$^{13}CHF{=}CH^{35}Cl$	A	16228.5163(150)^b	132.737	130.693	133.282	132.372	−0.765
	B	3715.67378(16)^b	4.954	4.458	4.055	4.371	−0.048
	C	3019.82425(110)^b	11.286	10.938	10.621	10.844	−0.014
CH_2CHF							
parent	A	64584.672(51)^c	621.788$^{\div}$	598.167$^{\div,d}$	560.655	583.609$^{\div}$	−6.124
	B	10636.809(9)^c	51.469	50.904	50.051	49.846	−0.321
	C	9118.108(6)^c	64.804	64.023	62.742	63.061	−0.023
$^{13}CH_2{=}CHF$	A	64211.333(108)^c	618.011	594.727	561.185	579.104	−6.054
	B	10295.265(18)^c	49.444	48.936	47.669	47.914	−0.303
	C	8858.851(13)^c	62.181	61.460	59.979	60.514	−0.023
$CH_2{=}^{13}CHF$	A	62977.398(77)^c	593.475	570.774	534.036	555.232	−5.830
	B	10634.218(13)^c	50.674	50.117	49.211	49.118	−0.321
	C	9083.166(9)^c	64.106	63.331	61.999	62.387	−0.023
$CHD_{trans}{=}CHF$	A	63789.713(78)^c	620.156	597.513	561.334	581.180	−5.970
	B	9668.180(14)^c	46.520	45.775	45.227	45.337	−0.268
	C	8383.947(9)^c	57.442	56.593	55.621	56.060	−0.021
$CHD_{trans}{=}CDF$	A	49547.985(99)^c	412.297	396.933	372.264	387.014	−3.610
	B	9667.173(15)^c	47.369	46.572	46.321	46.487	−0.268
	C	8076.940(10)^c	56.099	55.244	54.452	55.016	−0.021
$CHD_{cis}{=}CHF$	A	53609.855(227)^c	505.265	486.924	468.429	479.313	−4.220
	B	10278.245(39)^c	42.840	42.027	40.994	41.537	−0.300
	C	8610.352(25)^c	57.367	56.443	55.315	56.001	−0.021
$CHD_{cis}{=}CDF$	A	42818.339(211)^c	349.962	336.962	323.245	331.684	−2.705
	B	10274.671(44)	45.018	44.168	43.556	44.183	−0.299
	C	8272.260(40)	56.296	55.385	54.517	55.306	−0.020
$CH_2{=}CDF$	A	49930.986(91)^c	410.252	394.410	366.205	383.924	−3.669
	B	10635.434(15)^c	52.550	51.930	51.823	51.522	−0.321
	C	8753.124(9)^c	63.015	62.225	61.340	61.746	−0.022
$CD_2{=}CHF$	A	52621.501(67)^c	489.304	471.372	451.437	464.058	−4.056
	B	9401.010(11)^c	40.485	39.599	39.278	39.441	−0.254
	C	7964.335(8)^c	51.949	51.023	50.378	50.811	−0.019
$CD_2{=}CDF$	A	42257.769(52)^c	343.848	331.064	316.640	326.417	−2.626
	B	9397.708(13)^c	42.281	41.359	41.298	41.561	−0.254
	C	7676.414(9)^c	51.143	50.227	49.734	50.293	−0.019

Graphical symbol denotes: ÷ VTZ.
References: a) 61; b) 62; c) 63; d) 64.

— Table 1 continued —

		$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B^\beta_{\mathrm{vib}}$				$\Delta B^\beta_{\mathrm{el}}$
			CCSD(T)	MP2	B3LYP/SNSD	B3LYP/AVTZ	
oxirane							
parent	A	25483.79(3)[a]	228.075$^{\div,d}$	224.217$^{\div}$	209.684	214.360	−1.405
	B	22120.76(3)[a]	236.345	230.690	224.084	227.205	0.199
	C	14097.71(3)[a]	155.431	153.725	146.508	145.863	0.244
^{13}C	A	25291.89(6)[a]	225.305	225.506	206.567	204.896	−1.375
	B	21597.77(6)[a]	227.096	221.400	215.471	219.555	0.180
	C	13825.75(6)[a]	151.103	149.936	142.410	143.742	0.233
^{18}O	A	23992.83(11)[a]	207.615	208.062	190.190	188.394	−1.228
	B	22121.58(12)[a]	235.976	229.890	223.819	228.106	0.199
	C	13628.56(13)[a]	147.890	146.753	139.237	140.470	0.233
D	A	24252.47(6)[a]	219.999	219.577	203.299	202.278	−1.214
	B	19905.34(6)[a]	201.315	195.710	191.813	195.094	0.123
	C	13327.40(6)[a]	141.009	139.483	133.385	134.655	0.213
D_2(*cis*)	A	22700.41(5)[a]	200.959	199.976	187.068	186.120	−1.127
	B	18318.39(5)[a]	180.963	175.700	172.764	175.867	0.139
	C	12650.08(5)[a]	128.839	127.082	122.229	123.482	0.190
^{13}C-D_2(*cis*)	A	22555.61(4)[a]	198.489	197.631	184.746	183.803	−1.114
	B	17963.42(4)[a]	175.203	170.160	167.122	170.097	0.132
	C	12438.85(4)[a]	125.665	123.999	119.157	120.372	0.183
^{18}O-D_2(*cis*)	A	21424.03(5)[a]	183.723	183.067	170.596	169.639	−0.990
	B	18317.20(5)[a]	180.534	175.220	172.344	175.440	0.139
	C	12243.45(5)[a]	123.009	121.376	116.570	117.701	0.183
D_2(*trans*)	A	22943.19(3)[a]	203.744	202.818	189.377	188.479	−1.122
	B	18198.47(3)[a]	179.817	174.610	171.930	174.981	0.135
	C	12585.27(3)[a]	128.459	126.726	121.993	123.191	0.181
^{13}C-D_2(*trans*)	A	22786.84(6)[a]	201.110	200.236	186.946	186.025	−1.108
	B	17852.32(7)[a]	174.177	169.220	166.339	169.287	0.127
	C	12377.50(6)[a]	125.315	123.677	118.921	120.096	0.175
^{18}O-D_2(*trans*)	A	21646.74(9)[a]	186.089	185.413	172.467	171.503	−0.983
	B	18202.46(10)[a]	179.416	174.200	171.574	174.615	0.135
	C	12186.66(9)[a]	122.663	121.057	116.366	117.424	0.174
dioxirane							
parent	A	28976.762(78)[b]	311.$^{\div,e}$	265.267$^{\div}$	242.360	246.275	−1.070
	B	25056.382(86)[b]	147.	112.283	138.079	129.544	−2.168
	C	14779.889(65)[b]	149.	124.265	127.950	126.077	0.016
D	A	25157.48(11)[b]	216.	218.707	202.432	205.689	−0.827
	B	24154.97(10)[b]	142.	115.938	141.161	133.230	−1.999
	C	14003.461(72)[b]	137.	112.969	116.679	115.027	0.003
$^{18}O_2$	A	28120.96(21)[b]	253.	255.137	232.968	236.525	−0.979
	B	22491.83(22)[b]	123.	92.674	115.050	107.790	−1.747
	C	13648.58(23)[b]	132.	109.837	113.578	111.819	0.021
^{13}C	A	28012.641(68)[b]	246.	250.103	227.777	231.620	−1.013
	B	25056.772(86)[b]	147.	112.417	137.633	129.089	−2.168
	C	14524.118(75)[b]	145.	121.518	124.612	122.856	0.012
***trans*-glyoxal**							
parent	A	55290.612(51)[c]	716.510$^{\div,c}$	714.492$^{\div}$	723.318	740.494	−29.418
	B	4798.037(14)[c]	21.852	23.236	22.412	23.108	−0.215
	C	4416.898(14)[c]	22.120	23.023	22.010	22.569	−0.078
D	A	44482.968(99)[c]	528.840	524.436	530.071	542.820	−18.932
	B	4786.426(33)[c]	21.303	22.558	21.766	22.420	−0.214
	C	4323.139(33)[c]	21.709	22.366	21.406	21.919	−0.075
D2	A	37036.423(63)[c]	412.714	408.985	413.114	422.860	−13.066
	B	4773.547(24)[c]	20.960	22.103	21.349	21.964	−0.213
	C	4230.257(24)[c]	21.200	21.729	20.825	21.290	−0.071
^{13}C	A	53412.969(54)[c]	667.980	665.702	673.385	689.321	−27.414
	B	4760.611(24)[c]	21.467	22.861	22.085	22.781	−0.212
	C	4372.871(24)[c]	21.736	22.560	21.586	22.142	−0.077

Graphical symbol denotes: ÷ VTZ.

References: a) 65; b) 66; c) 67; d) 68; e) calculated as differences of the values reported in Tables V and III in ref 69.

— Table 1 continued —

		$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B^\beta_{\mathrm{vib}}$				$\Delta B^\beta_{\mathrm{el}}$
			CCSD(T)	MP2	B3LYP/SNSD	B3LYP/AVTZ	
***cis*-acrolein**							
parent	A	22831.6496(161)[a]	61.154÷	59.095÷	57.086	53.878	−3.019
	B	6241.0470(29)[a]	62.222	60.389	55.610	56.775	−0.303
	C	4902.2063(28)[a]	41.147	39.587	37.225	37.403	−0.018
^{13}C1	A	22565.122(21)[b]	57.582	55.688	54.438	50.640	−2.950
	B	6200.653(4)[b]	61.341	59.516	54.468	55.835	−0.298
	C	4864.975(3)[b]	40.382	38.837	36.349	36.628	−0.018
^{13}C2	A	22485.459(22)[b]	58.549	56.664	54.604	50.977	−2.933
	B	6198.712(4)[b]	61.184	59.385	54.694	56.028	−0.298
	C	4860.028(3)[b]	40.338	38.813	36.506	36.771	−0.018
^{13}C3	A	22574.762(18)[b]	59.590	57.653	57.074	53.045	−2.944
	B	6073.707(3)[b]	60.319	58.532	53.360	54.778	−0.288
	C	4786.881(2)[b]	40.122	38.603	36.019	36.348	−0.018
^{18}O4	A	22339.531(14)[b]	59.964	57.988	54.653	51.186	−2.892
	B	5973.952(3)[b]	58.836	57.052	52.855	54.040	−0.274
	C	4714.284(2)[b]	39.319	37.811	35.682	35.904	−0.015
D5	A	20811.966(16)[b]	69.447	67.075	68.501	65.764	−2.510
	B	6118.233(3)[b]	59.633	58.036	52.892	54.355	−0.291
	C	4729.863(3)[b]	38.496	37.067	34.700	35.012	−0.017
D6	A	20594.106(8)[b]	56.211	53.920	50.695	48.954	−2.472
	B	6128.360(2)[b]	61.086	59.429	55.697	56.753	−0.291
	C	4723.899(2)[b]	39.047	37.631	35.898	36.050	−0.018
D7	A	20796.961(20)[b]	71.042	67.680	69.578	65.236	−2.494
	B	6163.027(3)[b]	57.519	55.942	50.126	51.959	−0.296
	C	4755.207(3)[b]	37.813	36.375	33.603	34.078	−0.017
D8	A	22634.762(55)[b]	56.130	54.408	55.278	51.623	−2.956
	B	5770.070(10)[b]	55.850	54.103	49.653	50.912	−0.261
	C	4598.859(11)[b]	37.642	36.168	33.976	34.278	−0.017
***trans*-acrolein**							
parent	A	47353.729(9)[c]	482.993÷	497.298÷	473.458	492.126	−15.398
	B	4659.4894(4)[c]	28.669	26.958	26.919	26.837	−0.156
	C	4242.7034(4)[c]	27.453	25.617	26.036	26.113	−0.020
^{13}C1	A	46781.044(7)[b]	475.208	489.010	464.606	482.342	−15.029
	B	4644.7419(7)[b]	28.456	26.767	26.704	26.654	−0.155
	C	4225.8363(6)[b]	27.235	25.419	25.812	25.908	−0.019
^{13}C2	A	46518.949(6)[b]	459.947	474.033	451.761	470.312	−14.847
	B	4642.4397(7)[b]	28.356	26.680	26.629	26.553	−0.155
	C	4221.7446(6)[b]	27.083	25.279	25.695	25.779	−0.020
^{13}C3	A	47255.232(6)[b]	481.141	496.201	472.233	490.822	−15.340
	B	4520.7955(6)[b]	27.720	26.050	26.008	25.897	−0.148
	C	4126.6426(6)[b]	26.574	24.784	25.185	25.228	−0.019
^{18}O4	A	47262.882(6)[b]	486.424	500.581	476.595	495.348	−15.343
	B	4428.1025(6)[b]	26.698	25.074	25.078	24.998	−0.139
	C	4049.3455(6)[b]	25.692	23.957	24.368	24.432	−0.016
D5	A	39514.424(5)[b]	406.716	415.043	396.331	410.099	−10.715
	B	4651.701(6)[b]	28.231	26.604	26.462	26.408	−0.155
	C	4162.3476(6)[b]	26.914	25.196	25.515	25.617	−0.019
D6	A	39038.070(5)[b]	329.366	338.592	326.278	341.254	−10.408
	B	4647.9057(7)[b]	28.414	26.770	26.784	26.717	−0.156
	C	4153.6536(6)[b]	26.566	24.834	25.335	25.449	−0.019
D7	A	41654.613(5)[b]	415.963	428.714	412.017	427.176	−11.932
	B	4508.5717(6)[b]	26.155	24.374	24.374	24.290	−0.147
	C	4068.6004(5)[b]	25.274	23.425	23.885	23.956	−0.019
D8	A	46660.088(8)[b]	491.398	505.105	476.935	493.535	−14.937
	B	4356.7777(8)[b]	26.103	24.526	24.671	24.640	−0.138
	C	3985.4051(8)[b]	25.095	23.390	23.895	23.983	−0.019

