Supplementary Information for: Convergent Concordant Mode Approach: CMA-2A

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S1 Remarks

The supplementary information pertaining to each molecule in this benchmark study can be found in the TOC. For each molecule, the Cartesian coordinates of the structure optimized at CCSD(T)/cc-pVTZ are printed in Bohr. Second, the unnormalized natural internal coordinates are provided. Last, a table of vibrational frequencies are displayed. In each table, the CCSD(T)/cc-pVTZ and MP2/cc-pVTZ frequencies are printed in the first column. The third column corresponds to the CMA-0A frequencies. The last two columns correspond to the CMA-2A[(T)/TZ,MP2/TZ] ($\xi = 0.05$) frequencies and the corresponding number of off-diagonal elements for each molecule.

Contents

S1.1 Cyclopropane

Geometries

Table S1: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−1.42667652	0.00000000	−0.82369207
2	C	−0.00000000	0.00000000	1.64738415
3	C	1.42667652	−0.00000000	−0.82369207
4	H	−2.37936667	1.72210724	−1.37372799
5	H	−2.37936667	−1.72210724	−1.37372799
6	H	−0.00000000	−1.72210724	2.74745597
7	H	−0.00000000	1.72210724	2.74745597
8	H	2.37936667	1.72210724	−1.37372799
9	H	2.37936667	−1.72210724	−1.37372799

Natural Internal Coordinates

Table S2: Symmetrized, unnormalized natural internal coordinates for Cyclopropane.

1	$r_{2,3} + r_{1,2} + r_{1,3}$
2	$2r_{2,3} - r_{1,2} - r_{1,3}$
3	$r_{1,2} - r_{1,3}$
4	$r_{1,4} + r_{1,5} + r_{2,6} + r_{2,7} + r_{3,8} + r_{3,9}$
5	$2r_{1,4} + 2r_{1,5} - r_{2,6} - r_{2,7} - r_{3,8} - r_{3,9}$
6	$r_{2,6} + r_{2,7} - r_{3,8} - r_{3,9}$
7	$r_{1,4} - r_{1,5} + r_{2,6} - r_{2,7} + r_{3,8} - r_{3,9}$
8	$2r_{1,4} - 2r_{1,5} - r_{2,6} + r_{2,7} - r_{3,8} + r_{3,9}$
9	$r_{2,6} - r_{2,7} - r_{3,8} + r_{3,9}$
10	$4\phi_{4,1,5} - \phi_{4,1,2} - \phi_{4,1,3} - \phi_{5,1,2} - \phi_{5,1,3} + 4\phi_{6,2,7} - \phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3}$ $+4\phi_{8,3,9} - \phi_{8,3,1} - \phi_{8,3,2} - \phi_{9,3,1} - \phi_{9,3,2}$
11	$8\phi_{4,1,5} - 2\phi_{4,1,2} - 2\phi_{4,1,3} - 2\phi_{5,1,2} - 2\phi_{5,1,3} - 4\phi_{6,2,7} + \phi_{6,2,1} + \phi_{6,2,3} + \phi_{7,2,1} + \phi_{7,2,3}$ $-4\phi_{8,3,9} + \phi_{8,3,1} + \phi_{8,3,2} + \phi_{9,3,1} + \phi_{9,3,2}$
12	$4\phi_{6,2,7} - \phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3} - 4\phi_{8,3,9} + \phi_{8,3,1} + \phi_{8,3,2} + \phi_{9,3,1} + \phi_{9,3,2}$
13	$\phi_{4,1,2} + \phi_{4,1,3} - \phi_{5,1,2} - \phi_{5,1,3} + \phi_{6,2,1} + \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3} + \phi_{8,3,1} + \phi_{8,3,2}$ $-\phi_{9,3,1} - \phi_{9,3,2}$
14	$2\phi_{4,1,2} + 2\phi_{4,1,3} - 2\phi_{5,1,2} - 2\phi_{5,1,3} - \phi_{6,2,1} - \phi_{6,2,3} + \phi_{7,2,1} + \phi_{7,2,3} - \phi_{8,3,1} - \phi_{8,3,2}$ $+\phi_{9,3,1} + \phi_{9,3,2}$
15	$\phi_{6,2,1} + \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,3,1} - \phi_{8,3,2} + \phi_{9,3,1} + \phi_{9,3,2}$
16	$\phi_{4,1,2} - \phi_{4,1,3} + \phi_{5,1,2} - \phi_{5,1,3} + \phi_{6,2,1} - \phi_{6,2,3} + \phi_{7,2,1} - \phi_{7,2,3} + \phi_{8,3,1} - \phi_{8,3,2}$ $+\phi_{9,3,1} - \phi_{9,3,2}$
17	$2\phi_{4,1,2} - 2\phi_{4,1,3} + 2\phi_{5,1,2} - 2\phi_{5,1,3} - \phi_{6,2,1} + \phi_{6,2,3} - \phi_{7,2,1} + \phi_{7,2,3} - \phi_{8,3,1} + \phi_{8,3,2}$ $-\phi_{9,3,1} + \phi_{9,3,2}$
18	$\phi_{6,2,1} - \phi_{6,2,3} + \phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,3,1} + \phi_{8,3,2} - \phi_{9,3,1} + \phi_{9,3,2}$
19	$\phi_{4,1,2} - \phi_{4,1,3} - \phi_{5,1,2} + \phi_{5,1,3} + \phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} + \phi_{7,2,3} + \phi_{8,3,1} - \phi_{8,3,2}$ $-\phi_{9,3,1} + \phi_{9,3,2}$
20	$2\phi_{4,1,2} - 2\phi_{4,1,3} - 2\phi_{5,1,2} + 2\phi_{5,1,3} - \phi_{6,2,1} + \phi_{6,2,3} + \phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,3,1} + \phi_{8,3,2}$ $+\phi_{9,3,1} - \phi_{9,3,2}$
21	$\phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} + \phi_{7,2,3} - \phi_{8,3,1} + \phi_{8,3,2} + \phi_{9,3,1} - \phi_{9,3,2}$

Frequencies

Table S3: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	740.85	740.68	740.86	740.86	0
2	740.85	740.69	740.86	740.86	0
3	857.68	860.46	857.69	857.69	0
4	891.96	894.34	892.19	892.19	0
5	891.96	894.37	892.19	892.19	0
6	1060.52	1047.44	1060.34	1060.34	0
7	1060.52	1047.59	1060.34	1060.34	0
8	1088.57	1077.74	1088.57	1088.57	0
9	1160.87	1163.77	1160.87	1160.87	0
10	1214.39	1213.98	1214.43	1214.43	0
11	1217.35	1214.00	1217.35	1217.35	0
12	1217.35	1217.37	1217.35	1217.35	0
13	1478.32	1478.47	1478.31	1478.31	0
14	1478.32	1478.47	1478.31	1478.31	0
15	1528.61	1524.51	1528.58	1528.58	0
16	3146.29	3163.10	3146.29	3146.29	0
17	3146.29	3163.15	3146.30	3146.30	0
18	3156.95	3171.65	3156.89	3156.89	0
19	3228.73	3252.54	3228.70	3228.70	0
20	3228.73	3252.74	3228.81	3228.81	0
21	3248.62	3271.15	3248.62	3248.62	0

S1.2 Methane

Geometries

Table S4: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.00000000	0.00000000	0.00000000
2	H	0.00000000	−1.68028027	1.18813758
3	H	0.00000000	1.68028027	1.18813758
4	H	1.68028027	0.00000000	−1.18813758
5	H	−1.68028027	−0.00000000	−1.18813758

Natural Internal Coordinates

Table S5: Symmetrized, unnormalized natural internal coordinates for Methane.

1	$r_{1,2} + r_{1,3} + r_{1,4} + r_{1,5}$
2	$-r_{1,2} - r_{1,3} + r_{1,4} + r_{1,5}$
3	$-r_{1,2} + r_{1,3} - r_{1,4} + r_{1,5}$
4	$r_{1,2} - r_{1,3} - r_{1,4} + r_{1,5}$
5	$2\phi_{2,1,3} + 2\phi_{4,1,5} - \phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5}$
6	$\phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} + \phi_{3,1,5}$
7	$-\phi_{2,1,3} + \phi_{4,1,5}$
8	$-\phi_{2,1,4} + \phi_{3,1,5}$
9	$\phi_{2,1,5} - \phi_{3,1,4}$

Frequencies

Table S6: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1343.99	1343.17	1344.00	1344.00	0
2	1343.99	1343.17	1344.00	1344.00	0
3	1343.99	1343.24	1344.00	1344.00	0
4	1570.80	1578.60	1570.80	1570.80	0
5	1570.80	1578.60	1570.80	1570.80	0
6	3034.66	3045.57	3034.64	3034.64	0
7	3153.78	3178.77	3153.78	3153.78	0
8	3153.78	3178.77	3153.78	3153.78	0
9	3153.78	3179.02	3153.80	3153.80	0

S1.3 Ammonia

Geometries

Table S7: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	N	−0.13335323	−0.00000078	−0.00000000
2	H	0.61762190	−1.76309423	−0.00000000
3	H	0.61761729	0.88155253	1.52688219
4	H	0.61761729	0.88155253	−1.52688219

Natural Internal Coordinates

Table S8: Symmetrized, unnormalized natural internal coordinates for Ammonia.

