Supporting Information for: The Accuracy of Rotational Parameters Predicted by High-level Quantum-Chemical Calculations: The Case Study of Sulfur-Containing Molecules of Astrochemical Interest

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Table I: Experimental values and best theoretical estimates (CCSD(T)/CBS(Q,5) + core/cc-pCVTZ + ΔB_0^i level) for the rotational constants B_0^i of all the isotopologues considered in the benchmark I study. The last column reports the computed vibrational corrections to the rotational constants at fc-CCSD(T)/cc-pVTZ level. The number in parentheses represents the standard deviation in units of the last significant digits. All values are given in MHz.

Molecule	Isotopologues	Reference	Experimental B_0	Best theo. B_0	ΔB_0^i
OCS	$^{16}O^{12}C^{32}S$	1	6081.4921150(52)	6088.4	17.9
	$^{16}O^{13}C^{32}S$	2	6061.92381(13)	6068.8	17.6
	$^{17}O^{12}C^{32}S$	3	5883.67234(25)	5890.3	17.2
	$^{16}O^{12}C^{34}S$	2	5932.833775(88)	5939.5	17.4
	$^{16}O^{12}C^{36}S$	3	5799.69204(37)	5806.2	16.8
	$^{18}O^{12}C^{32}S$	2	5704.85720(37)	5711.3	16.5
	$^{16}O^{13}C^{34}S$	2	5911.73162(71)	5918.4	17.0
	$^{18}O^{12}C^{34}S$	2	5559.96933(45)	5566.3	15.9
	$^{18}O^{13}C^{32}S$	4	5691.06046(48)	5697.5	16.2
	$^{16}O^{13}C^{36}S$	4	5777.17194(28)	5783.7	16.5
	$^{18}O^{12}C^{36}S$	4	5430.18962(74)	5436.3	15.4
	$^{18}O^{13}C^{34}S$	4	5544.87195(78)	5551.1	15.7
CS	$^{12}C^{32}S$	5	24495.55884(15)	24521.7	86.6
	$^{12}C^{34}S$	5	24103.548378(53)	24129.1	84.5
	$^{12}C^{33}S$	6	24293.25862(154)	24319.2	85.5
	$^{12}C^{36}S$	7	23754.3821(29)	23779.6	82.7
	$^{13}C^{32}S$	6	23123.78795(198)	23148.2	79.4
	$^{13}C^{33}S$	7	22921.3796(27)	22945.7	78.4
	$^{13}C^{34}S$	7	22731.53495(27)	22755.6	77.4
CS^+	$^{12}C^{32}S^+$	8	25908.8560(41)	26220.7	94.0
HCS	$D^{12}C^{32}S$	9	557076.(660)*	569819.3	-24909.5

*This experimental rotational constant is excluded from the benchmark analysis due to is high uncertainty

Table I: (continued)

Molecule	Isotopologues	Reference	Experimental B_0	Best theo. B_0	ΔB_0^i
		9	17899.58155	18005.2	64.7
		9	17235.78155	17392.1	97.8
HSO	$H^{32}S^{16}O$	10	299483.90(12)	300761.2	2098.0
		10	20502.7847(10)	20590.5	67.1
		10	19135.6989(10)	19219.6	119.0
	$D^{32}S^{16}O$	10	158726.938(71)	159229.5	647.3
		10	19836.533(89)	19919.0	64.5
		10	17570.206(87)	17645.2	118.0
HSC	$H^{32}S^{12}C$	11	295038.877(80)	296707.4	1128.6
		11	21038.331(30)	21065.6	-3.7
		11	19562.055(30)	19601.0	69.8
	$D^{32}S^{12}C$	11	155927.68(160)	156439.4	192.8
		11	20431.7169(140)	20470.3	18.0
		11	17980.2247(133)	18023.2	95.1
H_2S	$H_2^{32}S$	12	310583.57681(33)	311174.8	436.7
		12	270367.68173(51)	270019.6	171.7
		12	141820.025852(31)	141977.9	2735.6
	$H_2^{36}S$	13	308539.7387(185)	309128.7	430.0
		13	270366.3105(219)	270018.0	173.3
		13	141387.9835(110)	141545.5	2723.6
	$H_2^{34}S$	14	309502.3997(103)	310092.4	433.1
		14	270366.9368(98)	270018.7	172.6
		14	141591.8242(93)	141749.5	2729.3
	$H_2^{33}S$	12	310025.8404(11)	310616.4	434.9