Graphical symbol denotes: ÷ VTZ.
References: a) 70; b) 71; c) 72.

— Table 1 continued —

		$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B^\beta_{\mathrm{vib}}$				$\Delta B^\beta_{\mathrm{el}}$
			CCSD(T)	MP2	B3LYP/SNSD	B3LYP/AVTZ	
pyridazine							
parent	A	6242.95134(14)^a	52.504$^{\aleph0,a}$	49.825$^{\div}$	49.074	48.838	−0.352
	B	5961.09283(13)^a	43.231	41.088	38.810	39.542	−0.457
	C	3048.71390(20)^a	24.608	23.562	22.823	22.979	0.057
^{13}C3	A	6112.22807(85)^a	51.177	48.473	47.824	47.613	−0.344
	B	5961.31709(85)^a	42.965	40.909	38.559	39.285	−0.457
	C	3017.24769(87)^a	24.248	23.216	22.490	22.646	0.056
^{13}C4	A	6217.71925(61)^a	51.903	49.250	48.423	48.226	−0.350
	B	5848.36612(60)^a	42.297	40.203	38.053	38.754	−0.444
	C	3013.02887(23)^a	24.184	23.158	22.428	22.588	0.056
^{15}N	A	6218.91097(66)^a	51.850	49.252	48.377	48.192	−0.349
	B	5857.40185(51)^a	42.393	40.272	38.138	38.829	−0.444
	C	3015.70923(32)^a	24.199	23.178	22.442	22.602	0.056
C3-D	A	5962.40668(41)^a	43.525	41.345	39.249	39.954	−0.454
	B	5828.17973(46)^a	47.450	45.043	44.523	44.370	−0.323
	C	2946.68605(33)^a	23.438	22.440	21.827	21.979	0.055
C4-D	A	6192.44445(15)^a	51.475	48.973	48.078	47.968	−0.358
	B	5598.11888(13)^a	39.904	37.795	36.137	36.736	−0.414
	C	2939.56879(11)^a	23.281	22.287	21.659	21.818	0.055
C3,C4-D	A	5854.14225(16)^a	46.381	44.086	42.797	42.899	−0.372
	B	5539.31505(15)^a	40.458	38.364	37.449	37.897	−0.376
	C	2845.68651(15)^a	22.231	21.281	20.760	20.917	0.053
C3,C5-D	A	5889.76581(36)^a	46.464	44.063	42.782	42.806	−0.379
	B	5498.78296(32)^a	40.330	38.333	37.425	37.891	−0.370
	C	2843.27858(12)^a	22.206	21.257	20.741	20.885	0.053
C3,C6-D	A	5959.19500(34)^a	43.434	41.310	39.509	40.209	−0.457
	B	5460.41809(33)^a	43.429	41.151	40.698	40.583	−0.307
	C	2848.96352(12)^a	22.330	21.371	20.865	21.012	0.053
C4,C5-D	A	6002.7188(12)^a	49.449	46.882	46.445	46.286	−0.338
	B	5388.7995(11)^a	37.638	35.767	34.068	34.663	−0.413
	C	2839.10005(55)^a	21.124	21.153	20.615	20.761	0.053
C3,C4,C5-D	A	5622.36606(24)^a	45.092	42.684	42.255	42.255	−0.314
	B	5385.21892(23)^a	37.693	35.873	35.016	35.016	−0.414
	C	2750.18252(30)^a	21.124	20.222	19.940	19.940	0.052
C3,C4,C6-D	A	5732.55746(16)^a	42.375	40.356	38.748	39.258	−0.418
	B	5299.11962(15)^a	40.482	38.299	38.039	38.067	−0.312
	C	2753.23394(14)^a	21.208	20.297	19.878	20.018	0.052
C3,C4,C5,C6-D	A	5385.76388(45)^a	37.727	35.930	34.502	35.111	−0.413
	B	5275.67750(46)^a	41.303	39.058	38.973	38.858	−0.297
	C	2664.70726(65)^a	20.198	19.333	18.988	19.122	0.050
^{13}C,C4-D	A	6079.770(15)^a	50.156	47.686	46.730	46.622	−0.357
	B	5587.211(15)^a	39.732	37.615	36.068	36.654	−0.408
	C	2910.9599(10)^a	22.957	21.965	21.356	21.508	0.055
cyclobutene							
parent	A	12892.88(1)^b	126.618$^{\div}$	125.391$^{\div}$	119.566	123.077	−0.404
	B	12226.11(1)^b	97.422	93.253	89.061	89.904	−0.488
	C	6816.25(1)^b	61.901	60.641	57.906	59.375	−0.077
^{13}C1	A	12784.79(1)^b	123.951	122.532	116.841	120.227	−0.403
	B	12015.61(1)^b	95.618	91.782	87.509	88.398	−0.466
	C	6720.51(1)^b	60.558	59.332	56.615	58.051	−0.074
^{13}C3	A	12742.89(1)^b	122.942	121.423	115.708	119.093	−0.402
	B	12033.87(1)^b	96.268	92.532	88.248	89.145	−0.465
	C	6714.54(1)^b	60.566	59.344	56.617	58.061	−0.074
C1-D	A	12658.77(1)^b	118.211	115.963	110.617	113.550	−0.421
	B	11220.97(1)^b	89.056	86.302	82.660	83.801	−0.385
	C	6432.01(1)^b	56.562	55.405	53.010	54.356	−0.068
C3-D	A	12419.27(1)^b	115.896	113.733	108.880	111.671	−0.402
	B	11431.62(1)^b	94.114	91.016	87.409	88.462	−0.403
	C	6557.96(1)^b	58.448	57.170	54.845	56.158	−0.071

Graphical symbols denote: $\div$ VTZ; $\aleph0$ ANO0.

References: a) from the Total corrections reported in Table III of ref. 73 and subtracting their $\Delta B^\beta_{\mathrm{el}}$ (0.309, 0.395, and 0.062 MHz for A, B, and C, respectively). b) 74, the factor 505531 MHz amu Å^2 has been used for conversions from amu Å^2 to MHz, as indicated in Table 7.

Table 2: $(B_0^\beta)^{\mathrm{EXP}}$, B3LYP/SNSD $\Delta B_{\mathrm{vib}}^\beta$ and $\Delta B_{\mathrm{el}}^\beta$ ($g^{\beta\beta}$ at the B3LYP/AVTZ level) contributions for molecules belonging to the GeomSNS set not presented in Table 1. All data are in MHz.

		$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B_{\mathrm{vib}}^\beta$	$\Delta B_{\mathrm{el}}^\beta$
glycolaldehyde				
parent	A	18446.25696(134)[a]	37.488	−1.303
	B	6525.99578(51)[a]	108.126	−0.268
	C	4969.23452(50)[a]	65.778	−0.047
$H^{13}COCH_2OH$	A	18259.420856(138)[b]	33.931	−1.274
	B	6472.436365(46)[b]	106.747	−0.265
	C	4924.607952(39)[b]	64.649	−0.047
$HCO^{13}CH_2OH$	A	18142.347585(137)[b]	34.362	−1.272
	B	6486.371688(42)[b]	106.165	−0.264
	C	4924.025217(38)[b]	64.159	−0.047
$HC^{18}OCH_2OH$	A	18087.0469(48)[c]	39.532	−1.268
	B	6242.8120(18)[c]	102.027	−0.243
	C	4778.4877(20)[c]	62.998	−0.043
$HCOCH_2^{18}OH$	A	18085.3081(46)[c]	32.027	−1.226
	B	6239.3692(21)[c]	103.178	−0.247
	C	4776.3858(30)[c]	63.149	−0.043
$HCOCH_2OD$	A	17490.68230(18)[d]	63.529	−1.154
	B	6499.72649(12)[d]	98.345	−0.267
	C	4882.948293(76)[d]	60.233	−0.045
$DCOCH_2OH$	A	17150.99706(21)[d]	43.173	−1.106
	B	6362.87482(10)[d]	101.266	−0.259
	C	4778.922377(73)[d]	60.593	−0.044
HCOCHDOH	A	16987.80362(18)[d]	40.081	−1.128
	B	6385.430683(91)[d]	104.775	−0.254
	C	4843.811766(70)[d]	63.763	−0.045
DCOCHDOH	A	15862.45361(17)[d]	43.035	−0.966
	B	6233.230843(90)[d]	98.658	−0.246
	C	4663.584048(65)[d]	58.969	−0.043
ethenol				
parent	A	59660.80(2)[e]	557.543	−2.662
	B	10561.665(3)[e]	67.801	−0.382
	C	8965.786(3)[e]	69.567	−0.002
$H_2C{=}^{13}CHOH$	A	58385.65(2)[e]	534.876	−2.541
	B	10561.069(3)[e]	66.899	−0.381
	C	8935.768(3)[e]	68.741	−0.002
$H_2^{13}C{=}CHOH$	A	59362.26(2)[e]	556.265	−2.630
	B	10233.319(3)[e]	65.009	−0.359
	C	8721.587(2)[e]	66.947	−0.002
$H_2C{=}CH^{18}OH$	A	59430.52(2)[e]	553.697	−2.669
	B	10025.964(3)[e]	63.431	−0.342
	C	8571.915(2)[e]	65.362	−0.001
$H_2C{=}CHOD$	A	52585.52(2)[e]	453.840	−2.145
	B	10320.499(3)[e]	64.505	−0.361
	C	8621.184(3)[e]	64.130	−0.002
$H_2C{=}CDOH$	A	47112.05(1)[e]	388.530	−1.624
	B	10560.543(3)[e]	69.068	−0.381
	C	8618.709(3)[e]	67.800	−0.001
$HD_cC{=}CHOH$	A	50260.32(1)[e]	466.719	−1.854
	B	10195.395(3)[e]	59.575	−0.357
	C	8468.432(3)[e]	62.566	−0.003
$HD_tC{=}CHOH$	A	58911.59(2)[e]	542.755	−2.628
	B	9624.171(3)[e]	61.671	−0.317
	C	8267.011(2)[e]	62.520	−0.002
$D_2C{=}CHOH$	A	49315.77(1)[e]	441.603	−1.801
	B	9350.327(3)[e]	56.019	−0.301
	C	7854.079(2)[e]	57.275	−0.003
$D_2C{=}CDOH$	A	40226.383(8)[e]	325.792	−1.171
	B	9347.259(2)[e]	57.640	−0.301
	C	7578.524(2)[e]	56.293	−0.002
propanal				
parent	A	16669.695(9)[f]	92.196	−0.809
	B	5893.496(3)[f]	62.958	−0.171
	C	4598.992(3)[f]	44.710	−0.029
$DCOCH_2CH_3$	A	15668.618(9)[f]	88.124	−0.709
	B	5752.546(3)[f]	61.001	−0.163
	C	4436.334(3)[f]	42.373	−0.027
$H^{13}COCH_2CH_3$	A	16536.994(12)[f]	89.476	−0.797
	B	5848.634(4)[f]	62.143	−0.168
	C	4561.588(4)[f]	43.994	−0.029
$HCO^{13}CH_2CH_3$	A	16394.706(6)[f]	89.247	−0.789
	B	5863.114(2)[f]	61.925	−0.169
	C	4559.363(3)[f]	43.811	−0.029
$HCOCH_2^{13}CH_3$	A	16505.355(10)[f]	89.377	−0.786
	B	5746.942(3)[f]	61.466	−0.163
	C	4497.083(4)[f]	43.737	−0.028
$HCOCHDCH_3$	A	15392.623(47)[f]	86.378	−0.701
	B	5789.676(12)[f]	61.448	−0.164
	C	4489.566(12)[f]	43.865	−0.029
$DCOCHDCH_3$	A	14524.314(18)[f]	82.315	−0.655
	B	5656.174(5)[f]	59.710	−0.161
	C	4335.220(5)[f]	41.676	−0.028
$HC^{18}OCH_2CH_3$	A	16333.613(71)[f]	91.185	−0.781
	B	5658.984(12)[f]	59.273	−0.155
	C	4430.429(16)[f]	42.566	−0.026
$HCOCH_2CH_2D_o$	A	15609.154(7)[f]	83.888	−0.696
	B	5741.151(3)[f]	59.428	−0.163
	C	4479.589(3)[f]	42.657	−0.028
$HCOCH_2CH_2D_p$	A	16602.445(27)[f]	99.674	−0.799
	B	5482.571(11)[f]	55.687	−0.149
	C	4341.234(10)[f]	40.057	−0.027
$HCOCH_2CD_2H_o$	A	15571.225(16)[f]	91.834	−0.690
	B	5354.224(46)[f]	52.725	−0.143
	C	4238.962(44)[f]	38.328	−0.025
$HCOCH_2CD_2H_p$	A	14699.873(94)[f]	77.362	−0.605
	B	5587.716(28)[f]	56.920	−0.155
	C	4373.944(27)[f]	40.830	−0.026
benzene				
parent	B	5689.27(1)[g]	39.925	−0.245
	C	–	20.800	0.087
C_6D_6	B	4707.31(15)[h]	31.430	−0.167
	C	–	16.139	0.059
$^{13}C_6H_6$	B	5337.92(6)[h]	36.102	−0.215
	C	–	18.843	0.076
$^{13}C_6D_6$	B	4464.37(2)[i]	28.787	−0.151
	C	–	14.805	0.053
cyclopropane				
parent	B	20093.317(30)[j]	207.504	0.287
	C	12522.3(90)[j]	145.594	0.469
$C_3H_4D_2$	A	18835.662(18)[j]	190.245	0.252
	B	16370.2703(70)[j]	152.250	0.190
	C	11409.2285(67)[j]	125.239	0.386