1	$r_{1,2} + r_{1,3} + r_{1,4}$
2	$2r_{1,2} - r_{1,3} - r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{3,1,4}$
5	$\phi_{2,1,4} - \phi_{3,1,4}$
6	$\gamma_{2,1,3,4} + \gamma_{3,1,4,2} + \gamma_{4,1,2,3}$

Frequencies

Table S9: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1109.21	1097.96	1109.22	1109.22	0
2	1687.93	1683.54	1687.93	1687.93	0
3	1687.93	1683.58	1687.93	1687.93	0
4	3471.91	3483.02	3471.91	3471.91	0
5	3597.54	3623.41	3597.54	3597.54	0
6	3597.54	3623.57	3597.54	3597.54	0

S1.4 Silane

Geometries

Table S10: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	Si	0.00000000	0.00000000	0.00000000
2	H	0.00000000	−2.28308541	1.61437763
3	H	0.00000000	2.28308541	1.61437763
4	H	2.28308541	0.00000000	−1.61437763
5	H	−2.28308541	0.00000000	−1.61437763

Natural Internal Coordinates

Table S11: Symmetrized, unnormalized natural internal coordinates for Silane.

1	$r_{1,2} + r_{1,3} + r_{1,4} + r_{1,5}$
2	$-r_{1,2} - r_{1,3} + r_{1,4} + r_{1,5}$
3	$-r_{1,2} + r_{1,3} - r_{1,4} + r_{1,5}$
4	$r_{1,2} - r_{1,3} - r_{1,4} + r_{1,5}$
5	$2\phi_{2,1,3} + 2\phi_{4,1,5} - \phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5}$
6	$\phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} + \phi_{3,1,5}$
7	$-\phi_{2,1,3} + \phi_{4,1,5}$
8	$-\phi_{2,1,4} + \phi_{3,1,5}$
9	$\phi_{2,1,5} - \phi_{3,1,4}$

Frequencies

Table S12: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	933.79	949.08	933.79	933.79	0
2	933.80	949.08	933.80	933.80	0
3	933.80	949.14	933.80	933.80	0
4	985.48	1000.33	985.48	985.48	0
5	985.49	1000.33	985.49	985.49	0
6	2250.62	2270.48	2250.62	2250.62	0
7	2255.36	2274.13	2255.36	2255.36	0
8	2255.36	2274.13	2255.36	2255.36	0
9	2255.36	2274.24	2255.36	2255.36	0

S1.5 Benzene

Geometries

Table S13: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.00000000	2.64096559	−0.00000000
2	C	−2.28714329	1.32048279	−0.00000000
3	C	−2.28714329	−1.32048279	0.00000000
4	C	−0.00000000	−2.64096559	0.00000000
5	C	2.28714329	−1.32048279	0.00000000
6	C	2.28714329	1.32048279	−0.00000000
7	H	0.00000000	4.68777554	−0.00000000
8	H	−4.05973271	2.34388777	−0.00000000
9	H	−4.05973271	−2.34388777	0.00000000
10	H	−0.00000000	−4.68777554	0.00000000
11	H	4.05973271	−2.34388777	0.00000000
12	H	4.05973271	2.34388777	−0.00000000

Natural Internal Coordinates

Frequencies

Table S14: Symmetrized, unnormalized natural internal coordinates for Benzene.

1	$r_{1,2} + r_{2,3} + r_{3,4} + r_{4,5} + r_{5,6} + r_{6,1}$
2	$r_{1,2} - r_{2,3} + r_{3,4} - r_{4,5} + r_{5,6} - r_{6,1}$
3	$2r_{1,2} + r_{2,3} - r_{3,4} - 2r_{4,5} - r_{5,6} + r_{6,1}$
4	$r_{2,3} + r_{3,4} - r_{5,6} - r_{6,1}$
5	$2r_{1,2} - r_{2,3} - r_{3,4} + 2r_{4,5} - r_{5,6} - r_{6,1}$
6	$r_{2,3} - r_{3,4} + r_{5,6} - r_{6,1}$
7	$r_{1,7} + r_{2,8} + r_{3,9} + r_{4,10} + r_{5,11} + r_{6,12}$
8	$r_{1,7} - r_{2,8} + r_{3,9} - r_{4,10} + r_{5,11} - r_{6,12}$
9	$2r_{1,7} + r_{2,8} - r_{3,9} - 2r_{4,10} - r_{5,11} + r_{6,12}$
10	$r_{2,8} + r_{3,9} - r_{5,11} - r_{6,12}$
11	$2r_{1,7} - r_{2,8} - r_{3,9} + 2r_{4,10} - r_{5,11} - r_{6,12}$
12	$r_{2,8} - r_{3,9} + r_{5,11} - r_{6,12}$
13	$\phi_{6,1,2} - \phi_{1,2,3} + \phi_{2,3,4} - \phi_{3,4,5} + \phi_{4,5,6} - \phi_{5,6,1}$
14	$2\phi_{6,1,2} - \phi_{1,2,3} - \phi_{2,3,4} + 2\phi_{3,4,5} - \phi_{4,5,6} - \phi_{5,6,1}$
15	$\phi_{1,2,3} - \phi_{2,3,4} + \phi_{4,5,6} - \phi_{5,6,1}$
16	$\phi_{7,1,2} - \phi_{7,1,6} + \phi_{8,2,3} - \phi_{8,2,1} + \phi_{9,3,4} - \phi_{9,3,2} + \phi_{10,4,5} - \phi_{10,4,3} + \phi_{11,5,6} - \phi_{11,5,4} + \phi_{12,6,1} - \phi_{12,6,5}$
17	$\phi_{7,1,2} - \phi_{7,1,6} - \phi_{8,2,3} + \phi_{8,2,1} + \phi_{9,3,4} - \phi_{9,3,2} - \phi_{10,4,5} + \phi_{10,4,3} + \phi_{11,5,6} - \phi_{11,5,4} - \phi_{12,6,1} + \phi_{12,6,5}$
18	$2\phi_{7,1,2} - 2\phi_{7,1,6} + \phi_{8,2,3} - \phi_{8,2,1} - \phi_{9,3,4} + \phi_{9,3,2} - 2\phi_{10,4,5} + 2\phi_{10,4,3} - \phi_{11,5,6} + \phi_{11,5,4} + \phi_{12,6,1} - \phi_{12,6,5}$
19	$\phi_{8,2,3} - \phi_{8,2,1} + \phi_{9,3,4} - \phi_{9,3,2} - \phi_{11,5,6} + \phi_{11,5,4} - \phi_{12,6,1} + \phi_{12,6,5}$
20	$2\phi_{7,1,2} - 2\phi_{7,1,6} - \phi_{8,2,3} + \phi_{8,2,1} - \phi_{9,3,4} + \phi_{9,3,2} + 2\phi_{10,4,5} - 2\phi_{10,4,3} - \phi_{11,5,6} + \phi_{11,5,4} - \phi_{12,6,1} + \phi_{12,6,5}$
21	$\phi_{8,2,3} - \phi_{8,2,1} - \phi_{9,3,4} + \phi_{9,3,2} + \phi_{11,5,6} - \phi_{11,5,4} - \phi_{12,6,1} + \phi_{12,6,5}$
22	$\tau_{1,2,3,4} - \tau_{2,3,4,5} + \tau_{3,4,5,6} - \tau_{4,5,6,1} + \tau_{5,6,1,2} - \tau_{6,1,2,3}$
23	$\tau_{1,2,3,4} - \tau_{3,4,5,6} + \tau_{4,5,6,1} - \tau_{6,1,2,3}$
24	$-\tau_{1,2,3,4} + 2\tau_{2,3,4,5} - \tau_{3,4,5,6} - \tau_{4,5,6,1} + 2\tau_{5,6,1,2} - \tau_{6,1,2,3}$
25	$\gamma_{7,1,2,6} + \gamma_{8,2,3,1} + \gamma_{9,3,4,2} + \gamma_{10,4,5,3} + \gamma_{11,5,6,4} + \gamma_{12,6,1,5}$
26	$\gamma_{7,1,2,6} - \gamma_{8,2,3,1} + \gamma_{9,3,4,2} - \gamma_{10,4,5,3} + \gamma_{11,5,6,4} - \gamma_{12,6,1,5}$
27	$2\gamma_{7,1,2,6} + \gamma_{8,2,3,1} - \gamma_{9,3,4,2} - 2\gamma_{10,4,5,3} - \gamma_{11,5,6,4} + \gamma_{12,6,1,5}$
28	$\gamma_{8,2,3,1} + \gamma_{9,3,4,2} - \gamma_{11,5,6,4} - \gamma_{12,6,1,5}$
29	$2\gamma_{7,1,2,6} - \gamma_{8,2,3,1} - \gamma_{9,3,4,2} + 2\gamma_{10,4,5,3} - \gamma_{11,5,6,4} - \gamma_{12,6,1,5}$
30	$\gamma_{8,2,3,1} - \gamma_{9,3,4,2} + \gamma_{11,5,6,4} - \gamma_{12,6,1,5}$