Table I: (continued)

Molecule	Isotopologues	Reference	Experimental B_0	Best theo. B_0	ΔB_0^i
		12	270367.3005(16)	270019.1	172.2
		12	141702.4195(10)	141860.2	2732.4
	$HD^{32}S$	15	292351.303(135)	292572.9	499.4
		15	147861.801(54)	147837.9	170.0
		15	96704.119(54)	96838.2	1504.5
	$D_2^{32}S$	16	164571.118(45)	164981.2	177.2
		16	135380.313(45)	135142.9	56.5
		16	73244.068(71)	73337.4	1005.0
H_2CS	$H_2^{12}C^{32}S$	17	291613.34(1)	292709.2	1934.6
		17	17698.99488(27)	17722.8	77.3
		17	16652.49866(21)	16675.7	110.2
	$HD^{12}C^{32}S$	18	202716.66(217)	203270.3	1055.4
		18	16111.38339(610)	16131.5	67.0
		18	14890.97584(603)	14911.3	97.4
	$D_2^{12}C^{32}S$	18	146400.546(284)	146691.9	743.2
		18	14904.7104(116)	14923.3	58.8
		18	13495.4298(116)	13513.2	86.9
	$H_2^{12}C^{34}S$	18	291708.3(169)	292707.8	1935.9
		18	17389.1451(120)	17411.8	75.7
		18	16376.6721(120)	16400.1	107.6
	$H_2^{13}C^{32}S$	19	291673.(22)	292723.9	1919.8
		19	16999.209(10)	17021.7	72.4
		19	16030.811(10)	16053.6	103.2
	$H_2^{12}C^{33}S$	19	291673.(22)	292708.4	1935.3

Table I: (continued)

Molecule	Isotopologues	Reference	Experimental B_0	Best theo. B_0	ΔB_0^i
		19	17539.37(2)	17562.4	76.4
		19	16510.16(2)	16533.6	108.9
C_3S	$^{12}C^{12}C^{12}C^{32}S$	20	2890.37959(29)	2892.0	-1.3
	$^{12}C^{12}C^{12}C^{34}S$	20	2820.3691561(98)	2822.0	-1.3
	$^{13}C^{12}C^{12}C^{32}S$	20	2783.061702(138)	2784.6	-1.4
	$^{12}C^{13}C^{12}C^{32}S$	20	2861.370962(52)	2863.0	-1.1
	$^{12}C^{12}C^{13}C^{32}S$	20	2890.385095(157)	2892.0	-1.4
	$^{13}C^{12}C^{12}C^{34}S$	20	2714.80987(48)	2716.3	-1.4
	$^{12}C^{13}C^{12}C^{34}S$	20	2790.96122(42)	2792.6	-1.0
	$^{12}C^{12}C^{13}C^{34}S$	20	2820.29073(26)	2821.9	-1.3
	$^{13}C^{12}C^{13}C^{32}S$	20	2783.09143(26)	2784.7	-1.4
	$^{12}C^{13}C^{13}C^{32}S$	20	2861.39905(34)	2863.0	-1.1
C_3O	$^{12}C^{12}C^{12}C^{16}O$	21	4810.88641(10)	4810.7	-13.4
	$^{12}C^{12}C^{12}C^{18}O$	22	4572.294(1)	4572.2	-12.6
	$^{13}C^{12}C^{12}C^{16}O$	22	4632.840(2)	4632.6	-13.2
	$^{12}C^{13}C^{12}C^{16}O$	22	4784.246(1)	4784.1	-12.4
	$^{12}C^{12}C^{13}C^{16}O$	22	4797.966(1)	4797.7	-13.5
HCO^+	$H^{12}C^{16}O^+$	23	44594.42866(16)	44631.5	235.2
	$D^{12}C^{16}O^+$	24	36019.76763(41)	36045.7	167.6
	$H^{13}C^{16}O^+$	24	43377.3019(17)	43413.3	225.9
	$D^{13}C^{16}O^+$	24	35366.7096(47)	35392.2	163.1
	$H^{12}C^{18}O^+$	25	42581.281(46)	42616.5	220.0
	$D^{12}C^{18}O^+$	26	34413.78556(18)	34438.5	156.8
	$H^{12}C^{17}O^+$	27	43528.9253(19)	43565.0	227.1