Subscripts c and t stand for *c*is and *t*rans, respectively. Subscripts p and o stand for in *p*lane and *o*ut of plane, respectively.
References: a) 75; b) 76; c) 77; d) 78; e) 79; f) 80; g) 81; h) 82; i) 83; j) 84.

— Table 2 continued —

		$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B^\beta_{\mathrm{vib}}$	$\Delta B^\beta_{\mathrm{el}}$			$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B^\beta_{\mathrm{vib}}$	$\Delta B^\beta_{\mathrm{el}}$
propene					***cis*-methyl formate**				
parent	A	46083.05[a]	380.629	−2.487	parent	A	19982.19530(56)[d]	15.552	−1.480
	B	9305.27[a]	73.152	−0.213		B	6914.03971(17)[d]	108.164	−0.153
	C	8134.16[a]	68.239	0.046		C	5304.49791(17)[d]	68.666	−0.049
$CH_2=^{13}CHCH_3$	A	45298.48[a]	364.457	−2.400	$DCOOCH_3$	A	18475.71[e]	20.189	−1.270
	B	9303.28[a]	72.300	−0.213		B	6768.41[e]	104.838	−0.145
	C	8107.14[a]	67.405	0.046		C	5109.70[e]	64.761	−0.045
$CH_2=CH^{13}CH_3$	A	46167.22[a]	377.477	−2.460	$HCOOCH_2D_p$	A	19921.587052(980)[h]	38.918	−1.477
	B	9047.94[a]	70.336	−0.203		B	6415.266933(180)[h]	92.790	−0.133
	C	7932.98[a]	65.870	0.044		C	5004.268277(200)[h]	59.929	−0.044
$CHD_c=CHCH_3$	A	40217.26[a]	338.328	−1.945	$HCOOCH_2D_o$	A	18516.681258(830)[h]	21.626	−1.270
	B	9040.09[a]	65.065	−0.191		B	6730.195643(190)[h]	98.134	−0.145
	C	7729.66[a]	62.135	0.042		C	5164.955356(180)[h]	64.670	−0.047
$CH_2=CDCH_3$	A	38154.2[b]	273.435	−1.697	$HCOOCD_3$	A	17261.81[f]	40.335	−1.107
	B	9301.80[b]	73.081	−0.212		B	6101.92[f]	84.321	−0.120
	C	7837.18[b]	66.043	0.043		C	4778.01[f]	55.213	−0.041
$CH_2=CHCH_2D_p$	A	40539.78[a]	332.267	−1.860	$H^{13}COOCH_3$	A	19798.73249(43)[d]	12.962	−1.454
	B	9066.99[a]	70.895	−0.209		B	6864.74991(14)[d]	106.796	−0.150
	C	7765.98[a]	63.164	0.041		C	5262.53086(13)[d]	67.562	−0.048
$CH_2=CHCH_2D_o$	A	43281.76[a]	335.168	−2.190	$HCOO^{13}CH_3$	A	19765.12[e]	12.660	−1.449
	B	8659.02[a]	67.930	−0.183		B	6742.65[e]	105.477	−0.146
	C	7718.11[a]	63.601	0.041		C	5188.08[e]	67.184	−0.048
$CH_2=CDCH_2D_o$	A	36180.[c]	246.813	−1.526	$HC^{18}OOCH_3$	A	19525.80[e]	18.179	−1.406
	B	8654.53[c]	67.375	−0.184		B	6617.19[e]	102.122	−0.139
	C	7449.49[c]	61.661	0.038		C	5097.25[e]	65.611	−0.044
$CHD_c=CHCH2D_p$	A	35710.[c]	300.888	−1.498	$HCO^{18}OCH_3$	A	19323.00[e]	13.182	−1.384
	B	8821.61[c]	62.913	−0.187		B	6848.97[e]	105.231	−0.151
	C	7397.33[c]	57.311	0.038		C	5219.01[e]	66.074	−0.048
$CHD_c=CHCH2D_o$	A	38200.[c]	301.019	−1.739	$HCOOCD_2H_p$	A	17281.949265(420)[g]	21.724	−1.106
	B	8411.37[c]	60.544	−0.166		B	6540.604314(110)[g]	96.140	−0.137
	C	7340.45[c]	58.083	0.037		C	5041.990952(120)[g]	62.222	−0.045
$CHD_t=CDCH3$	A	37960.[c]	274.858	−1.659	$HCOOCD_2H_o$	A	18482.353793(330)[g]	41.286	−1.269
	B	8546.43[c]	65.636	−0.181		B	6261.052643(100)[g]	85.733	−0.127
	C	7289.36[c]	59.691	0.037		C	4884.201398(110)[g]	57.187	−0.043
$CH_2=CHCHD_pD_o$	A	38220.[c]	302.753	−1.659	**CH_2F_2**				
	B	8469.44[c]	65.615	−0.181	parent	A	49142.87203(230)[i]	514.764	−2.060
	C	7395.45[c]	59.024	0.037		B	10604.82258(53)[i]	61.021	−0.238
$CH_2=CHCHD_oD_o$	A	39730.[c]	324.770	−1.905		C	9249.75702(49)[i]	69.366	−0.205
	B	8111.44[c]	62.878	−0.161	^{13}C	A	47730.7563(23)[i]	486.777	−1.964
	C	7370.87[c]	57.785	0.037		B	10606.21792(60)[i]	59.610	−0.238
$CD_2=CHCH_3$	A	39820.[c]	333.925	−1.870		C	9199.02313(63)[i]	68.152	−0.204
	B	8347.03[c]	59.789	−0.165	D_2	A	34745.2222(98)[j]	319.808	−1.075
	C	7203.75[c]	56.838	0.037		B	10241.4230(30)[j]	63.952	−0.222
$CHD_t=CHCH_2D_p$	A	40360.[c]	334.094	−1.817		C	8831.8102(26)[j]	65.793	−0.190
	B	8324.23[c]	63.515	−0.179	D	A	40682.063(15)[j]	393.531	−1.445
	C	7210.10[c]	56.984	0.036		B	10454.4883(44)[j]	62.596	−0.232
$CHD_t=CHCH_2D_o$	A	43040.[c]	336.831	−2.128		C	9008.9616(40)[j]	67.212	−0.196
	B	7976.26[c]	61.273	−0.158	$^{13}CD_2$	A	34138.387(19)[j]	307.646	−1.047
	C	7164.02[c]	57.444	0.036		B	10242.7414(59)[j]	62.625	−0.222
$^{13}CH_2=CHCH_3$	A	45999.181	377.680	−2.476		C	8792.5874(57)[j]	64.627	−0.189
	B	9048.328	70.525	−0.199	**CCl_2F_2**				
	C	7930.844	66.015	0.044	parent	A	4118.87378(12)[k]	19.418	−0.063
$CH_2=CDCH_2D_p$	A	34060.[c]	247.147	−1.311		B	2638.674317(88)[k]	12.253	−0.032
	B	9058.28[c]	71.125	−0.208		C	2233.691145(88)[k]	10.306	−0.026
	C	7483.72[c]	61.083	0.039	^{13}C	A	4115.71380(67)[l]	18.978	−0.063
$CHD_c=CDCH_3$	A	33720.[c]	253.078	−1.372		B	2638.94282(58)[l]	11.988	−0.032
	B	9038.74[c]	65.294	−0.192		C	2232.85263(57)[l]	10.090	−0.026
	C	7451.01[c]	60.213	0.039	^{37}Cl	A	4092.0152(13)[l]	19.225	−0.062
$CHD_t=CHCH_3$	A	45912.6[b]	383.457	−2.417		B	2582.2212(13)[l]	11.896	−0.031
	B	8548.00(8)[b]	65.631	−0.182		C	2185.4417(13)[l]	10.017	−0.025
	C	7542.20(0)[b]	61.442	0.040					

Subscripts c and t stand for *c*is and *t*rans, respectively. Subscripts p and o stand for in *p*lane and *o*ut of plane, respectively.
References: a) 85, the factor 505531 MHz amu Å^2 has been used for conversions from amu Å^2 to MHz, as indicated in Table III; b) 86; c) 87; d) 88; e) 89, the authors informed us with a private communication that these values have been obtained making new fits of data from ref. 90; f) 90; g) 91; h) 92; i) 93; j) 94; k) 95; l) 96.