Table S15: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	401.34	402.87	401.34	401.34	0
2	401.34	402.88	401.34	401.34	0
3	607.13	603.07	607.14	607.14	0
4	607.13	603.08	607.14	607.14	0
5	674.67	682.19	674.80	674.67	1
6	685.29	687.72	685.29	685.29	0
7	856.44	859.05	856.44	856.44	0
8	856.44	859.05	856.44	856.44	0
9	959.08	958.03	959.08	959.08	0
10	959.08	958.05	959.08	959.08	0
11	966.66	971.83	966.57	966.66	1
12	1004.54	1003.25	1004.54	1004.54	0
13	1010.33	1012.70	1010.33	1010.33	0
14	1054.36	1053.52	1054.37	1054.37	0
15	1054.36	1053.53	1054.37	1054.37	0
16	1158.88	1164.22	1163.79	1158.88	1
17	1190.57	1190.37	1190.61	1190.61	0
18	1190.57	1190.38	1190.61	1190.61	0
19	1328.17	1364.96	1323.88	1328.17	0
20	1370.18	1439.45	1370.18	1370.18	1
21	1506.94	1497.84	1506.94	1506.94	0
22	1506.94	1497.85	1506.94	1506.94	0
23	1637.23	1624.57	1637.21	1637.21	0
24	1637.23	1624.59	1637.21	1637.21	0
25	3169.39	3186.60	3169.39	3169.39	0
26	3180.74	3198.06	3180.74	3180.74	0
27	3180.74	3198.12	3180.74	3180.74	0
28	3198.33	3214.52	3198.33	3198.33	0
29	3198.33	3214.58	3198.33	3198.33	0
30	3209.15	3224.30	3209.15	3209.15	0

S1.6 Cyclopropene

Geometries

Table S16: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.00000000	−0.00000000	1.67420069
2	H	0.00001614	−1.72642240	2.78915742
3	H	−0.00001614	1.72642240	2.78915742
4	C	1.22917808	0.00000291	−0.90945117
5	C	−1.22917808	−0.00000291	−0.90945117
6	H	2.98721276	−0.00000494	−1.92768856
7	H	−2.98721276	0.00000494	−1.92768856

Natural Internal Coordinates

Table S17: Symmetrized, unnormalized natural internal coordinates for Cyclopropene.

1	$r_{1,4} + r_{1,5} + r_{4,5}$
2	$r_{1,4} - r_{1,5}$
3	$-r_{1,4} - r_{1,5} + 2r_{4,5}$
4	$r_{1,2} + r_{1,3}$
5	$r_{1,2} - r_{1,3}$
6	$r_{4,6} + r_{5,7}$
7	$r_{4,6} - r_{5,7}$
8	$4\phi_{2,1,3} - \phi_{3,1,4} - \phi_{3,1,5} - \phi_{2,1,4} - \phi_{2,1,5}$
9	$\phi_{3,1,4} + \phi_{3,1,5} - \phi_{2,1,4} - \phi_{2,1,5}$
10	$\phi_{3,1,4} - \phi_{3,1,5} + \phi_{2,1,4} - \phi_{2,1,5}$
11	$\phi_{3,1,4} - \phi_{3,1,5} - \phi_{2,1,4} + \phi_{2,1,5}$
12	$\phi_{6,4,1} - \phi_{6,4,5} + \phi_{7,5,1} - \phi_{7,5,4}$
13	$\phi_{6,4,1} - \phi_{6,4,5} - \phi_{7,5,1} + \phi_{7,5,4}$
14	$\gamma_{6,4,1,5} + \gamma_{7,5,1,4}$
15	$\gamma_{6,4,1,5} - \gamma_{7,5,1,4}$

Frequencies

Table S18: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	575.68	584.69	575.69	575.69	0
2	791.69	790.47	791.95	791.95	0
3	824.74	838.84	825.12	825.12	0
4	927.46	929.75	927.54	927.54	0
5	1020.59	1023.63	1020.26	1020.26	0
6	1042.08	1033.50	1042.90	1042.90	0
7	1074.23	1064.44	1073.27	1073.27	0
8	1108.96	1111.63	1108.97	1108.97	0
9	1158.16	1153.88	1158.16	1158.16	0
10	1524.77	1526.62	1524.75	1524.75	0
11	1682.96	1677.34	1682.94	1682.94	0
12	3071.86	3088.42	3071.85	3071.85	0
13	3143.03	3167.07	3143.02	3143.02	0
14	3264.57	3280.37	3264.57	3264.57	0
15	3310.75	3326.63	3310.75	3310.75	0

S1.7 Allene

Geometries

Table S19: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.00000000	0.00000000	−0.00000001
2	C	0.00000000	0.00000000	−2.48178976
3	C	0.00000000	0.00000000	2.48178971
4	H	−1.75641355	0.00000000	−3.53278972
5	H	1.75641355	0.00000000	−3.53278972
6	H	0.00000000	−1.75641338	3.53279007
7	H	0.00000000	1.75641338	3.53279007

Natural Internal Coordinates

Table S20: Symmetrized, unnormalized natural internal coordinates for Allene.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$r_{2,4} + r_{2,5} + r_{3,6} + r_{3,7}$
4	$r_{2,4} + r_{2,5} - r_{3,6} - r_{3,7}$
5	$r_{2,4} - r_{2,5} + r_{3,6} - r_{3,7}$
6	$r_{2,4} - r_{2,5} - r_{3,6} + r_{3,7}$
7	$2\phi_{4,2,5} - \phi_{1,2,4} - \phi_{1,2,5} + 2\phi_{6,3,7} - \phi_{1,3,6} - \phi_{1,3,7}$
8	$2\phi_{4,2,5} - \phi_{1,2,4} - \phi_{1,2,5} - 2\phi_{6,3,7} + \phi_{1,3,6} + \phi_{1,3,7}$
9	$\phi_{1,2,4} - \phi_{1,2,5} + \phi_{1,3,6} - \phi_{1,3,7}$
10	$\phi_{1,2,4} - \phi_{1,2,5} - \phi_{1,3,6} + \phi_{1,3,7}$
11	$\tau_{4,2,3,6} + \tau_{4,2,3,7} + \tau_{5,2,3,6} + \tau_{5,2,3,7}$
12	$\gamma_{1,2,4,5} + \gamma_{1,3,7,6}$
13	$\gamma_{1,2,4,5} - \gamma_{1,3,7,6}$
14	$\alpha^x_{4,2,1,3} - \alpha^x_{5,2,1,3} + \alpha^x_{6,3,1,2} - \alpha^x_{7,3,1,2}$
15	$\alpha^x_{4,2,1,3} - \alpha^x_{5,2,1,3} - \alpha^x_{6,3,1,2} + \alpha^x_{7,3,1,2}$

Frequencies

Table S21: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	347.95	356.60	348.20	348.20	0
2	347.95	356.61	348.21	348.21	0
3	856.73	855.11	856.73	856.73	0
4	856.73	855.14	856.73	856.73	0
5	870.31	892.05	870.31	870.31	0
6	1017.66	1011.09	1017.57	1017.57	0
7	1017.78	1011.11	1017.70	1017.70	0
8	1080.75	1082.06	1080.76	1080.76	0
9	1438.38	1433.30	1438.41	1438.41	0
10	1488.52	1481.35	1488.52	1488.52	0
11	2012.15	2009.82	2012.12	2012.12	0
12	3142.75	3159.36	3142.80	3142.80	0
13	3144.28	3159.72	3144.20	3144.20	0
14	3226.41	3247.56	3226.41	3226.41	0
15	3226.41	3247.74	3226.45	3226.45	0

S1.8 Spiropentane

Geometries

Table S22: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.00000000	−0.00000000	0.00000000
2	C	−1.02524750	−1.02524750	−2.39918091
3	C	1.02524750	1.02524750	−2.39918091
4	C	1.02524750	−1.02524750	2.39918091
5	C	−1.02524750	1.02524750	2.39918091
6	H	−0.46577708	−2.91033012	−2.96611806
7	H	−2.91033012	−0.46577708	−2.96611806
8	H	0.46577708	2.91033012	−2.96611806
9	H	2.91033012	0.46577708	−2.96611806
10	H	0.46577708	−2.91033012	2.96611806
11	H	2.91033012	−0.46577708	2.96611806
12	H	−0.46577708	2.91033012	2.96611806
13	H	−2.91033012	0.46577708	2.96611806

Natural Internal Coordinates

Frequencies

Table S23: Symmetrized, unnormalized natural internal coordinates for Spiropentane.