Table I: (continued)

Molecule	Isotopologues	Reference	Experimental B_0	Best theo. B_0	ΔB_0^i
SO	$^{32}S^{16}O$	28	21523.55568(26)	21613.2	81.6
	$^{34}S^{16}O$	28	21102.73094(43)	21190.5	79.2
	$^{32}S^{17}O$	28	20677.80826(76)	20763.7	76.8
	$^{32}S^{18}O$	28	19929.2786(42)	20011.9	72.7
HCS^+	$H^{12}C^{32}S^+$	29	21337.14071(66)	21349.9	98.2
	$D^{12}C^{32}S^+$	29	18018.26343(54)	18028.1	69.7
	$H^{13}C^{32}S^+$	29	20444.4949(15)	20456.7	92.9
	$H^{12}C^{34}S^+$	29	20991.57316(79)	21004.1	96.1
CCS	$^{12}C^{12}C^{32}S$	30	6477.57036(71)	6492.6	5.5
	$^{12}C^{12}C^{34}S$	30	6335.88395(107)	6350.4	5.2
SO_2	$^{32}S^{16}O^{16}O$	31	60778.549784(294)	60754.4	-233.3
		31	10318.073534(51)	10348.1	40.0
		31	8799.703401(45)	8822.2	44.0
	$^{33}S^{16}O^{16}O$	32	59856.47852(176)	59832.7	-229.1
		32	10318.29808(36)	10348.3	39.8
		32	8780.13926(38)	8802.6	43.7
	$^{34}S^{16}O^{16}O$	33	58991.1829500(5101)	58967.8	-225.2
		33	10318.5099300(899)	10348.5	39.6
		33	8761.3024810(972)	8783.6	43.5
	$^{32}S^{17}O^{16}O$	32	59883.72807(64)	59860.0	-227.0
		32	10008.214186(143)	10037.3	38.5
		32	8555.136601(137)	8577.1	42.3
	$^{32}S^{18}O^{16}O$	33	59101.1689600(26823)	59077.9	-221.3
		33	9724.6428400(5571)	9752.9	37.0

Table I: (continued)

Molecule	Isotopologues	Reference	Experimental B_0	Best theo. B_0	ΔB_0^i
		33	8331.560181(5109)	8352.9	40.8

Table II: Experimental values for all the rotational constants B_0^i considered in the benchmark II study. The number in parentheses represents the standard deviation in units of the last significant digits. All values are given in MHz.