— Table 2 continued —

		$(B_0^\beta)^{\text{EXP}}$	$-\Delta B^\beta_{\text{vib}}$	$\Delta B^\beta_{\text{el}}$			$(B_0^\beta)^{\text{EXP}}$	$-\Delta B^\beta_{\text{vib}}$	$\Delta B^\beta_{\text{el}}$
CH_2Cl_2					**$CHClF_2$**				
parent	*A*	32002.23(6)[a]	289.383	−0.064	parent	*A*	10234.70311(28)[f,g]	60.426	−0.215
	B	3320.24(4)[a]	14.966	−0.025		*B*	4861.25340(13)[f,g]	20.836	−0.057
	C	3065.19(4)[a]	17.285	−0.031		*C*	3507.43791(10)[f,g]	18.866	−0.050
^{13}C	*A*	30746.54(10)[b]	271.905	−0.065	^{13}C	*A*	10204.19195(41)[f]	59.403	−0.214
	B	3320.66(11)[b]	14.552	−0.025		*B*	4846.02214(21)[f]	20.398	−0.057
	C	3053.48(10)[b]	16.957	−0.031		*C*	3503.34990(24)[f]	18.483	−0.049
D	*A*	27197.75(52)[a]	221.553	−0.056	D	*A*	9804.9203(45)[h]	59.304	−0.199
	B	3305.84(54)[a]	14.978	−0.025		*B*	4749.2119(19)[h]	20.964	−0.055
	C	3027.21(51)[a]	16.852	−0.031		*C*	3500.4025(20)[h]	19.058	−0.049
D_2	*A*	23676.52(16)[a]	179.356	−0.049	^{37}Cl	*A*	10233.85975(28)[f]	60.655	−0.215
	B	3285.08(6)[a]	15.017	−0.025		*B*	4717.14876(12)[f]	20.016	−0.054
	C	2993.98(6)[a]	16.599	−0.030		*C*	3431.84796(10)[f]	18.322	−0.047
^{37}Cl	*A*	31878.65(10)[a]	288.523	−0.060	^{37}ClD	*A*	9803.9417(59)[h]	59.191	−0.199
	B	3231.26(9)[a]	14.498	−0.024		*B*	4610.1091(26)[h]	20.182	−0.052
	C	2988.18(8)[a]	16.721	−0.030		*C*	3424.3312(28)[h]	18.478	−0.047
$^{37}Cl_2$	*A*	31755.7(14)[a]	287.663	−0.057	**pyridine**				
	B	3142.4(16)[a]	14.038	−0.023	parent	*A*	6039.2516(6)[i]	45.557	−0.288
	C	2911.0(14)[a]	16.167	−0.028		*B*	5804.9116(6)[i]	38.880	−0.343
^{37}ClD	*A*	27091.23(65)[a]	220.866	−0.053		*C*	2959.2117(6)[i]	21.980	0.071
	B	3217.01(71)[a]	14.506	−0.024	^{13}C2	*A*	5963.13(4)[j]	44.271	−0.285
	C	2951.23(65)[a]	16.309	−0.029		*B*	5758.90(3)[j]	38.969	−0.332
$^{37}ClD_2$	*A*	23581.80(40)[a]	178.776	−0.046		*C*	2928.96(1)[j]	21.645	0.069
	B	3197.80(42)[a]	14.544	−0.024	^{13}C3	*A*	5956.57(5)[j]	44.168	−0.285
	C	2919.87(37)[a]	16.071	−0.029		*B*	5756.00(4)[j]	38.855	−0.331
glyoxylic acid						*C*	2926.63(1)[j]	21.635	0.069
parent	*A*	10966.8683(18)[c]	107.657	−0.913	^{13}C4	*A*	6039.46(3)[j]	45.333	−0.287
	B	4606.00801(29)[c]	30.374	−0.190		*B*	5676.03(2)[j]	37.790	−0.328
	C	3242.15287(26)[c]	26.197	−0.035		*C*	2925.40(1)[j]	21.603	0.069
DCOCOOH	*A*	10276.7(8)[d]	94.680	−0.798	^{15}N	*A*	6039.45(8)[j]	45.379	−0.306
	B	4573.66(6)[d]	30.337	−0.188		*B*	5680.37(6)[j]	39.712	−0.283
	C	3163.85(6)[d]	24.886	−0.033		*C*	2926.54(2)[j]	21.593	0.066
DCOCOOD	*A*	9777.0(1.0)[d]	91.645	−0.722	D(-C2)	*A*	5900.8828(5)[i]	42.363	−0.312
	B	4569.88(7)[d]	29.270	−0.187		*B*	5558.5214(5)[i]	38.715	−0.282
	C	3113.17(7)[d]	24.230	−0.032		*C*	2861.7137(5)[i]	21.056	0.065
H^{13}COCOOH	*A*	10861.3(7)[d]	104.260	−0.894	D(-C3)	*A*	5889.1923(10)[i]	41.981	−0.288
	B	4577.03(6)[d]	30.288	−0.188		*B*	5555.0518(10)[i]	38.494	−0.300
	C	3218.60(6)[d]	25.827	−0.034		*C*	2858.0310(10)[i]	20.917	0.066
HCOCOOD	*A*	10422.262(136)[e]	103.765	−0.824	D(-C4)	*A*	6039.9967(10)[i]	45.877	−0.288
	B	4600.668(4)[e]	29.239	−0.189		*B*	5420.0697(9)[i]	35.256	−0.328
	C	3190.305(10)[e]	25.477	−0.034		*C*	2855.8194(8)[i]	20.887	0.069
HC^{18}OCOOH	*A*	10965.74(27)[e]	107.467	−0.913					
	B	4349.089(10)[e]	28.743	−0.170					
	C	3112.754(25)[e]	24.995	−0.032					
HCOC^{18}OOH	*A*	10737.525(92)[e]	110.220	−0.880					
	B	4414.702(5)[e]	26.974	−0.173					
	C	3126.948(10)[e]	24.547	−0.032					
HCOCO^{18}OH	*A*	10264.66(13)[e]	95.324	−0.796					
	B	4579.313(7)[e]	31.187	−0.188					
	C	3165.071(18)[e]	25.729	−0.033					
HCO^{13}COOH	*A*	10975.1(9.5)[e]	106.619	−0.913					
	B	4591.17(26)[e]	29.922	−0.188					
	C	3236.77(24)[e]	25.861	−0.034					

References: a) 97; b) 98; c) 99; d) 100; e) 101. f) 102; g) 103; h) 104; i) 105; j) 106;

— Table 2 continued —

		$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B^\beta_{\mathrm{vib}}$	$\Delta B^\beta_{\mathrm{el}}$			$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B^\beta_{\mathrm{vib}}$	$\Delta B^\beta_{\mathrm{el}}$
thiophene					**furan**				
parent	A	8041.77[a]	60.941	0.395	parent	A	9447.1210(10)[i]	80.171	−0.506
	B	5418.12[a]	30.319	0.200		B	9246.7419(10)[i]	65.581	−0.485
	C	3235.77[a]	22.237	−0.087		C	4670.8234(10)[i]	38.812	0.132
C2-D	A	7437.32[a]	53.293	0.338	C2-D	A	9280.3433(14)[i]	68.532	−0.493
	B	5413.61[a]	30.467	0.199		B	8638.6241(14)[i]	67.557	−0.424
	C	3131.82[a]	21.093	−0.081		C	4472.1266(13)[i]	36.228	0.121
C3-D	A	7856.13[a]	58.753	0.376	C3-D	A	9383.709(2)[i]	76.216	−0.502
	B	5138.14[a]	28.174	0.179		B	8490.524(2)[i]	60.352	−0.413
	C	3105.23[a]	20.876	−0.080		C	4455.483(2)[i]	36.059	0.120
C3,C4-D	A	7616.99[a]	56.256	0.355	C2,C3,C4,C5-D	A	8056.5022(9)[i]	53.129	−0.368
	B	4914.50[a]	26.488	0.165		B	7688.0556(9)[i]	58.796	−0.334
	C	2985.99[a]	19.703	−0.074		C	3932.5863(9)[i]	29.701	0.094
C2,C3,C4,C5-D	A	6587.67[a]	44.052	0.265	C2,C5-D	A	9033.6024(7)[i]	62.967	−0.463
	B	4905.66[a]	26.717	0.164		B	8160.7819(6)[i]	64.322	−0.377
	C	2810.88[a]	17.898	−0.065		C	4285.8610(6)[i]	33.882	0.112
^{13}C2	A	7852.89[a]	59.153	0.377	C3,C4-D	A	8819.6010(7)[j]	71.906	−0.440
	B	5418.34[a]	30.065	0.200		B	8248.8750(16)[j]	55.453	−0.387
	C	3204.81[a]	21.913	−0.085		C	4260.5864(9)[j]	33.647	0.110
^{13}C3	A	7981.43[a]	60.096	0.389	^{13}C2	A	9295.41[k]	71.932	−0.496
	B	5319.23[a]	29.645	0.192		B	9178.23[k]	71.068	−0.483
	C	3190.63[a]	21.795	−0.084		C	4616.25[k]	38.157	0.129
^{34}S	A	8042.29[a]	60.811	0.395	^{13}C3	A	9403.73[k]	77.657	−0.503
	B	5274.23[a]	29.301	0.189		B	9043.68[k]	65.289	−0.468
	C	3183.70[a]	21.729	−0.084		C	4608.15[k]	38.037	0.129
***trans*-formic acid**					^{18}O	A	9447.66[k]	79.448	−0.506
parent	A	77512.229(70)[b]	382.599	−12.259		B	8841.72[k]	62.330	−0.443
	B	12055.105(12)[b]	89.219	−0.614		C	4565.37[k]	37.584	0.127
	C	10416.114(11)[b]	90.514	−0.159	***cis*-formic acid**				
H^{13}COOH	A	75580.8793(39)[c]	349.972	−11.660	parent	A	86461.6124(12)[l]	703.100	−22.370
	B	12053.56994(40)[c]	87.955	−0.613		B	11689.18149(16)[l]	68.263	−0.494
	C	10379.0003(35)[c]	89.023	−0.157		C	10283.99126(15)[l]	76.688	−0.129
DCOOH	A	57709.23401(70)[d]	285.853	−6.794	H^{13}COOH	A	84201.819(19)[m]	664.964	−21.255
	B	12055.98357(20)[d]	88.421	−0.614		B	11687.5239(28)[m]	67.273	−0.494
	C	9955.61289(19)[d]	86.322	−0.145		C	10249.6623(28)[m]	75.736	−0.129
D^{13}COOH	A	56787.65(24)[e]	267.974	−6.584	DCOOH	A	62653.4395(87)[m]	506.338	−15.926
	B	12054.043(49)[e]	87.204	−0.613		B	11690.1692(18)[m]	67.547	−0.462
	C	9927.130(53)[e]	84.923	−0.144		C	9837.9145(18)[m]	75.137	−0.121
DC^{18}OOH	A	56979.36(16)[e]	285.918	−6.582	HCOOD	A	83962.785(22)[m]	641.978	−16.062
	B	11397.9890(26)[e]	82.240	−0.546		B	10883.9413(29)[m]	63.614	−0.428
	C	9482.4113(22)[e]	80.919	−0.129		C	9624.9421(29)[m]	69.050	−0.119
DCO^{18}OH	A	57440.16(28)[e]	280.366	−6.756	DCOOD	A	61507.409(11)[m]	475.469	−11.645
	B	11382.628(11)[e]	82.677	−0.550		B	10884.5356(22)[m]	63.016	−0.404
	C	9484.547(13)[e]	81.021	−0.135		C	9237.0082(22)[m]	67.863	−0.112
HCOOD	A	66099.43368(200)[f]	354.903	−9.013	HC^{18}OOH	A	85388.388(35)[m]	704.617	−22.000
	B	11762.55737(28)[f]	82.293	−0.582		B	11058.5903(40)[m]	62.811	−0.417
	C	9969.964321(282)[f]	83.319	−0.146		C	9778.6232(40)[m]	71.078	−0.109
DCOOD	A	50816.53186(135)[f]	267.453	−5.340	HCO^{18}OH	A	85175.320(26)[m]	674.640	−21.353
	B	11759.89095(21)[f]	82.306	−0.581		B	11093.7328(33)[m]	64.293	−0.477
	C	9534.172828(207)[f]	79.699	−0.134		C	9803.3164(33)[m]	71.902	−0.122
HC^{18}OOH	A	76526.465(15)[g]	382.326	−5.181					
	B	11397.1065(25)[g]	83.002	−0.580					
	C	9904.6859(20)[g]	84.636	−0.133					
HCO^{18}OH	A	77201.3076(88)[g]	375.302	−11.887					
	B	11383.7761(18)[g]	83.407	−0.546					
	C	9905.9491(12)[g]	84.751	−0.140					
D^{13}COOD	A	50031.88(44)[h]	255.194	−12.193					
	B	11756.1655(151)[h]	79.142	−0.552					
	C	9503.6307(195)[h]	77.304	−0.146					

References: a) 107; b) 108; c) 109; d) 110; e) 111; f) 112; g) 113; h) 114; i) 115; j) 116; k) 117; l) 118; m) 119.