1	$r_{1,2} + r_{1,3} + r_{2,3} + r_{1,4} + r_{1,5} + r_{4,5}$
2	$r_{1,2} + r_{1,3} + r_{2,3} - r_{1,4} - r_{1,5} - r_{4,5}$
3	$-r_{1,2} - r_{1,3} + 2r_{2,3} - r_{1,4} - r_{1,5} + 2r_{4,5}$
4	$-r_{1,2} - r_{1,3} + 2r_{2,3} + r_{1,4} + r_{1,5} - 2r_{4,5}$
5	$r_{1,2} - r_{1,3} + r_{1,4} - r_{1,5}$
6	$r_{1,2} - r_{1,3} - r_{1,4} + r_{1,5}$
7	$r_{2,6} + r_{2,7} + r_{3,8} + r_{3,9} + r_{4,10} + r_{4,11} + r_{5,12} + r_{5,13}$
8	$r_{2,6} + r_{2,7} + r_{3,8} + r_{3,9} - r_{4,10} - r_{4,11} - r_{5,12} - r_{5,13}$
9	$r_{2,6} + r_{2,7} - r_{3,8} - r_{3,9} + r_{4,10} + r_{4,11} - r_{5,12} - r_{5,13}$
10	$r_{2,6} + r_{2,7} - r_{3,8} - r_{3,9} - r_{4,10} - r_{4,11} + r_{5,12} + r_{5,13}$
11	$r_{2,6} - r_{2,7} + r_{3,8} - r_{3,9} + r_{4,10} - r_{4,11} + r_{5,12} - r_{5,13}$
12	$r_{2,6} - r_{2,7} + r_{3,8} - r_{3,9} - r_{4,10} + r_{4,11} - r_{5,12} + r_{5,13}$
13	$r_{2,6} - r_{2,7} - r_{3,8} + r_{3,9} + r_{4,10} - r_{4,11} - r_{5,12} + r_{5,13}$
14	$r_{2,6} - r_{2,7} - r_{3,8} + r_{3,9} - r_{4,10} + r_{4,11} + r_{5,12} - r_{5,13}$
15	$\phi_{2,1,4} + \phi_{3,1,4} - \phi_{2,1,5} - \phi_{3,1,5}$
16	$\phi_{2,1,4} - \phi_{3,1,4} + \phi_{2,1,5} - \phi_{3,1,5}$
17	$\phi_{2,1,4} - \phi_{3,1,4} - \phi_{2,1,5} + \phi_{3,1,5}$
18	$4\phi_{6,2,7} - \phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3} + 4\phi_{8,3,9} - \phi_{8,3,1} - \phi_{8,3,2} - \phi_{9,3,1} - \phi_{9,3,2}$ $+4\phi_{10,4,11} - \phi_{10,4,1} - \phi_{10,4,5} - \phi_{11,4,1} - \phi_{11,4,5} + 4\phi_{12,5,13} - \phi_{12,5,1} - \phi_{12,5,4} - \phi_{13,5,1} - \phi_{13,5,4}$
19	$4\phi_{6,2,7} - \phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3} + 4\phi_{8,3,9} - \phi_{8,3,1} - \phi_{8,3,2} - \phi_{9,3,1} - \phi_{9,3,2}$ $-4\phi_{10,4,11} + \phi_{10,4,1} + \phi_{10,4,5} + \phi_{11,4,1} + \phi_{11,4,5} - 4\phi_{12,5,13} + \phi_{12,5,1} + \phi_{12,5,4} + \phi_{13,5,1} + \phi_{13,5,4}$
20	$4\phi_{6,2,7} - \phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3} - 4\phi_{8,3,9} + \phi_{8,3,1} + \phi_{8,3,2} + \phi_{9,3,1} + \phi_{9,3,2}$ $+4\phi_{10,4,11} - \phi_{10,4,1} - \phi_{10,4,5} - \phi_{11,4,1} - \phi_{11,4,5} - 4\phi_{12,5,13} + \phi_{12,5,1} + \phi_{12,5,4} + \phi_{13,5,1} + \phi_{13,5,4}$
21	$4\phi_{6,2,7} - \phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3} - 4\phi_{8,3,9} + \phi_{8,3,1} + \phi_{8,3,2} + \phi_{9,3,1} + \phi_{9,3,2}$ $-4\phi_{10,4,11} + \phi_{10,4,1} + \phi_{10,4,5} + \phi_{11,4,1} + \phi_{11,4,5} + 4\phi_{12,5,13} - \phi_{12,5,1} - \phi_{12,5,4} - \phi_{13,5,1} - \phi_{13,5,4}$
22	$\phi_{6,2,1} + \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3} + \phi_{8,3,1} + \phi_{8,3,2} - \phi_{9,3,1} - \phi_{9,3,2} + \phi_{10,4,1} + \phi_{10,4,5}$ $-\phi_{11,4,1} - \phi_{11,4,5} + \phi_{12,5,1} + \phi_{12,5,4} - \phi_{13,5,1} - \phi_{13,5,4}$
23	$\phi_{6,2,1} + \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3} + \phi_{8,3,1} + \phi_{8,3,2} - \phi_{9,3,1} - \phi_{9,3,2} - \phi_{10,4,1} - \phi_{10,4,5}$ $+\phi_{11,4,1} + \phi_{11,4,5} - \phi_{12,5,1} - \phi_{12,5,4} + \phi_{13,5,1} + \phi_{13,5,4}$
24	$\phi_{6,2,1} + \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,3,1} - \phi_{8,3,2} + \phi_{9,3,1} + \phi_{9,3,2} + \phi_{10,4,1} + \phi_{10,4,5}$ $-\phi_{11,4,1} - \phi_{11,4,5} - \phi_{12,5,1} - \phi_{12,5,4} + \phi_{13,5,1} + \phi_{13,5,4}$
25	$\phi_{6,2,1} + \phi_{6,2,3} - \phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,3,1} - \phi_{8,3,2} + \phi_{9,3,1} + \phi_{9,3,2} - \phi_{10,4,1} - \phi_{10,4,5}$ $+\phi_{11,4,1} + \phi_{11,4,5} + \phi_{12,5,1} + \phi_{12,5,4} - \phi_{13,5,1} - \phi_{13,5,4}$
26	$\phi_{6,2,1} - \phi_{6,2,3} + \phi_{7,2,1} - \phi_{7,2,3} + \phi_{8,3,1} - \phi_{8,3,2} + \phi_{9,3,1} - \phi_{9,3,2} + \phi_{10,4,1} - \phi_{10,4,5}$ $+\phi_{11,4,1} - \phi_{11,4,5} + \phi_{12,5,1} - \phi_{12,5,4} + \phi_{13,5,1} - \phi_{13,5,4}$
27	$\phi_{6,2,1} - \phi_{6,2,3} + \phi_{7,2,1} - \phi_{7,2,3} + \phi_{8,3,1} - \phi_{8,3,2} + \phi_{9,3,1} - \phi_{9,3,2} - \phi_{10,4,1} + \phi_{10,4,5}$ $-\phi_{11,4,1} + \phi_{11,4,5} - \phi_{12,5,1} + \phi_{12,5,4} - \phi_{13,5,1} + \phi_{13,5,4}$
28	$\phi_{6,2,1} - \phi_{6,2,3} + \phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,3,1} + \phi_{8,3,2} - \phi_{9,3,1} + \phi_{9,3,2} + \phi_{10,4,1} - \phi_{10,4,5}$ $+\phi_{11,4,1} - \phi_{11,4,5} - \phi_{12,5,1} + \phi_{12,5,4} - \phi_{13,5,1} + \phi_{13,5,4}$
29	$\phi_{6,2,1} - \phi_{6,2,3} + \phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,3,1} + \phi_{8,3,2} - \phi_{9,3,1} + \phi_{9,3,2} - \phi_{10,4,1} + \phi_{10,4,5}$ $-\phi_{11,4,1} + \phi_{11,4,5} + \phi_{12,5,1} - \phi_{12,5,4} + \phi_{13,5,1} - \phi_{13,5,4}$
30	$\phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} + \phi_{7,2,3} + \phi_{8,3,1} - \phi_{8,3,2} - \phi_{9,3,1} + \phi_{9,3,2} + \phi_{10,4,1} - \phi_{10,4,5}$ $-\phi_{11,4,1} + \phi_{11,4,5} + \phi_{12,5,1} - \phi_{12,5,4} - \phi_{13,5,1} + \phi_{13,5,4}$
31	$\phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} + \phi_{7,2,3} + \phi_{8,3,1} - \phi_{8,3,2} - \phi_{9,3,1} + \phi_{9,3,2} - \phi_{10,4,1} + \phi_{10,4,5}$ $+\phi_{11,4,1} - \phi_{11,4,5} - \phi_{12,5,1} + \phi_{12,5,4} + \phi_{13,5,1} - \phi_{13,5,4}$
32	$\phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} + \phi_{7,2,3} - \phi_{8,3,1} + \phi_{8,3,2} + \phi_{9,3,1} - \phi_{9,3,2} + \phi_{10,4,1} - \phi_{10,4,5}$ $-\phi_{11,4,1} + \phi_{11,4,5} - \phi_{12,5,1} + \phi_{12,5,4} + \phi_{13,5,1} - \phi_{13,5,4}$
33	$\phi_{6,2,1} - \phi_{6,2,3} - \phi_{7,2,1} + \phi_{7,2,3} - \phi_{8,3,1} + \phi_{8,3,2} + \phi_{9,3,1} - \phi_{9,3,2} - \phi_{10,4,1} + \phi_{10,4,5}$ $+\phi_{11,4,1} - \phi_{11,4,5} + \phi_{12,5,1} - \phi_{12,5,4} - \phi_{13,5,1} + \phi_{13,5,4}$