Molecule	Isotopologues	Reference	Experimental B_0
OCS	$^{16}O^{12}C^{32}S$	1	6081.4921150(52)
	$^{16}O^{13}C^{32}S$	2	6061.92381(13)
	$^{17}O^{12}C^{32}S$	3	5883.67234(25)
	$^{16}O^{12}C^{34}S$	2	5932.833775(88)
	$^{16}O^{12}C^{36}S$	3	5799.69204(37)
	$^{18}O^{12}C^{32}S$	2	5704.85720(37)
	$^{16}O^{13}C^{34}S$	2	5911.73162(71)
	$^{18}O^{12}C^{34}S$	2	5559.96933(45)
	$^{18}O^{13}C^{32}S$	4	5691.06046(48)
	$^{16}O^{13}C^{36}S$	4	5777.17194(28)
	$^{18}O^{12}C^{36}S$	4	5430.18962(74)
	$^{18}O^{13}C^{34}S$	4	5544.87195(78)
CS	$^{12}C^{32}S$	5	24495.55884(15)
	$^{12}C^{34}S$	5	24103.548378(53)
	$^{12}C^{33}S$	6	24293.25862(154)
	$^{12}C^{36}S$	7	23754.3821(29)
	$^{13}C^{32}S$	6	23123.78795(198)
	$^{13}C^{33}S$	7	22921.3796(27)
	$^{13}C^{34}S$	7	22731.53495(27)

Table II: (continued)

Molecule	Isotopologues	Reference	Experimental B_0
H_2S	$H_2^{32}S$	12	310583.57681(33)
		12	270367.68173(51)
		12	141820.025852(31)
	$H_2^{36}S$	13	308539.7387(185)
		13	270366.3105(219)
		13	141387.9835(110)
	$H_2^{34}S$	14	309502.3997(103)
		14	270366.9368(98)
		14	141591.8242(93)
	$H_2^{33}S$	12	310025.8404(11)
		12	270367.3005(16)
		12	141702.4195(10)
	$HD^{32}S$	15	292351.303(135)
		15	147861.801(54)
		15	96704.119(54)
	$D_2^{32}S$	16	164571.118(45)
		16	135380.313(45)
		16	73244.068(71)
PN	$^{31}P^{14}N$	34	23495.20419(41)
	$^{31}p^{15}N$	34	22421.70815(52)
SiS	$^{28}Si^{32}S$	35	9055.373025(134)
	$^{29}Si\ ^{32}S$	36	8889.19077(57)
	$^{30}Si\ ^{32}S$	36	8734.42487(63)
	$^{28}Si\ ^{34}S$	36	8807.68415(56)

Table II: (continued)

Molecule	Isotopologues	Reference	Experimental B_0
HBS	$H^{11}B^{32}S$	37	19083.010866(215)
	$H^{10}B^{32}S$	37	20080.2457361(956)
	$D^{11}B^{32}S$	37	15937.943127(165)
	$D^{10}B^{32}S$	37	16563.353201(102)
HCl	$H^{35}Cl$	38	312989.27878(14)
	$H^{37}Cl$	38	312519.10033(14)
	$D^{35}Cl$	39	161656.24855(27)
	$D^{37}Cl$	39	161183.12953(23)
HCP	$H^{12}C^{31}P$	40	19975.991629 (74)
	$H^{13}C^{31}P$	41	19139.31165(89)
	$D^{12}C^{31}P$	42	16984.36032(96)
	$D^{13}C^{31}P$	41	16427.5191(13)
FCP	$^{19}F^{12}C^{31}P$	43	5257.803751(48)
	$^{19}F^{13}C^{31}P$	43	5250.163726(77)
ClCP	$^{35}Cl^{12}C^{31}P$	44	3020.2968(30)
	$^{37}Cl^{12}C^{31}P$	44	2941.204(41)
	$^{35}Cl^{13}C^{31}P$	44	3020.039(22)
FBS	$^{19}F^{11}B^{32}S$	45	4953.855086(89)
	$^{19}F^{10}B^{32}S$	45	4963.163 68(10)
	$^{19}F^{11}B^{34}S$	45	4828.373 688(91)
	$^{19}F^{10}B^{34}S$	45	4838.770 58(13)
	$^{19}F^{11}B^{33}S$	45	4889.222 21(11)
	$^{19}F^{10}B^{33}S$	45	4899.084 09(14)