— Table 2 continued —

		$(B_0^\beta)^{\rm EXP}$	$-\Delta B_{\rm vib}^\beta$	$\Delta B_{\rm el}^\beta$			$(B_0^\beta)^{\rm EXP}$	$-\Delta B_{\rm vib}^\beta$	$\Delta B_{\rm el}^\beta$
dimethyl ether					**aziridine**				
parent	A	38788.162(25)[a]	95.332	−0.656	parent	A	22736.191870(86)[b]	239.356	−0.536
	B	10056.509(6)[a]	152.569	−0.051		B	21192.460228(82)[b]	210.531	0.261
	C	8886.804(5)[a]	118.168	−0.113		C	13383.16422(11)[b]	160.053	0.384
$(CH_3)_2^{18}O$	A	37172.343(19)[a]	67.976	−0.584	ND	A	20678.35(2)[c]	202.187	0.227
	B	10058.257(5)[a]	150.790	−0.051		B	20583.08(2)[c]	212.769	−0.438
	C	8799.546(4)[a]	114.422	−0.110		C	12796.97(2)[c]	151.297	0.358
$^{13}CH_3OCH_3$	A	38615.722(21)[a]	91.384	−0.653	CD_c	A	21832.15(1)[c]	230.958	−0.426
	B	9795.652(5)[a]	147.525	−0.049		B	19088.17(1)[c]	180.236	0.162
	C	8673.639(5)[a]	114.762	−0.107		C	12653.83(1)[c]	144.778	0.343
$CH_3OCH_2D_p$	A	38281.541(38)[a]	144.119	−0.630	CD_t	A	21775.24(1)[c]	228.410	−0.428
	B	9309.206(10)[a]	133.607	−0.044		B	19097.61(1)[c]	183.144	0.167
	C	8277.943(8)[a]	103.791	−0.097		C	12689.57(1)[c]	147.727	0.336
$CH_3OCH_2D_o$	A	34764.242(38)[a]	102.011	−0.539	^{15}N	A	22046.37(2)[c]	227.066	−0.500
	B	9642.43(10)[a]	142.030	−0.048		B	21186.75(2)[c]	210.353	0.262
	C	8537.205(8)[a]	111.994	−0.103		C	13142.74(2)[c]	155.663	0.371
$CH_3OCD_2H_p$	A	31492.884(32)[a]	102.924	−0.450	^{13}C	A	22600.73(1)[c]	236.688	−0.513
	B	9226.434(8)[a]	134.645	−0.043		B	20684.72(1)[c]	202.542	0.233
	C	8256.869(7)[a]	106.687	−0.098		C	13132.66(1)[c]	155.582	0.369
$CH_3OCD_2H_o$	A	34199.914(32)[a]	141.378	−0.515	^{15}ND	A	20685.03(2)[c]	201.726	0.229
	B	8976.858(8)[a]	125.761	−0.042		B	20051.67(2)[c]	203.202	−0.411
	C	7984.112(7)[a]	99.388	−0.090		C	12596.36(2)[c]	147.583	0.348
CH_3OCD_3	A	30912.357(24)[a]	134.370	−0.428	CD_2	A	20883.91(1)[c]	218.466	−0.368
	B	8635.549(6)[a]	120.939	−0.038		B	17299.26(1)[c]	160.331	0.111
	C	7747.481(6)[a]	95.436	−0.086		C	12116.01(1)[c]	136.870	0.311
$^{13}CH_3OCD_3$	A	30795.899(34)[a]	131.582	−0.428	**pyrrole**				
	B	8414.195(9)[a]	117.142	−0.036	parent	A	9130.63231(96)[d]	74.754	−0.480
	C	7561.704(8)[a]	92.823	−0.082		B	9001.36348(93)[d]	69.949	−0.336
$CH_3^{18}OCD_3$	A	29779.220(32)[a]	113.732	−0.386		C	4532.10977(97)[d]	37.193	0.181
	B	8633.634(8)[a]	119.521	−0.038	^{15}N	A	9131.09(2)[e]	74.362	−0.480
	C	7672.081(7)[a]	92.572	−0.084		B	8807.26(2)[e]	68.696	−0.323
$CH_3O^{13}CD_3$	A	30847.90(45)[a]	131.995	−0.429		C	4482.47(2)[e]	36.748	0.176
	B	8469.347(11)[a]	117.954	−0.036	$^{13}C2$	A	9021.879(12)[e]	70.876	−0.371
	C	7609.406(9)[a]	93.403	−0.083		B	8892.736(12)[e]	71.106	−0.421
$(CD_3)_2O$	A	25696.425(10)[a]	143.467	−0.305		C	4477.737(12)[e]	36.526	0.176
	B	7483.852(3)[a]	97.076	−0.028	$^{13}C3$	A	9099.129(9)[e]	73.507	−0.453
	C	6798.089(2)[a]	78.750	−0.067		B	8803.137(9)[e]	68.494	−0.341
$CD_3OCH_2D_p$	A	30632.923(36)[a]	162.801	−0.374		C	4473.678(9)[e]	36.499	0.176
	B	8024.522(12)[a]	106.955	−0.032	N-D	A	9130.77(2)[e]	74.686	−0.480
	C	7239.067(8)[a]	84.498	−0.076		B	8340.83(2)[e]	59.866	−0.290
$CD_3OCH_2D_o$	A	28274.150(33)[a]	129.082	−0.359		C	4358.66(2)[e]	34.070	0.166
	B	8306.515(10)[a]	113.255	−0.033	C2-D	A	9018.39(3)[e]	70.939	−0.357
	C	7460.470(7)[a]	91.182	−0.075		B	8361.84(3)[e]	64.612	−0.385
$CD_3OCD_2H_p$	A	26050.220(17)[a]	123.646	−0.353		C	4338.30(3)[e]	34.707	0.165
	B	7976.282(5)[a]	107.283	−0.032	C3-D	A	9089.06(2)[e]	73.422	−0.436
	C	7226.842(4)[a]	87.469	−0.075		B	8272.45(2)[e]	62.384	−0.313
$CD_3OCD_2H_o$	A	27945.018(22)[a]	151.724	−0.364		C	4330.20(2)[e]	34.701	0.165
	B	7757.271(6)[a]	101.425	−0.033					
	C	6996.412(5)[a]	81.417	−0.075					
$^{13}CD_3OCD_3$	A	25649.234(31)[a]	141.550	−0.305					
	B	7338.549(13)[a]	94.573	−0.027					
	C	6674.675(9)[a]	76.949	−0.064					

Subscripts c and t stand for *c*is and *t*rans, respectively. Subscripts p and o stand for in *p*lane and *o*ut of plane, respectively.
References: a) 120; b) 121; c) 122; d) 123. e) 124.

		$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B^\beta_{\mathrm{vib}}$	$\Delta B^\beta_{\mathrm{el}}$
maleic-anhydride				
parent	A	6842.486(13)[a]	49.339	−0.422
	B	2467.614(8)[a]	13.915	−0.067
	C	1813.627(8)[a]	11.037	−0.015
D_2	A	6106.159(7)[a]	41.481	−0.376
	B	2423.551(3)[a]	13.629	−0.066
	C	1734.998(3)[a]	10.377	−0.014
^{13}C2	A	6841.501(33)[a]	48.988	−0.422
	B	2452.607(9)[a]	13.741	−0.066
	C	1805.442(6)[a]	10.911	−0.015
^{13}C3	A	6691.282(23)[a]	47.678	−0.412
	B	2462.240(6)[a]	13.868	−0.067
	C	1799.954(5)[a]	10.920	−0.015
^{18}O1	A	6688.643(24)[a]	48.814	−0.412
	B	2467.808(8)[a]	13.679	−0.067
	C	1802.755(5)[a]	10.886	−0.015
^{18}O6	A	6790.337(44)[a]	48.929	−0.419
	B	2354.397(11)[a]	13.141	−0.064
	C	1748.276(8)[a]	10.543	−0.014
^{13}C2,D_2	A	6104.567(25)[a]	41.177	−0.376
	B	2409.078(8)[a]	13.459	−0.065
	C	1727.440(5)[a]	10.260	−0.014
^{13}C3,D_2	A	5993.203(28)[a]	40.213	−0.369
	B	2418.373(7)[a]	13.579	−0.065
	C	1723.126(5)[a]	10.264	−0.014
^{18}O1,D_2	A	5971.996(16)[a]	40.935	−0.368
	B	2423.742(6)[a]	13.442	−0.066
	C	1724.104(4)[a]	10.244	−0.014
^{18}C6,D_2	A	6058.195(14)[a]	40.923	−0.373
	B	2314.121(5)[a]	12.926	−0.063
	C	1674.540(3)[a]	9.939	−0.014
pyrazole				
parent	A	9618.77584(85)[b]	78.631	−0.412
	B	9412.54381(82)[b]	79.175	−0.676
	C	4755.85007(98)[b]	41.264	0.164
D(-N1)	A	9455.230(5)[c]	80.590	−0.643
	B	8859.733(5)[c]	65.804	−0.382
	C	4572.847(4)[c]	37.819	0.151
D(-C3)	A	9435.783(4)[c]	77.067	−0.613
	B	8774.190(4)[c]	70.857	−0.396
	C	4545.189(3)[c]	38.560	0.150
D-(C4)	A	9566.176(10)[c]	81.191	−0.502
	B	8617.847(9)[c]	66.417	−0.488
	C	4532.324(9)[c]	38.263	0.149
D-(C5)	A	9537.304(4)[c]	75.909	−0.470
	B	8677.868(3)[c]	71.457	−0.521
	C	4542.381(3)[c]	38.438	0.149
^{15}N1	A	9488.641(4)[c]	80.741	−0.543
	B	9339.851(4)[c]	75.229	−0.526
	C	4705.424(4)[c]	40.755	0.161
^{15}N2	A	9618.304(4)[c]	77.934	−0.411
	B	9180.010(4)[c]	76.959	−0.643
	C	4695.610(3)[c]	40.514	0.160
^{13}C3	A	9457.566(6)[c]	75.059	−0.524
	B	9340.099(6)[c]	79.714	−0.539
	C	4697.835(6)[c]	40.496	0.160
^{13}C4	A	9582.358(6)[c]	79.894	−0.463
	B	9193.394(8)[c]	74.867	−0.594
	C	4690.511(8)[c]	40.439	0.159
^{13}C5	A	9571.674(5)[c]	76.019	−0.425
	B	9223.004(5)[c]	78.614	−0.634
	C	4695.634(4)[c]	40.478	0.159