Table S24: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	293.06	292.70	293.07	293.07	0
2	297.15	293.90	297.18	297.18	0
3	297.15	293.94	297.18	297.18	0
4	598.43	599.04	598.50	598.50	0
5	786.27	787.57	786.27	786.27	0
6	786.27	787.58	786.27	786.27	0
7	840.13	838.36	840.14	840.14	0
8	897.42	896.82	897.50	897.50	0
9	897.42	896.84	897.50	897.50	0
10	900.83	898.59	901.91	900.88	1
11	1019.25	1006.35	1018.43	1019.33	1
12	1027.32	1027.54	1027.39	1027.39	0
13	1054.41	1050.78	1058.08	1054.41	1
14	1076.02	1064.14	1072.42	1076.03	0
15	1077.33	1064.21	1077.35	1077.35	0
16	1077.33	1067.66	1077.35	1077.35	1
17	1173.46	1171.62	1173.46	1173.46	0
18	1183.50	1180.66	1183.45	1183.45	0
19	1189.88	1183.00	1189.86	1189.86	0
20	1189.88	1183.01	1189.86	1189.86	0
21	1439.26	1439.83	1439.24	1439.24	0
22	1468.81	1467.34	1468.78	1468.78	0
23	1468.81	1467.34	1468.78	1468.78	0
24	1501.43	1497.87	1501.40	1501.40	0
25	1596.21	1586.54	1596.15	1596.15	0
26	3130.04	3146.05	3130.04	3130.04	0
27	3130.04	3146.13	3130.04	3130.04	0
28	3134.85	3148.68	3134.85	3134.85	0
29	3135.93	3151.11	3135.93	3135.93	0
30	3212.32	3235.55	3212.32	3212.32	0
31	3213.22	3236.81	3213.22	3213.22	0
32	3225.32	3247.84	3225.32	3225.32	0
33	3225.32	3247.93	3225.32	3225.32	0

S1.9 Aluminum Trichloride

Geometries

Table S25: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	Al	0.00000000	0.00000000	0.00000069
2	Cl	0.00000000	0.00000000	−3.92579486
3	Cl	0.00000000	3.39983903	1.96289716
4	Cl	0.00000000	−3.39983903	1.96289716

Natural Internal Coordinates

Table S26: Symmetrized, unnormalized natural internal coordinates for Aluminum Trichloride.

1	$r_{1,2} + r_{1,3} + r_{1,4}$
2	$2r_{1,2} - r_{1,3} - r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{3,1,4}$
5	$\phi_{2,1,4} - \phi_{3,1,4}$
6	$\gamma_{2,1,3,4} + \gamma_{3,1,4,2} + \gamma_{4,1,2,3}$

Frequencies

Table S27: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	147.27	146.23	147.27	147.27	0
2	147.29	146.24	147.29	147.29	0
3	207.49	206.64	207.49	207.49	0
4	388.75	388.95	388.75	388.75	0
5	628.44	628.70	628.44	628.44	0
6	628.44	628.71	628.44	628.44	0

S1.10 Aluminium Trifluoride

Geometries

Table S28: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	Al	0.00000000	0.00000000	0.00000081
2	F	0.00000000	0.00000000	−3.08479068
3	F	0.00000000	2.67150833	1.54239476
4	F	0.00000000	−2.67150833	1.54239476

Natural Internal Coordinates

Table S29: Symmetrized, unnormalized natural internal coordinates for Aluminium Trifluoride.

1	$r_{1,2} + r_{1,3} + r_{1,4}$
2	$2r_{1,2} - r_{1,3} - r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{3,1,4}$
5	$\phi_{2,1,4} - \phi_{3,1,4}$
6	$\gamma_{2,1,3,4} + \gamma_{3,1,4,2} + \gamma_{4,1,2,3}$

Frequencies

Table S30: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	244.84	245.46	244.85	244.85	0
2	244.99	245.47	244.98	244.98	0
3	301.32	301.60	301.32	301.32	0
4	695.29	697.03	695.29	695.29	0
5	962.28	965.75	962.28	962.28	0
6	962.29	965.79	962.28	962.28	0

S1.11 Boron Trichloride

Geometries

Table S31: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	B	0.00000000	0.00000000	0.00000105
2	Cl	0.00000000	0.00000000	−3.29682188
3	Cl	0.00000000	2.85513240	1.64841078
4	Cl	0.00000000	−2.85513240	1.64841078

Natural Internal Coordinates

Table S32: Symmetrized, unnormalized natural internal coordinates for Boron Trichloride.

1	$r_{1,2} + r_{1,3} + r_{1,4}$
2	$2r_{1,2} - r_{1,3} - r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{3,1,4}$
5	$\phi_{2,1,4} - \phi_{3,1,4}$
6	$\gamma_{2,1,3,4} + \gamma_{3,1,4,2} + \gamma_{4,1,2,3}$

Frequencies

Table S33: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	257.16	256.31	257.17	257.17	0
2	257.22	256.31	257.22	257.22	0
3	462.52	461.48	462.52	462.52	0
4	476.79	476.64	476.79	476.79	0
5	972.61	966.90	972.61	972.61	0
6	972.62	966.93	972.61	972.61	0

S1.12 Boron Trifluoride

Geometries

Table S34: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	B	0.00000000	0.00000000	−0.00000000
2	F	0.00000000	−2.14848994	1.24043124
3	F	0.00000000	−0.00000000	−2.48086249
4	F	−0.00000000	2.14848994	1.24043124

Natural Internal Coordinates

Table S35: Symmetrized, unnormalized natural internal coordinates for Boron Trifluoride.

1	$r_{1,2} + r_{1,3} + r_{1,4}$
2	$2r_{1,2} - r_{1,3} - r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{3,1,4}$
5	$\phi_{2,1,4} - \phi_{3,1,4}$
6	$\gamma_{2,1,3,4} + \gamma_{3,1,4,2} + \gamma_{4,1,2,3}$

Frequencies

Table S36: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	483.70	483.53	483.71	483.71	0
2	483.70	483.55	483.71	483.71	0
3	700.10	700.36	700.10	700.10	0
4	899.30	900.36	899.30	899.30	0
5	1493.14	1492.98	1493.14	1493.14	0
6	1493.14	1493.05	1493.14	1493.14	0

S1.13 Tetrachloromethane

Geometries

Table S37: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.00000000	0.00000000	0.00000006
2	Cl	0.00000000	−2.73683182	1.93523230
3	Cl	0.00000000	2.73683182	1.93523230
4	Cl	2.73683173	0.00000000	−1.93523231
5	Cl	−2.73683173	0.00000000	−1.93523231

Natural Internal Coordinates

Table S38: Symmetrized, unnormalized natural internal coordinates for Tetrachloromethane.