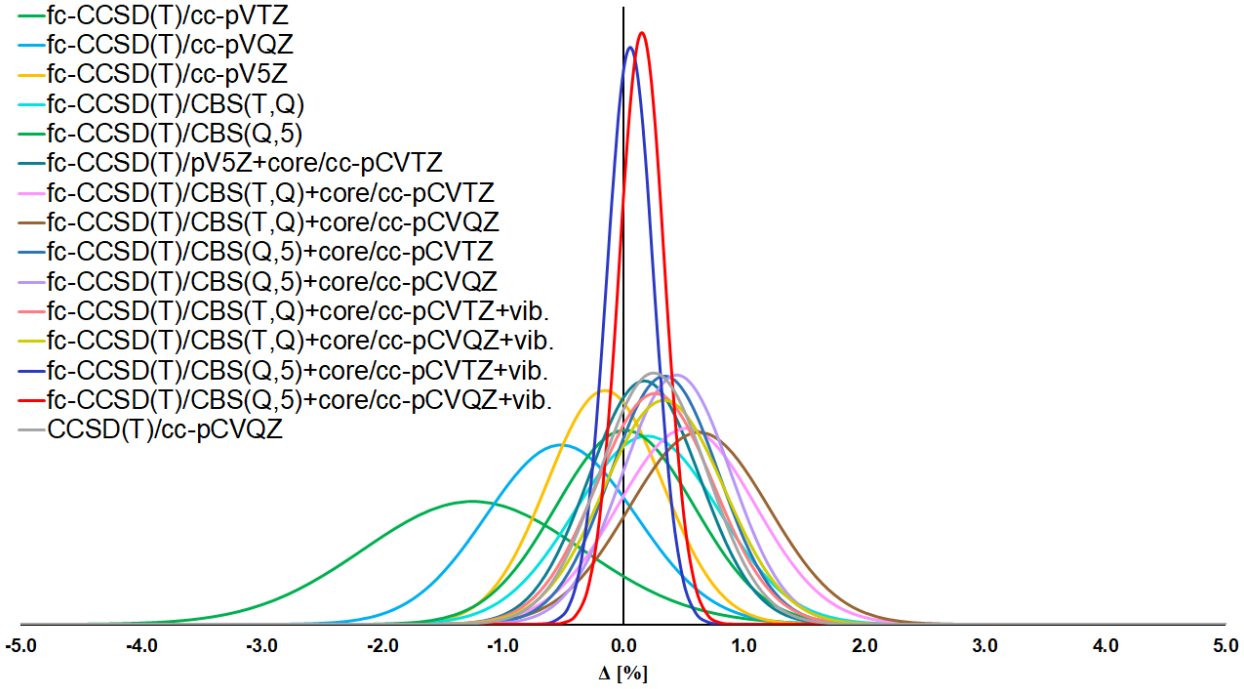

Figure 1: Normal distribution of relative errors in the computed rotational constants with respect to experimentally determined B_0^i values.