		$(B_0^\beta)^{\mathrm{EXP}}$	$-\Delta B^\beta_{\mathrm{vib}}$	$\Delta B^\beta_{\mathrm{el}}$
***cis*-hexatriene**				
parent	A	14651.2292(7)[d]	190.342	−1.325
	B	1583.1814(1)[d]	6.941	−0.021
	C	1429.4619(1)[d]	6.827	0.003
^{13}C1	A	14606.201(1)[d]	190.557	−1.321
	B	1543.538(1)[d]	6.724	−0.020
	C	1396.6539(4)[d]	6.632	0.003
^{13}C2	A	14581.503(1)[d]	187.643	−1.319
	B	1571.686(1)[d]	6.889	−0.021
	C	1419.4331(4)[d]	6.758	0.003
^{13}C3	A	14411.130(3)[d]	185.878	−1.304
	B	1580.989(1)[d]	6.895	−0.021
	C	1425.3504(7)[d]	6.794	0.003
D_2(-C1)	A	13898.545(3)[e]	173.335	−1.256
	B	1475.897(1)[e]	6.354	−0.020
	C	1334.859(1)[e]	6.183	0.003
D_{trans}(-C1)	A	14072.587(2)[e]	183.904	−1.272
	B	1524.966(2)[e]	6.522	−0.020
	C	1376.482(1)[e]	6.484	0.003
D_{cis}(-C1)	A	14494.602(5)[e]	181.545	−1.310
	B	1528.795(4)[e]	6.765	−0.020
	C	1383.628(3)[e]	6.532	0.003
D(-C2)	A	13871.177(2)[e]	181.805	−1.254
	B	1577.942(1)[e]	6.612	−0.021
	C	1417.502(1)[e]	6.531	0.003
D(-C3)	A	13512.527(4)[e]	156.783	−1.220
	B	575.8974(5)[e]	7.350	−0.021
	C	411.9484(6)[e]	7.008	0.003
imidazole				
parent	A	9725.326(12)[f]	79.977	−0.524
	B	9374.011(12)[f]	73.551	−0.559
	C	4771.928(12)[f]	40.060	0.158
D(-N1)	A	9668.881(20)[f]	79.708	−0.579
	B	8699.529(18)[f]	62.798	−0.434
	C	4578.384(18)[f]	36.648	0.144
D(-C2)	A	9388.993(26)[f]	73.275	−0.522
	B	8896.784(26)[f]	70.580	−0.473
	C	4566.963(24)[f]	37.484	0.145
D(-C4)	A	9486.409(48)[f]	77.266	−0.620
	B	8778.562(36)[f]	66.602	−0.382
	C	4558.162(26)[f]	37.374	0.145
D(-C5)	A	9586.929(42)[f]	76.666	−0.456
	B	8684.701(30)[f]	66.652	−0.524
	C	4555.635(20)[f]	37.197	0.143
^{15}N1	A	9695.278(26)[f]	79.760	−0.554
	B	9188.170(26)[f]	71.877	−0.510
	C	4716.172(22)[f]	39.532	0.154
^{15}N3	A	9721.546(22)[f]	79.361	−0.511
	B	9135.778(22)[f]	71.311	−0.540
	C	4708.472(18)[f]	39.284	0.155
^{13}C2	A	9522.309(62)[f]	76.662	−0.461
	B	9354.007(62)[f]	73.960	−0.596
	C	4717.455(62)[f]	39.352	0.155
^{13}C4	A	9573.922(60)[f]	78.712	−0.580
	B	9286.009(60)[f]	71.878	−0.477
	C	4712.609(56)[f]	39.311	0.155
^{13}C5	A	9632.227(74)[f]	77.525	−0.469
	B	9225.537(62)[f]	72.981	−0.584
	C	4710.987(54)[f]	39.298	0.154
D(-N1),D(-C2)	A	8941.68(20)[f]	70.949	−0.545
	B	8631.60(20)[f]	62.252	−0.380
	C	4390.68(20)[f]	34.451	0.133

References: a) 125; b) 126; c) 127; d) 128; e) 129; f) 130.

— Table 2 continued —

		$(B_0^\beta)^{\rm EXP}$	$-\Delta B_{\rm vib}^\beta$	$\Delta B_{\rm el}^\beta$			$(B_0^\beta)^{\rm EXP}$	$-\Delta B_{\rm vib}^\beta$	$\Delta B_{\rm el}^\beta$
butadiene					**ethene**				
parent	A	41682.658(21)[a]	419.959	−6.402	parent	A	145837.641(1)[f]	1497.895	−35.042
	B	4433.504(3)[a]	27.421	−0.106		B	30010.919(1)[f]	199.069	−1.998
	C	4008.042(6)[a]	25.936	0.020		C	24824.194(1)[f]	247.042	0.616
^{13}C1	A	41634.934(18)[b]	419.929	−6.386	$H_2^{13}CCH_2$	A	145835.5(1.7)[g]	1495.376	−35.042
	B	4307.067(9)[b]	26.460	−0.100		B	29263.1(7)[g]	191.781	−1.900
	C	3904.050(9)[b]	25.081	0.019		C	24309.6(7)[g]	238.692	0.590
^{13}C2^{13}C3	A	40607.152(21)[c]	397.827	−6.079	$HDCCH_2$	A	120093.521(70)[h]	1108.958	−23.763
	B	4405.162(3)[c]	26.884	−0.104		B	27470.737(26)[h]	172.930	−1.667
	C	3974.762(6)[c]	25.378	0.020		C	22297.745(14)[h]	213.212	0.496
D_2(-C1)	A	36599.086(12)[a]	357.859	−4.915	D_2CCH_2	A	97496.7(1.8)[h]	801.171	−15.587
	B	4041.9524(9)[a]	23.709	−0.088		B	25675.260(44)[h]	156.800	−1.457
	C	3640.6340(9)[a]	22.436	0.017		C	20268.791(40)[h]	188.560	0.410
D(-C2)D(-C3)	A	30589.695(15)[d]	265.758	−3.428	*cis*-HDCCHD	A	99667.262(89)[h]	872.687	−16.308
	B	4415.250(9)[d]	26.939	−0.105		B	25417.208(41)[h]	148.820	−1.427
	C	3858.848(9)[d]	24.672	0.019		C	20199.073(24)[h]	184.854	0.406
D_t(-C1)D_t(-C4)	A	40165.531(18)[e]	399.641	−5.940	D_2CCD_2	A	73199.01(60)[i]	555.820	−8.773
	B	3918.248(6)[e]	23.756	−0.082		B	22032.1(2)[i]	127.017	−1.069
	C	3570.792(6)[e]	22.428	0.016		C	16893.8(2)[i]	146.799	0.284
D_c(-C1)D_c(-C4)	A	34172.553(18)[e]	340.570	−4.283					
	B	4137.607(9)[e]	22.899	−0.092					
	C	3691.350(9)[e]	21.930	0.017					
D_c(-C1)D_t(-C4)	A	36713.688(21)[e]	367.655	−4.948					
	B	4029.630(21)[e]	23.260	−0.087					
	C	3631.695(18)[e]	22.172	0.017					

Subscripts c and t stand for *c*is and *t*rans, respectively.
References: a) 131; b) 132; c) 133; d) 134; e) 135; f) 136; g) 137; h) 138; i) 139.

Table 3: $(B_0^\beta)^{\rm EXP}$, B3LYP/SNSD $\Delta B_{\rm vib}^\beta$ and $\Delta B_{\rm el}^\beta$ ($g^{\beta\beta}$ at the B3LYP/AVTZ level) contributions for fluoropyridines. All data are in MHz.

		$(B_0^\beta)^{\rm EXP}$	$-\Delta B_{\rm vib}^\beta$	$\Delta B_{\rm el}^\beta$			$(B_0^\beta)^{\rm EXP}$	$-\Delta B_{\rm vib}^\beta$	$\Delta B_{\rm el}^\beta$
2-fluoropyridine					**3-fluoropyridine**				
parent	A	5870.88105(19)[a]	43.805	−0.303	parent	A	5829.70195(13)[a]	42.639	−0.312
	B	2699.98571(10)[a]	15.801	−0.067		B	2637.49103(7)[a]	14.761	−0.073
	C	1849.24259(7)[a]	12.051	0.022		C	1815.65619(6)[a]	11.494	0.019
^{15}N	A	5779.4641(3)[a]	42.767	−0.293	^{15}N	A	5737.4876(4)[a]	41.682	−0.301
	B	2699.09638(11)[a]	15.735	−0.066		B	2617.99299(21)[a]	14.572	−0.072
	C	1839.65857(11)[a]	11.936	0.021		C	1797.43686(17)[a]	11.321	0.018
^{13}C2	A	5871.2147(7)[a]	43.458	−0.303	^{13}C2	A	5738.82484(21)[a]	41.858	−0.302
	B	2690.64398(18)[a]	15.599	−0.066		B	2637.31634(11)[a]	14.666	−0.073
	C	1844.89037(16)[a]	11.915	0.022		C	1806.66088(9)[a]	11.939	0.019
^{13}C3	A	5769.5965(6)[a]	42.888	−0.293	^{13}C3	A	5829.97704(27)[a]	42.369	−0.312
	B	2699.73699(18)[a]	15.715	−0.067		B	2627.64595(15)[a]	14.555	−0.072
	C	1838.95575(15)[a]	11.941	0.021		C	1811.01379(12)[a]	11.361	0.019
^{13}C4	A	5778.6121(5)[a]	42.875	−0.293	^{13}C4	A	5729.26706(24)[a]	41.673	−0.302
	B	2677.95903(17)[a]	15.608	−0.066		B	2636.95880(13)[a]	14.688	−0.073
	C	1829.72561(16)[a]	11.878	0.021		C	1805.54353(11)[a]	11.388	0.018
^{13}C5	A	5870.8586(6)[a]	43.598	−0.303	^{13}C5	A	5734.58904(29)[a]	41.689	−0.304
	B	2650.54112(20)[a]	15.498	−0.064		B	2618.25406(16)[a]	14.612	−0.071
	C	1825.91289(20)[a]	11.856	0.021		C	1797.27550(13)[a]	11.342	0.018
^{13}C6	A	5775.7229(5)[a]	42.884	−0.294	^{13}C6	A	5829.94366(25)[a]	42.363	−0.312
	B	2682.96409(16)[a]	15.617	−0.066		B	2592.19215(13)[a]	14.510	−0.070
	C	1831.77113(16)[a]	11.887	0.021		C	1794.09782(11)[a]	11.315	0.018

References: a) 140;

Table 4: $(B_0^\beta)^{\rm EXP}$, $\Delta B_{\rm vib}^\beta$ and $\Delta B_{\rm el}^\beta$ ($g^{\beta\beta}$ at the B3LYP/AVTZ level) for *trans*-1-chloro-2-fluoroethylene. All data are in MHz.

***trans*-CHFCHCl**		$(B_0^\beta)^{\rm EXP}$	$-\Delta B_{\rm vib}^\beta$		$\Delta B_{\rm el}^\beta$
			CCSD(T)/VTZ[a]	B3LYP/SNSD	
parent	A	53655.7296(13)[b]	542.590	505.722	−4.615
	B	2476.60705(40)[b]	9.530	9.372	−0.034
	C	2366.41041(45)[b]	10.672	10.430	−0.015
$CDF{=}CD^{35}Cl$	A	36119.5308(18)[b]	299.024	280.102	−2.089
	B	2466.1772(27)[b]	9.466	9.340	−0.033
	C	2307.5064(12)[b]	10.534	10.325	−0.015
$CDF{=}CH^{35}Cl$	A	43786.717(19)[b]	427.869	397.209	−3.084
	B	2466.640(20)[b]	9.222	9.085	−0.033
	C	2334.144(20)[b]	10.429	10.200	−0.015
$CHF{=}CD^{35}Cl$	A	42810.6833(22)[b]	340.527	318.286	−2.920
	B	2476.0507(34)[b]	9.694	9.544	−0.034
	C	2339.6221(43)[b]	10.706	10.478	−0.015
$CHF{=}CH^{37}Cl$	A	53612.9224(17)[b]	541.505	504.437	−4.605
	B	2415.96632(38)[b]	9.268	9.111	−0.032
	C	2310.90479(41)[b]	10.359	10.122	−0.015
$CDF{=}CD^{37}Cl$	A	36093.02672(63)[b]	298.529	279.833	−2.084
	B	2405.054(7)[b]	9.202	9.077	−0.032
	C	2253.834(7)[b]	10.227	10.022	−0.014
$CDF{=}CH^{37}Cl$	A	43763.8174(32)[b]	427.607	397.036	−3.080
	B	2405.669(85)[b]	8.962	8.828	−0.032
	C	2279.400(85)[b]	10.118	9.896	−0.014
$CHF{=}CD^{37}Cl$	A	42766.8580(24)[b]	339.312	317.071	−2.910
	B	2415.2413(42)[b]	9.430	9.284	−0.032
	C	2285.1521(42)[b]	10.399	10.178	−0.014

a) CCSD(T) $\Delta B_{\rm vib}^\beta$ from ref. 64.
b) $(B_0^\beta)^{\rm EXP}$ from ref. 141.