1	$r_{1,2} + r_{1,3} + r_{1,4} + r_{1,5}$
2	$-r_{1,2} - r_{1,3} + r_{1,4} + r_{1,5}$
3	$-r_{1,2} + r_{1,3} - r_{1,4} + r_{1,5}$
4	$r_{1,2} - r_{1,3} - r_{1,4} + r_{1,5}$
5	$2\phi_{2,1,3} + 2\phi_{4,1,5} - \phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5}$
6	$\phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} + \phi_{3,1,5}$
7	$-\phi_{2,1,3} + \phi_{4,1,5}$
8	$-\phi_{2,1,4} + \phi_{3,1,5}$
9	$\phi_{2,1,5} - \phi_{3,1,4}$

Frequencies

Table S39: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	218.41	217.54	218.42	218.42	0
2	218.44	217.55	218.42	218.42	0
3	316.69	315.68	316.69	316.69	0
4	316.70	315.68	316.73	316.73	0
5	316.79	315.70	316.76	316.76	0
6	463.23	461.64	463.23	463.23	0
7	802.53	788.95	802.54	802.54	0
8	802.56	788.95	802.55	802.55	0
9	802.57	789.03	802.57	802.57	0

S1.14 Tetrafluoromethane

Geometries

Table S40: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.00000000	0.00000000	0.00000000
2	F	0.00000000	−2.03544624	1.43927784
3	F	−0.00000000	2.03544624	1.43927784
4	F	2.03544624	0.00000000	−1.43927784
5	F	−2.03544624	−0.00000000	−1.43927784

Natural Internal Coordinates

Table S41: Symmetrized, unnormalized natural internal coordinates for Tetrafluoromethane.

1	$r_{1,2} + r_{1,3} + r_{1,4} + r_{1,5}$
2	$-r_{1,2} - r_{1,3} + r_{1,4} + r_{1,5}$
3	$-r_{1,2} + r_{1,3} - r_{1,4} + r_{1,5}$
4	$r_{1,2} - r_{1,3} - r_{1,4} + r_{1,5}$
5	$2\phi_{2,1,3} + 2\phi_{4,1,5} - \phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5}$
6	$\phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} + \phi_{3,1,5}$
7	$-\phi_{2,1,3} + \phi_{4,1,5}$
8	$-\phi_{2,1,4} + \phi_{3,1,5}$
9	$\phi_{2,1,5} - \phi_{3,1,4}$

Frequencies

Table S42: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	440.04	440.48	440.04	440.04	0
2	440.04	440.49	440.04	440.04	0
3	638.99	640.34	639.00	639.00	0
4	638.99	640.34	639.00	639.00	0
5	638.99	640.38	639.00	639.00	0
6	923.21	925.21	923.21	923.21	0
7	1323.00	1312.62	1323.00	1323.00	0
8	1323.00	1312.62	1323.00	1323.00	0
9	1323.00	1312.80	1323.00	1323.00	0

S1.15 Dichloromethane

Geometries

Table S43: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.00000000	1.52259374	0.00000000
2	Cl	−2.78829097	−0.33831409	0.00000000
3	Cl	2.78829098	−0.33831426	0.00000000
4	H	−0.00000018	2.67397215	−1.69354225
5	H	−0.00000018	2.67397215	1.69354225

Natural Internal Coordinates

Table S44: Symmetrized, unnormalized natural internal coordinates for Dichloromethane.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$r_{1,4} + r_{1,5}$
4	$r_{1,4} - r_{1,5}$
5	$4\phi_{2,1,3} - \phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5}$
6	$\phi_{2,1,4} + \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5}$
7	$\phi_{2,1,4} - \phi_{2,1,5} + \phi_{3,1,4} - \phi_{3,1,5}$
8	$\phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} + \phi_{3,1,5}$
9	$-\phi_{2,1,3} - \phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5} + 5\phi_{4,1,5}$

Frequencies

Table S45: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	284.60	284.30	284.60	284.60	0
2	723.57	725.46	723.58	723.58	0
3	776.83	774.86	776.86	776.86	0
4	906.97	909.44	906.97	906.97	0
5	1180.95	1185.94	1180.95	1180.95	0
6	1293.06	1291.47	1293.05	1293.05	0
7	1474.48	1477.10	1474.48	1474.48	0
8	3127.54	3142.79	3127.54	3127.54	0
9	3202.53	3224.11	3202.53	3202.53	0

S1.16 Difluoromethane

Geometries

Table S46: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.00000000	1.04690947	−0.00000000
2	F	−2.07913590	−0.44653109	0.00000000
3	F	2.07913592	−0.44653108	0.00000000
4	H	−0.00000010	2.18482447	−1.71602833
5	H	−0.00000010	2.18482447	1.71602833

Natural Internal Coordinates

Table S47: Symmetrized, unnormalized natural internal coordinates for Difluoromethane.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$r_{1,4} + r_{1,5}$
4	$r_{1,4} - r_{1,5}$
5	$4\phi_{2,1,3} - \phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5}$
6	$\phi_{2,1,4} + \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5}$
7	$\phi_{2,1,4} - \phi_{2,1,5} + \phi_{3,1,4} - \phi_{3,1,5}$
8	$\phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} + \phi_{3,1,5}$
9	$-\phi_{2,1,3} - \phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5} + 5\phi_{4,1,5}$

Frequencies

Table S48: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	536.99	538.02	536.99	536.99	0
2	1141.59	1138.11	1141.60	1141.60	0
3	1142.17	1144.15	1142.20	1142.20	0
4	1202.57	1207.65	1202.58	1202.58	0
5	1292.33	1297.51	1292.33	1292.33	0
6	1482.31	1487.77	1482.28	1482.28	0
7	1556.46	1565.86	1556.46	1556.46	0
8	3075.76	3092.64	3075.76	3075.76	0
9	3148.01	3173.45	3148.00	3148.00	0

S1.17 Formic Acid

Geometries

Table S49: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	H	0.05468955	2.84555164	−0.00000000
2	C	0.18775950	0.78180753	−0.00000000
3	O	2.12426566	−0.40608921	−0.00000000
4	O	−2.14789723	−0.23081035	0.00000000
5	H	−1.91525954	−2.04634183	0.00000000

Natural Internal Coordinates

Table S50: Symmetrized, unnormalized natural internal coordinates for Formic Acid.

1	$r_{2,3}$
2	$r_{2,4}$
3	$r_{2,1}$
4	$r_{4,5}$
5	$\phi_{2,4,5}$
6	$2\phi_{3,2,4} - \phi_{3,2,1} - \phi_{4,2,1}$
7	$\phi_{3,2,1} - \phi_{4,2,1}$
8	$\tau_{1,2,4,5} + \tau_{3,2,4,5}$
9	$\gamma_{1,2,3,4}$

Frequencies

Table S51: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	629.41	629.42	629.42	629.42	0
2	675.64	684.33	675.68	675.64	1
3	1061.21	1067.48	1061.18	1061.21	1
4	1137.12	1132.56	1137.64	1137.37	1
5	1326.19	1315.23	1326.02	1326.25	1
6	1415.80	1415.99	1415.64	1415.64	0
7	1824.55	1822.20	1824.47	1824.47	0
8	3089.21	3106.69	3089.21	3089.21	0
9	3764.00	3775.33	3764.00	3764.00	0

S1.18 Formaldehyde

Geometries

Table S52: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.00000000	0.00000000	1.14423616
2	H	0.00000000	−1.76987484	2.24620597
3	H	0.00000000	1.76987484	2.24620597
4	O	−0.00000000	0.00000000	−1.14151276

Natural Internal Coordinates

Table S53: Symmetrized, unnormalized natural internal coordinates for Formaldehyde.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$r_{1,4}$
4	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{3,1,4}$
5	$\phi_{2,1,4} - \phi_{3,1,4}$
6	$\gamma_{4,1,2,3}$

Frequencies

Table S54: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1192.19	1206.13	1192.19	1192.19	0
2	1274.88	1278.43	1274.88	1274.88	0
3	1543.21	1550.09	1543.24	1543.24	0
4	1780.76	1775.33	1780.75	1780.75	0
5	2929.23	2946.14	2929.22	2929.22	0
6	2995.85	3017.92	2995.85	2995.85	0

S1.19 Singlet Carbene

Geometries

Table S55: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.00000000	−0.00000000	0.19071799
2	H	0.00000000	−1.62640634	−1.13542319
3	H	0.00000000	1.62640634	−1.13542319

Natural Internal Coordinates

Table S56: Symmetrized, unnormalized natural internal coordinates for Singlet Carbene.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$\phi_{2,1,3}$

Frequencies

Table S57: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1406.59	1421.07	1406.59	1406.59	0
2	2912.05	2939.49	2912.05	2912.05	0
3	2983.12	3014.35	2983.12	2983.12	0

S1.20 Chloromethane

Geometries

Table S58: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	2.32154417	−0.00000390	0.00000000
2	Cl	−1.05377924	0.00000143	0.00000000
3	H	2.97370152	1.94601045	0.00000000
4	H	2.97370577	−0.97300677	1.68529621
5	H	2.97370577	−0.97300677	−1.68529621

Natural Internal Coordinates

Table S59: Symmetrized, unnormalized natural internal coordinates for Chloromethane.