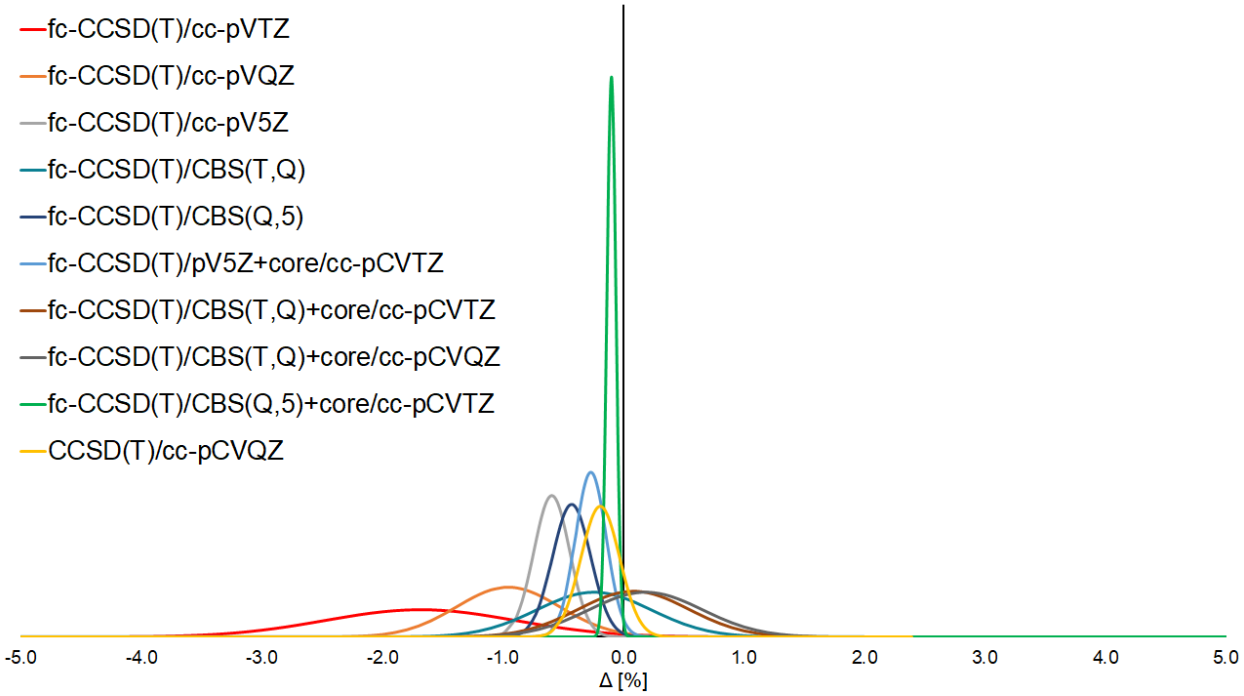

Figure 2: Normal distribution of relative errors in the comparison between calculated B_e^i and the best theoretical values obtained at the fc-CCSD(T)/CBS(Q,5)+core/cc-pCVQZ level.

Table III: Theoretical rotational parameters obtained for $HCCS^+$ in MHz.

Parameter	Theoretical value
B_e	6026.92
ΔB_0	4.20
B_0	6022.72 [(a)]
D	1.20×10^{-3} [(b)]
H	-6.35×10^{-11} [(b)]
γ	-24.07[(c)]

[(a)] fc-CCSD(T)/CBS(5,6) + core/cc-pCVQZ + ΔT + ΔQ + ΔB_0^i/cc-pCVQZ.
[(b)] CCSD(T)/cc-pCVQZ.
[(c)] CCSD/aug-cc-pCVQZ.

Table IV: Rotational parameters obtained for $HOCS^+$ and $HSCO^+$. All values are in MHz.