Table 5: $(B_0^\beta)^{\rm EXP}$, B3LYP/SNSD $\Delta B_{\rm vib}^\beta$ and $\Delta B_{\rm el}^\beta$ ($g^{\beta\beta}$ at the B3LYP/AVTZ level) for pyrimidine. All data are in MHz.

pyrimidine		$(B_0^\beta)^{\rm EXP}$	$-\Delta B_{\rm vib}^\beta$	$\Delta B_{\rm el}^\beta$
parent	A	6276.82802(19)[a]	45.041	−0.342
	B	6067.16590(18)[a]	41.001	−0.402
	C	3084.44917(17)[a]	22.396	0.051
^{13}C2	A	6152.684(4)[a]	43.954	−0.328
	B	6067.554(3)[a]	40.641	−0.402
	C	3054.27(2)[a]	22.043	0.050
^{13}C4	A	6256.102(4)[a]	44.429	−0.343
	B	5957.231(4)[a]	40.203	−0.384
	C	3050.846(8)[a]	22.024	0.050
^{13}C5	A	6132.820(3)[a]	43.775	−0.327
	B	6067.375(2)[a]	40.807	−0.402
	C	3049.33(3)[a]	22.041	0.050
^{15}N	A	6253.962(4)[a]	44.517	−0.343
	B	5954.185(4)[a]	40.111	−0.383
	C	3049.541(7)[a]	22.018	0.050

a) $(B_0^\beta)^{\rm EXP}$ from ref. 142.

Table 6: Comparison between the r_0 and r_e^{SE} geometries estimated using $\Delta B_{\mathrm{vib}}^{\beta}$ from CCSD(T), MP2, B3LYP/SNSD and B3LYP/AVTZ cubic force fields. Distances in Å, angles in degrees.

	r_e^{SE}	Δr_e^{SE}			Δr_0
	CCSD(T)	MP2	B3LYP/SNSD	B3LYP/AVTZ	
		– linear molecules –			
HCN^a					
r(H-C)	$1.0651^{\times,\dagger}$	$+0.0001^{\times,\dagger}$	$-0.0006^{\dagger}$	$-0.0007^{\dagger}$	-0.0027
r(C-N)	1.1533	-0.0004	$+0.0003$	$+0.0002$	$+0.0035$
HNC^a					
r(H-N)	$0.9954^{\times,\dagger}$	$-0.0011^{\times,\dagger}$	$-0.0008^{\dagger}$	$-0.0001^{\dagger}$	-0.0091
r(N-C)	1.1685	$+0.0001$	$+0.0003$	$+0.0002$	$+0.0040$
HCO$^+$					
r(H-C)	$1.0919^{\times,\dagger}$	$+0.0002^{\times,\dagger}$	$-0.0003^{\dagger}$	$-0.0004^{\dagger}$	$+0.0002$
r(C-O)	1.1057	-0.0002	$+0.0000$	$+0.0001$	$+0.0034$
HNCCN^{+b}					
r(H-N)	$1.0133^{\asymp,\dagger}$	$+0.0002^{\times,\dagger}$	$+0.0005^{\dagger}$	$+0.0000^{\dagger}$	-0.0075
r(N-C)	1.1406	-0.0007	-0.0014	-0.0004	-0.0006
r(C-C)	1.3724	$+0.0006$	$+0.0011$	$+0.0005$	$+0.0038$
r(C-N)	1.1634	-0.0013	-0.0027	-0.0008	-0.0050
HCCH^c					
r(C≡C)	$1.2030^{+,\dagger}$	$-0.0004^{\div,\dagger}$	$+0.0006^{\dagger}$	$+0.0005^{\dagger}$	$+0.0054$
r(C-H)	1.0617	$+0.0003$	-0.0006	-0.0010	-0.0045
HCCCCH^d					
r(C≡C)	$1.2084^{\times,\dagger}$	$-0.0007^{\div,\dagger}$	$-0.0014^{\dagger}$	$-0.0003^{\dagger}$	-0.0005
r(C-C)	1.3727	$+0.0009$	-0.0001	$+0.0005$	$+0.0024$
r(C-H)	1.0615	$+0.0008$	-0.0005	-0.0008	-0.0054
		– symmetric top molecules –			
SH$_3^{+e}$					
r(S-H)	$1.3500^{+,\dagger}$	$+0.0003^{\times,\dagger}$	$+0.0002^{\dagger}$	$+0.0001^{\dagger}$	$+0.0063$
a(H-S-H)	94.15	$+0.02$	-0.04	-0.04	$+0.04$
NH$_3{}^a$					
r(N-H)	$1.0110^{\times,\dagger}$	$+0.0003^{\times,\dagger}$	$+0.0001^{\dagger}$	$+0.0003^{\dagger}$	$+0.0040$
a(H-N-H)	106.94	-0.04	-0.07	-0.10	$+0.58$
H$_2$CCCH$_2$					
r(C=C)	$1.3066^{\div,\dagger}$	$+0.0001^{\div,\dagger}$	$+0.0009^{\dagger}$	$+0.0004^{\dagger}$	$+0.0030$
r(C-H)	1.0807	$+0.0001$	-0.0007	-0.0002	$+0.0026$
a(H-C-H)	118.26	$+0.02$	$+0.11$	$+0.09$	$+0.30$
		– asymmetric top molecules –			
H$_2$O^a					
r(O-H)	$0.9573^{\times,\dagger}$	$+0.0001^{\times,\dagger}$	$-0.0001^{\dagger}$	$+0.0002^{\dagger}$	-0.0006
a(H-O-H)	104.53	-0.00	-0.06	-0.06	$+0.40$

Graphical symbols denote: ÷ VTZ; ≍ VQZ; × CVQZ; + wCVQZ, † the inclusion of $\Delta B_{\mathrm{el}}^{\beta}$.

a) CCSD(T) $\Delta B_{\mathrm{vib}}^{\beta}$ from ref. 27.

b) CCSD(T) $\Delta B_{\mathrm{vib}}^{\beta}$ from ref. 28.

c) CCSD(T) $\Delta B_{\mathrm{vib}}^{\beta}$ from ref. 26.

d) CCSD(T) and MP2 $\Delta B_{\mathrm{vib}}^{\beta}$ from ref. 15.

e) CCSD(T) $\Delta B_{\mathrm{vib}}^{\beta}$ from ref. 48.

— Table 6 continued —

	r_e^{SE}	Δr_e^{SE}			Δr_0
	CCSD(T)	MP2	B3LYP/SNSD	B3LYP/AVTZ	
H_2CO[a]					
r(O-C)	$1.2047^{\times,\dagger}$	$+0.0000^{\times,\dagger}$	$+0.0004^{\dagger}$	$+0.0004^{\dagger}$	+0.0048
r(C-H)	1.1003	+0.0004	−0.0001	−0.0002	+0.0061
a(H-C-O)	121.65	+0.00	−0.03	−0.03	+0.01
CH_2ClF[b]					
r(C-H)	$1.0840^{\ddagger,\dagger}$	$+0.0005^{\div,\dagger}$	$+0.0002^{\dagger}$	$+0.0004^{\dagger}$	+0.0051
r(C-F)	1.3594	+0.0001	−0.0003	−0.0002	+0.0112
r(C-Cl)	1.7641	−0.0001	+0.0004	+0.0003	−0.0028
a(H-C-Cl)	107.96	+0.01	−0.03	+0.01	+1.38
a(H-C-H)	112.57	−0.05	−0.02	−0.01	−2.36
a(F-C-Cl)	110.02	+0.01	+0.00	+0.01	+0.16
CH_2CHF[c]					
r(C1-F)	$1.3424^{\div,\dagger}$	$+0.0001^{\div,\dagger}$	$-0.0012^{\dagger}$	$-0.0004^{\div,\dagger}$	+0.0150
r(C1-H)	1.0792	+0.0001	−0.0008	−0.0011	+0.0129
r(C1-C2)	1.3213	+0.0000	+0.0021	+0.0011	−0.0044
r(C2-H_{trans})	1.0772	+0.0003	−0.0004	+0.0002	+0.0002
r(C2-H_{cis})	1.0785	+0.0002	−0.0003	−0.0005	+0.0069
a(F-C1-H)	112.10	+0.00	+0.26	+0.35	−4.40
a(F-C1-C2)	121.72	−0.02	−0.04	−0.04	−0.15
a(C1-C2-H_{trans})	118.95	+0.00	−0.01	−0.06	−0.12
a(C1-C2-H_{cis})	121.32	+0.03	−0.03	−0.02	−0.30
***cis*-CHFCHCl**[d]					
r(C1-Cl)	$1.7129^{\div,\dagger}$	$-0.0001^{\div,\dagger}$	$-0.0005^{\dagger}$	$-0.0001^{\div,\dagger}$	+0.0142
r(C1-H)	1.0795	−0.0003	+0.0000	−0.0018	+0.0314
r(C1=C2)	1.3244	+0.0003	+0.0022	+0.0014	−0.0082
r(C2-F)	1.3313	−0.0001	−0.0007	−0.0005	+0.0050
r(C2-H)	1.0796	−0.0001	−0.0020	−0.0009	+0.0062
a(Cl-C1=C2)	123.08	−0.01	+0.00	−0.02	+0.05
a(H-C1=C2)	121.08	−0.07	−0.02	−0.30	+5.80
a(F-C2=C1)	122.56	+0.00	−0.09	−0.03	−0.29
a(H-C2=C1)	123.49	−0.02	−0.16	−0.11	+0.67
oxirane[e]					
r(C-C)	$1.4609^{\div,\dagger}$	$+0.0001^{\div,\dagger}$	$+0.0006^{\dagger}$	$+0.0006^{\dagger}$	+0.0111
r(C-O)	1.4274	+0.0000	+0.0007	+0.0007	+0.0083
r(C-H)	1.0816	+0.0003	−0.0002	−0.0004	+0.0007
a(C-O-C)	61.56	+0.00	−0.01	−0.01	+0.11
a(H-C-H)	116.25	−0.02	+0.08	+0.10	+0.38
a(H-C-O)	114.87	+0.01	−0.05	−0.05	−0.12

Graphical symbols denote: ÷ VTZ; ‡ CVTZ, † the inclusion of $\Delta B^{\beta}_{\mathrm{el}}$.

a) CCSD(T) $\Delta B^{\beta}_{\mathrm{vib}}$ from ref. 27.

b) CCSD(T) $\Delta B^{\beta}_{\mathrm{vib}}$ from ref. 60.

c) MP2 $\Delta B^{\beta}_{\mathrm{vib}}$ from ref. 64.

d) CCSD(T) and MP2 $\Delta B^{\beta}_{\mathrm{vib}}$ from ref. 64.

e) CCSD(T) $\Delta B^{\beta}_{\mathrm{vib}}$ from ref. 68.