1	$r_{1,2}$
2	$r_{1,3} + r_{1,4} + r_{1,5}$
3	$2r_{1,3} - r_{1,4} - r_{1,5}$
4	$r_{1,4} - r_{1,5}$
5	$2\phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2}$
6	$\phi_{4,1,2} - \phi_{5,1,2}$
7	$\phi_{3,1,2} + \phi_{4,1,2} + \phi_{5,1,2} - \phi_{3,1,4} - \phi_{4,1,5} - \phi_{5,1,3}$
8	$2\phi_{3,1,4} - \phi_{4,1,5} - \phi_{5,1,3}$
9	$\phi_{4,1,5} - \phi_{5,1,3}$

Frequencies

Table S60: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	746.24	750.33	746.24	746.24	0
2	1031.74	1035.40	1031.76	1031.76	0
3	1031.75	1035.40	1031.76	1031.76	0
4	1385.57	1385.91	1385.57	1385.57	0
5	1493.13	1498.37	1493.12	1493.12	0
6	1493.13	1498.39	1493.12	1493.12	0
7	3078.66	3092.10	3078.62	3078.62	0
8	3179.26	3202.42	3179.26	3179.26	0
9	3179.27	3202.54	3179.30	3179.30	0

S1.21 Thiomethanol

Geometries

Table S61: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.32717426	−0.02137589	0.00000000
2	S	1.11215342	0.08316595	0.00000000
3	H	−2.96283314	1.93620929	0.00000001
4	H	−3.04519469	−0.95084369	1.68762099
5	H	−3.04519470	−0.95084364	−1.68762102
6	H	1.48072095	−2.41834559	−0.00000002

Natural Internal Coordinates

Table S62: Symmetrized, unnormalized natural internal coordinates for Thiomethanol.

1	$r_{1,2}$
2	$r_{2,6}$
3	$r_{1,3} + r_{1,4} + r_{1,5}$
4	$r_{1,4} - r_{1,5}$
5	$2r_{1,3} - r_{1,4} - r_{1,5}$
6	$\phi_{1,2,6}$
7	$\phi_{3,1,2} + \phi_{4,1,2} + \phi_{5,1,2} - \phi_{3,1,4} - \phi_{3,1,5} - \phi_{4,1,5}$
8	$2\phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2}$
9	$\phi_{4,1,2} - \phi_{5,1,2}$
10	$2\phi_{3,1,4} - \phi_{3,1,5} - \phi_{4,1,5}$
11	$\phi_{3,1,5} - \phi_{4,1,5}$
12	$\tau_{3,1,2,6} + \tau_{4,1,2,6} + \tau_{5,1,2,6}$

Frequencies

Table S63: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	237.57	241.32	237.58	237.58	0
2	720.90	722.47	720.96	720.96	0
3	799.89	802.89	799.89	799.89	0
4	976.28	979.01	976.30	976.30	0
5	1099.81	1097.50	1099.81	1099.81	0
6	1362.14	1358.95	1362.14	1362.14	0
7	1482.93	1486.56	1482.92	1482.92	0
8	1497.03	1500.67	1497.01	1497.01	0
9	2712.63	2739.04	2712.64	2712.64	0
10	3059.91	3073.20	3059.91	3059.91	0
11	3150.01	3173.80	3150.01	3150.01	0
12	3151.27	3175.13	3151.27	3151.27	0

S1.22 Trichloromethane

Geometries

Table S64: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.00000070	0.89489730	0.00000000
2	H	0.00000088	2.93924961	0.00000000
3	Cl	−3.18361737	−0.13060258	0.00000000
4	Cl	1.59180855	−0.13060186	−2.75709409
5	Cl	1.59180855	−0.13060186	2.75709409

Natural Internal Coordinates

Table S65: Symmetrized, unnormalized natural internal coordinates for Trichloromethane.

1	$r_{1,2}$
2	$r_{1,3} + r_{1,4} + r_{1,5}$
3	$2r_{1,3} - r_{1,4} - r_{1,5}$
4	$r_{1,4} - r_{1,5}$
5	$2\phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2}$
6	$\phi_{4,1,2} - \phi_{5,1,2}$
7	$\phi_{3,1,2} + \phi_{4,1,2} + \phi_{5,1,2} - \phi_{3,1,4} - \phi_{3,1,5} - \phi_{4,1,5}$
8	$-\phi_{3,1,4} - \phi_{3,1,5} + 2\phi_{4,1,5}$
9	$\phi_{3,1,4} - \phi_{3,1,5}$

Frequencies

Table S66: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	261.66	260.93	261.69	261.69	0
2	261.72	260.94	261.69	261.69	0
3	368.48	367.99	368.48	368.48	0
4	678.57	679.33	678.57	678.57	0
5	789.88	782.53	789.98	789.98	0
6	789.90	782.54	789.98	789.98	0
7	1244.75	1243.31	1244.69	1244.69	0
8	1244.75	1243.33	1244.69	1244.69	0
9	3181.88	3198.65	3181.88	3181.88	0

S1.23 Trifluoromethan

Geometries

Table S67: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.68502199	−0.00000000	0.00000000
2	H	2.73949866	−0.00000000	0.00000000
3	F	−0.19266881	1.18093464	−2.04543880
4	F	−0.19266881	−2.36186929	−0.00000000
5	F	−0.19266881	1.18093464	2.04543880

Natural Internal Coordinates

Table S68: Symmetrized, unnormalized natural internal coordinates for Trifluoromethan.

1	$r_{1,2}$
2	$r_{1,3} + r_{1,4} + r_{1,5}$
3	$2r_{1,3} - r_{1,4} - r_{1,5}$
4	$r_{1,4} - r_{1,5}$
5	$2\phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2}$
6	$\phi_{4,1,2} - \phi_{5,1,2}$
7	$\phi_{3,1,2} + \phi_{4,1,2} + \phi_{5,1,2} - \phi_{3,1,4} - \phi_{3,1,5} - \phi_{4,1,5}$
8	$-\phi_{3,1,4} - \phi_{3,1,5} + 2\phi_{4,1,5}$
9	$\phi_{3,1,4} - \phi_{3,1,5}$

Frequencies

Table S69: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	514.80	515.45	514.81	514.81	0
2	514.80	515.48	514.81	514.81	0
3	710.23	711.57	710.23	710.23	0
4	1161.90	1164.53	1161.89	1161.89	0
5	1203.17	1197.08	1203.35	1203.35	0
6	1203.17	1197.12	1203.37	1203.37	0
7	1424.32	1427.20	1424.17	1424.17	0
8	1424.32	1427.23	1424.17	1424.17	0
9	3160.87	3181.06	3160.86	3160.86	0

S1.24 Methyl Nitrite

Geometries

Table S70: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−3.25927873	0.34172310	0.00000001
2	O	−0.88672134	−0.95845750	−0.00000001
3	N	1.10910462	0.84557965	0.00000003
4	O	3.08906348	−0.16302337	−0.00000001
5	H	−2.93271250	2.37633551	0.00000012
6	H	−4.31133488	−0.19761898	−1.68538742
7	H	−4.31133508	−0.19761956	1.68538715

Natural Internal Coordinates

Table S71: Symmetrized, unnormalized natural internal coordinates for Methyl Nitrite.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{3,4}$
4	$r_{1,5} + r_{1,6} + r_{1,7}$
5	$2r_{1,5} - r_{1,6} - r_{1,7}$
6	$r_{1,6} - r_{1,7}$
7	$\phi_{2,3,4}$
8	$\phi_{1,2,3}$
9	$\phi_{2,1,5} + \phi_{2,1,6} + \phi_{2,1,7} - \phi_{5,1,6} - \phi_{5,1,7} - \phi_{6,1,7}$
10	$2\phi_{2,1,5} - \phi_{2,1,6} - \phi_{2,1,7}$
11	$\phi_{2,1,6} - \phi_{2,1,7}$
12	$-\phi_{5,1,6} - \phi_{5,1,7} + 2\phi_{6,1,7}$
13	$\phi_{5,1,6} - \phi_{5,1,7}$
14	$\tau_{1,2,3,4}$
15	$\tau_{3,2,1,5} + \tau_{3,2,1,6} + \tau_{3,2,1,7}$

Frequencies

Table S72: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	79.74	99.66	79.93	79.77	2
2	220.92	229.50	220.89	220.92	2
3	380.32	375.76	380.49	380.49	0
4	595.01	575.13	598.57	598.57	0
5	847.80	827.78	846.95	846.95	0
6	1086.78	1082.35	1086.81	1086.81	0
7	1176.79	1179.55	1176.80	1176.80	1
8	1209.14	1204.43	1209.09	1209.09	0
9	1462.98	1462.45	1462.92	1462.92	0
10	1494.35	1499.64	1494.35	1494.35	1
11	1518.63	1524.68	1518.62	1518.62	0
12	1710.30	1670.96	1709.54	1709.54	0
13	3048.98	3060.46	3048.98	3048.98	0
14	3137.26	3160.80	3137.28	3137.28	0
15	3138.46	3161.15	3138.43	3138.43	0

S1.25 Nitromethane

Geometries

Table S73: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.64676127	−0.00000018	−0.00133681
2	N	0.17450660	0.00000001	−0.01682025
3	O	1.22490556	2.06093193	0.00501808
4	O	1.22490588	−2.06093176	0.00501808
5	H	−3.28037170	1.70855430	−0.93997613
6	H	−3.28037150	−1.70855540	−0.93997492
7	H	−3.22966507	0.00000052	1.97029345

Natural Internal Coordinates

Table S74: Symmetrized, unnormalized natural internal coordinates for Nitromethane.