Parameter	"This work"		Theoretical value[46]		Experimental values[47] [(a)]
	$HOCS^+$	$HSCO^+$	$HOCS^+$	$HSCO^+$	$HOCS^+$
A_e	758914.70	281415.53	-	-	-
ΔA_0	-20346.23	1943.86	-	-	-
A_0	779260.93 [(b)]	279471.67 [(b)]	777701.02	278498.47	782695.7(38)
B_e	5765.14	5706.48	-	-	-
ΔB_0	16.00	12.06	-	-	-
B_0	5749.14 [(b)]	5694.42 [(b)]	5753.87	5682.50	5750.551(49)
C_e	5721.67	5593.07	-	-	-
ΔC_0	19.52	18.04	-	-	-
C_0	5702.15 [(b)]	5575.03 [(b)]	5706.50	5577.59	5703.030(50)
D_J	1.01×10^{-3}[(c)]	1.48×10^{-3}[(c)]	1.02×10^{-3}	1.48×10^{-3}	$1.104(20) \times 10^{-3}$
D_K	649.01[(c)]	15.72[(c)]	655.47	0.14	993.68(77)
D_{JK}	0.27[(c)]	0.14[(c)]	0.268	15.65	0.2819(15)
d_1	-7.06×10^{-6} [(c)]	-3.00×10^{-5}[(c)]	-7.08×10^{-6}	-3.01×10^{-5}	$1.98(43) \times 10^{-5}$
d_2	-8.33×10^{-7} [(c)]	-3.79×10^{-6} [(c)]	-8.30×10^{-7}	-3.83×10^{-6}	-
H_J	1.02×10^{-11} [(c)]	-4.98×10^{-10} [(c)]	0.000	0.000	-
H_{JK}	2.12×10^{-7} [(c)]	3.56×10^{-7} [(c)]	0.22×10^{-6}	3.61×10^{-7}	-
H_{KJ}	-1.23×10^{-3} [(c)]	-1.77×10^{-4} [(c)]	-1.30×10^{-3}	-1.8×10^{-4}	-
H_K	2.75 [(c)]	-6.21×10^{-4} [(c)]	2.788	-6.5×10^{-4}	-
h_1	2.7×10^{-12} [(c)]	-6.4×10^{-12} [(c)]	0.000	0.000	-
h_2	2.4×10^{-12} [(c)]	1.68×10^{-11} [(c)]	0.000	0.000	-
h_3	3.0×10^{-13} [(c)]	1.8×10^{-12} [(c)]	0.000	0.000	-

[(a)] The number in parentheses represents the standard deviation in units of the last significant digits.
[(b)] fc-CCSD(T)/CBS(5,6) + core/cc-pCVQZ + ΔT + ΔQ + ΔB_0^i/cc-pCVQZ.
[(c)] CCSD(T)/cc-pCVQZ.

Table V: Rotational parameters of C_4S in MHz.

Parameter	Theoretical value	Experimental value[48] [(a)]
B_e	1521.59	-
ΔB_0	0.35	-
B_0	1521.24 [(b)]	1519.2062(3)
D	4.13×10^{-5} [(c)]	4.8×10^{-5}
H	2.0×10^{-13} [(d)]	-
λ	-	113840(60)
λ_D	-	$1.2(3) \times 10^{-2}$
γ	-3.95 [(e)]	-4.0(8)

[(a)] The number in parentheses represents the standard deviation in units of the last significant digits.
[(b)] fc-CCSD(T)/CBS(T,Q) + core/cc-pCVTZ + ΔB_0^i/cc-pVTZ.
[(c)] fc-CCSD(T)/cc-pVQZ.
[(d)] fc-CCSD(T)/cc-pVTZ.
[(e)] fc-CCSD/aug-cc-pVTZ

Table VI: Rotational parameters of C_5S in MHz.

Parameter	Theoretical value	Experimental value[48] [(a)]
B_e	922.32	-
ΔB_0	-0.83	-
B_0	923.15 [(b)]	922.7033(2)
D	1.19×10^{-5} [(c)]	$1.3(1) \times 10^{-5}$

[(a)] The number in parentheses represents the standard deviation in units of the last significant digits.
[(b)] fc-CCSD(T)/CBS(T,Q) + core/cc-pCVTZ + ΔB_0^i/cc-pVTZ.
[(c)] fc-CCSD(T)/cc-pVQZ.

Table VII: Rotational parameters obtained for HC_4S^+ in MHz.

Parameter	Theoretical value
B_e	1460.09
ΔB_0	-0.71
B_0	1460.80 [(a)]
D	3.60×10^{-5} [(b)]
H	0.1×10^{-12} [(c)]
γ	-4.34 [(d)]

[(a)] fc-CCSD(T)/CBS(T,Q) + core/cc-pCVTZ + ΔB_0^i/cc-pVTZ.
[(b)] fc-CCSD(T)/cc-pVQZ.
[(c)] fc-CCSD(T)/cc-pVTZ.
[(d)] fc-CCSD/aug-cc-pVTZ.

References

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