— Table 6 continued —

	r_e^{SE}	Δr_e^{SE}			Δr_0
	CCSD(T)	MP2	B3LYP/SNSD	B3LYP/AVTZ	
dioxirane[a]					
r(C-O)	1.3846$^{\div}$	+0.0000$^{\div,\dagger}$	+0.0004†	+0.0003†	+0.0068
r(O-O)	1.5133	+0.0014	+0.0007	+0.0011	+0.0059
r(C-H)	1.0853	+0.0001	−0.0003	−0.0002	−0.0016
a(H-C-H)	117.03	−0.06	+0.03	+0.02	−0.33
***trans*-glyoxal**[b]					
r(C=O)	1.2046$^{\div,\dagger}$	+0.0001$^{\div,\dagger}$	+0.0005†	+0.0003†	+0.0084
r(C-C)	1.5157	−0.0004	−0.0008	−0.0009	+0.0002
r(C-H)	1.1006	+0.0000	+0.0000	+0.0001	+0.0025
a(H-C-C)	115.23	+0.14	+0.14	+0.19	+0.19
a(O=C-H)	123.60	−0.14	−0.15	−0.20	+0.20
***cis*-acrolein**					
r(C1-C2)	1.4806$^{\div,\dagger}$	+0.0002$^{\div,\dagger}$	+0.0003†	+0.0005†	+0.0078
r(C2-C3)	1.3350	+0.0001	+0.0018	+0.0014	+0.0039
r(C1-O)	1.2108	+0.0004	−0.0006	+0.0000	+0.0016
r(C1-H)	1.1024	−0.0002	−0.0003	−0.0009	+0.0023
r(C2-H)	1.0824	+0.0000	−0.0017	−0.0014	+0.0040
r(C3-H8)	1.0808	+0.0012	−0.0008	+0.0003	+0.0176
r(C3-H7)	1.0797	+0.0003	−0.0011	−0.0009	−0.0001
a(C1-C2-C3)	121.21	+0.01	+0.12	−0.09	+0.18
a(O-C1-C2)	123.96	−0.01	−0.08	+0.11	+0.10
a(C2-C1-H)	115.83	−0.01	−0.02	+0.02	−0.50
a(C3-C2-H)	121.57	+0.04	+0.06	+0.05	−0.25
a(C2-C3-H_{cis})	119.85	−0.06	+0.01	−0.07	−1.26
a(C2-C3-H_{trans})	121.61	−0.01	+0.05	−0.01	−0.12
***trans*-acrolein**					
r(C1-C2)	1.4702$^{\div,\dagger}$	+0.0002$^{\div,\dagger}$	+0.0001†	−0.0004†	+0.0101
r(C2-C3)	1.3354	+0.0006	+0.0001	+0.0006	+0.0039
r(C1-O)	1.2103	+0.0003	+0.0006	+0.0006	+0.0019
r(C1-H)	1.1048	+0.0002	−0.0004	−0.0002	+0.0048
r(C2-H)	1.0814	+0.0001	+0.0003	+0.0001	−0.0005
r(C3-H7)	1.0825	+0.0001	+0.0001	+0.0000	+0.0047
r(C3-H8)	1.0795	−0.0001	−0.0003	−0.0004	+0.0038
a(C1-C2-C3)	120.18	+0.00	+0.03	+0.04	+0.00
a(O-C1-C2)	124.02	−0.02	−0.05	−0.03	−0.36
a(C2-C1-H)	115.08	−0.09	+0.03	+0.02	−0.38
a(C3-C2-H)	122.78	+0.03	+0.07	+0.06	+0.01
a(C2-C3-H_{cis})	120.46	+0.02	−0.02	−0.03	−0.55
a(C2-C3-H_{trans})	122.10	+0.02	−0.03	−0.05	−0.39

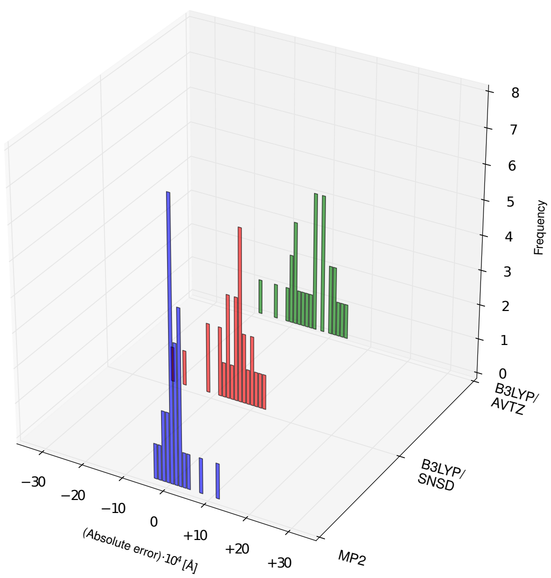
Graphical symbols denote: ÷ VTZ, † the inclusion of $\Delta B^{\beta}_{\mathrm{el}}$.
a) CCSD(T) r_e^{SE} from ref. 69.
b) CCSD(T) $\Delta B^{\beta}_{\mathrm{vib}}$ from ref. 67.

— Table 6 continued —

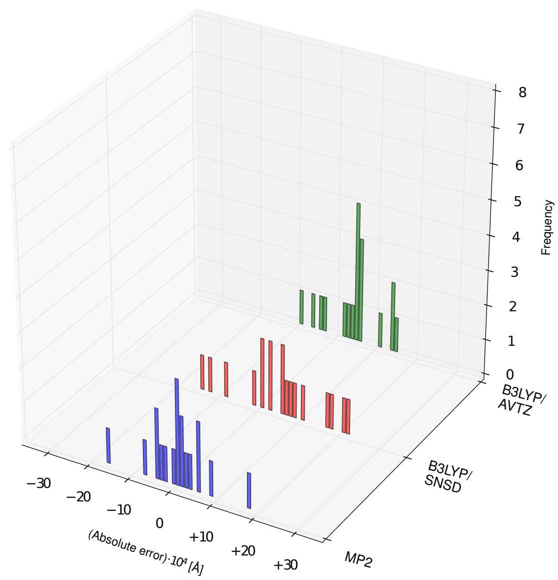
	r_e^{SE}	Δr_e^{SE}			Δr_0
	CCSD(T)	MP2	B3LYP/SNSD	B3LYP/AVTZ	
cyclobutene					
r(C1=C2)	$1.3406^{\div,\dagger}$	$-0.0003^{\dagger}$	$+0.0003^{\dagger}$	$+0.0002^{\dagger}$	+0.0072
r(C2-C3)	1.5141	+0.0004	+0.0008	+0.0006	+0.0069
r(C3-C4)	1.5639	−0.0002	+0.0007	+0.0003	+0.0088
r(C1-H)	1.0805	+0.0001	−0.0004	−0.0004	+0.0002
r(C3-H)	1.0894	+0.0003	−0.0002	+0.0000	+0.0029
a(C1-C2-C3)	94.23	+0.00	+0.00	+0.00	+0.01
a(C1-C2-H)	133.42	+0.05	+0.05	+0.02	+0.17
a(C4-C3-H)	114.64	+0.04	−0.04	−0.04	−0.07
a(H-C3-H)	109.09	+0.00	+0.10	+0.09	+0.13
pyridazine[a]					
r(N2-C3)	$1.3302^{\aleph 0,\dagger}$	$+0.0026^{\div,\dagger}$	$+0.0022^{\dagger}$	$+0.0014^{\dagger}$	+0.0093
r(C3-C4)	1.3938	−0.0016	−0.0012	−0.0006	+0.0010
r(C4-C5)	1.3761	+0.0018	+0.0017	+0.0015	+0.0104
r(C4-H)	1.0802	+0.0002	−0.0011	−0.0010	−0.0005
r(C3-H)	1.0810	+0.0001	−0.0006	−0.0006	+0.0012
a(C3-C4-C5)	116.85	+0.02	+0.01	+0.00	+0.00
a(N2-C3-C4)	123.86	−0.03	+0.01	+0.02	+0.05
a(H-C3-C4)	121.35	+0.06	+0.04	−0.01	+0.15
a(H-C4-C5)	122.37	−0.04	−0.05	−0.06	−0.11

Graphical symbols denote: ÷ VTZ; ℵ0 ANO0, † the inclusion of $\Delta B_{\mathrm{el}}^{\beta}$.
a) CCSD(T) r_e^{SE} from ref. 73.

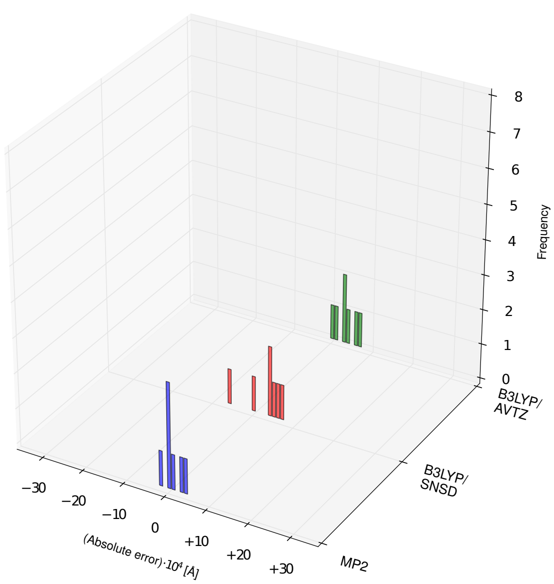
Figure 1: Statistical distributions of the MP2, B3LYP/SNSD and B3LYP/AVTZ deviations from the CCSD(T) SE equilibrium parameters for the molecules belonging to the GeomCC set (see Table 1 in the main text and Table 6 above).



(a) CH bonds

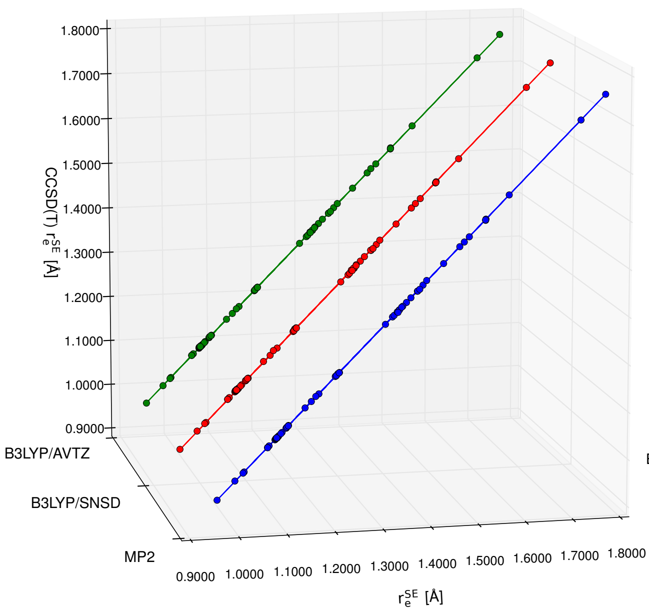


(b) CC bonds

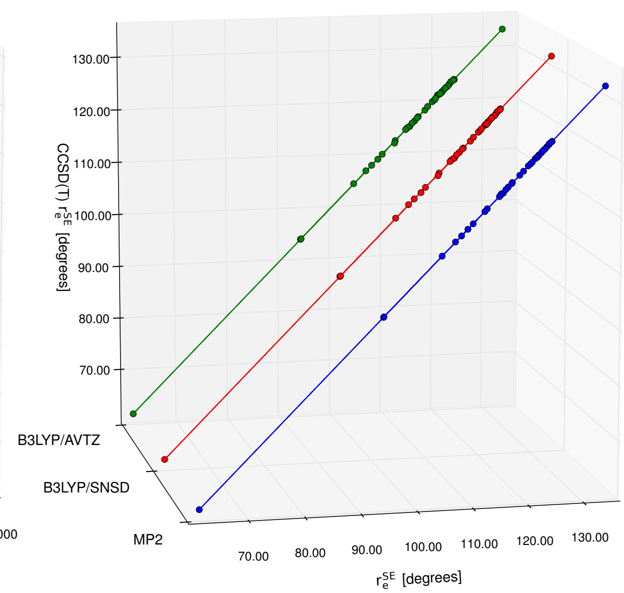


(c) CO bonds

Figure 2: CCSD(T) r_e^{SE} equilibrium parameters plotted versus the MP2, B3LYP/SNSD and B3LYP/AVTZ r_e^{SE} values for the molecules belonging to the GeomCC set (see Table 1 in the main text and Table 6 above).



(a) all bonds



(b) all angles

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