1	$r_{1,2}$
2	$r_{2,3} + r_{2,4}$
3	$r_{2,3} - r_{2,4}$
4	$r_{1,5} + r_{1,6} + r_{1,7}$
5	$-r_{1,5} - r_{1,6} + 2r_{1,7}$
6	$r_{1,5} - r_{1,6}$
7	$2\phi_{3,2,4} - \phi_{1,2,3} - \phi_{1,2,4}$
8	$\phi_{1,2,3} - \phi_{1,2,4}$
9	$\phi_{2,1,7} + \phi_{2,1,5} + \phi_{2,1,6} - \phi_{5,1,6} - \phi_{5,1,7} - \phi_{6,1,7}$
10	$2\phi_{2,1,7} - \phi_{2,1,5} - \phi_{2,1,6}$
11	$\phi_{2,1,5} - \phi_{2,1,6}$
12	$2\phi_{5,1,6} - \phi_{5,1,7} - \phi_{6,1,7}$
13	$\phi_{5,1,7} - \phi_{6,1,7}$
14	$\tau_{3,2,1,5} + \tau_{3,2,1,6} + \tau_{3,2,1,7} + \tau_{4,2,1,5} + \tau_{4,2,1,6} + \tau_{4,2,1,7}$
15	$\gamma_{1,2,3,4}$

Frequencies

Table S75: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	23.40	25.03	24.07	23.40	5
2	476.95	478.52	477.03	476.95	2
3	608.74	609.44	608.76	608.76	0
4	670.00	674.13	670.02	670.02	0
5	935.44	940.68	935.45	935.45	0
6	1110.76	1117.68	1113.47	1110.88	2
7	1142.47	1141.73	1142.54	1142.54	0
8	1409.56	1409.25	1409.64	1409.64	0
9	1425.54	1427.95	1425.42	1425.42	0
10	1475.67	1482.99	1476.79	1476.79	1
11	1487.85	1493.04	1487.83	1487.83	0
12	1642.57	1787.82	1639.70	1641.49	3
13	3088.79	3099.95	3088.81	3088.81	0
14	3186.71	3207.19	3186.69	3186.69	0
15	3215.04	3235.09	3215.04	3215.04	1

S1.26 Methylamine

Geometries

Table S76: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−1.40168824	−0.00000000	0.02605239
2	N	1.36882488	−0.00000000	−0.14039430
3	H	2.05503952	1.52392893	0.79571578
4	H	2.05503953	−1.52392892	0.79571579
5	H	−2.13608556	1.65964124	−0.95180826
6	H	−2.13608556	−1.65964127	−0.95180822
7	H	−2.16717853	0.00000003	1.95267120

Natural Internal Coordinates

Table S77: Symmetrized, unnormalized natural internal coordinates for Methylamine.

1	$r_{1,2}$
2	$r_{2,3} + r_{2,4}$
3	$r_{2,3} - r_{2,4}$
4	$r_{1,5} + r_{1,6} + r_{1,7}$
5	$-r_{1,5} - r_{1,6} + 2r_{1,7}$
6	$r_{1,5} - r_{1,6}$
7	$2\phi_{3,2,4} - \phi_{1,2,3} - \phi_{1,2,4}$
8	$\phi_{1,2,3} - \phi_{1,2,4}$
9	$\phi_{2,1,7} + \phi_{2,1,5} + \phi_{2,1,6} - \phi_{5,1,6} - \phi_{5,1,7} - \phi_{6,1,7}$
10	$2\phi_{2,1,7} - \phi_{2,1,5} - \phi_{2,1,6}$
11	$\phi_{2,1,5} - \phi_{2,1,6}$
12	$2\phi_{5,1,6} - \phi_{5,1,7} - \phi_{6,1,7}$
13	$\phi_{5,1,7} - \phi_{6,1,7}$
14	$\tau_{3,2,1,5} + \tau_{3,2,1,6} + \tau_{3,2,1,7} + \tau_{4,2,1,5} + \tau_{4,2,1,6} + \tau_{4,2,1,7}$
15	$\gamma_{1,2,3,4}$

Frequencies

Table S78: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	306.35	309.02	306.36	306.36	0
2	878.35	872.19	878.51	878.51	0
3	976.31	977.96	976.32	976.32	0
4	1065.57	1066.66	1065.60	1065.60	0
5	1188.02	1185.98	1187.95	1187.95	0
6	1359.39	1355.66	1359.40	1359.40	0
7	1458.06	1456.34	1458.08	1458.08	0
8	1508.16	1512.94	1508.13	1508.13	0
9	1527.65	1532.77	1527.65	1527.65	0
10	1667.46	1658.62	1667.45	1667.45	0
11	2996.98	3013.70	2997.33	2997.33	0
12	3079.94	3102.89	3079.58	3079.58	0
13	3115.36	3141.51	3115.38	3115.38	0
14	3498.27	3513.79	3498.26	3498.26	0
15	3579.12	3605.77	3579.12	3579.12	0

S1.27 Ethylene

Geometries

Table S79: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	1.26340450	0.00000000	0.00000000
2	H	2.33147619	−1.74616425	0.00000000
3	H	2.33147619	1.74616425	0.00000000
4	C	−1.26340450	0.00000000	−0.00000000
5	H	−2.33147619	−1.74616425	−0.00000000
6	H	−2.33147619	1.74616425	−0.00000000

Natural Internal Coordinates

Table S80: Symmetrized, unnormalized natural internal coordinates for Ethylene.

1	$r_{1,4}$
2	$r_{1,2} + r_{1,3} + r_{4,5} + r_{4,6}$
3	$r_{1,2} + r_{1,3} - r_{4,5} - r_{4,6}$
4	$r_{1,2} - r_{1,3} + r_{4,5} - r_{4,6}$
5	$r_{1,2} - r_{1,3} - r_{4,5} + r_{4,6}$
6	$\phi_{2,1,4} + \phi_{3,1,4} + \phi_{5,4,1} + \phi_{6,4,1}$
7	$\phi_{2,1,4} - \phi_{3,1,4} + \phi_{5,4,1} - \phi_{6,4,1}$
8	$\phi_{2,1,4} - \phi_{3,1,4} - \phi_{5,4,1} + \phi_{6,4,1}$
9	$\phi_{2,1,4} + \phi_{3,1,4} - \phi_{5,4,1} - \phi_{6,4,1}$
10	$\tau_{2,1,4,5} + \tau_{3,1,4,6}$
11	$\gamma_{1,4,5,6} + \gamma_{4,1,2,3}$
12	$\gamma_{1,4,5,6} - \gamma_{4,1,2,3}$

Frequencies

Table S81: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	823.04	820.93	823.05	823.05	0
2	941.84	957.22	941.84	941.84	0
3	966.67	981.28	966.67	966.67	0
4	1046.96	1070.98	1046.96	1046.96	0
5	1242.16	1238.74	1242.16	1242.16	0
6	1368.98	1373.22	1368.99	1368.99	0
7	1479.06	1479.21	1479.06	1479.06	0
8	1671.73	1666.27	1671.73	1671.73	0
9	3139.11	3155.69	3139.08	3139.08	0
10	3157.09	3173.05	3157.09	3157.09	0
11	3219.26	3241.74	3219.29	3219.29	0
12	3246.14	3268.43	3246.13	3246.13	0

S1.28 Tetrafluoroethylene

Geometries

Table S82: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.00000000	1.25411723	−0.00000000
2	F	−0.00000000	2.61971410	−2.07863349
3	F	−0.00000000	2.61971408	2.07863350
4	C	0.00000000	−1.25411723	−0.00000000
5	F	0.00000000	−2.61971410	−2.07863349
6	F	0.00000000	−2.61971408	2.07863350

Natural Internal Coordinates

Table S83: Symmetrized, unnormalized natural internal coordinates for Tetrafluoroethylene.

1	$r_{1,4}$
2	$r_{1,2} + r_{1,3} + r_{4,5} + r_{4,6}$
3	$r_{1,2} + r_{1,3} - r_{4,5} - r_{4,6}$
4	$r_{1,2} - r_{1,3} + r_{4,5} - r_{4,6}$
5	$r_{1,2} - r_{1,3} - r_{4,5} + r_{4,6}$
6	$\phi_{2,1,4} + \phi_{3,1,4} + \phi_{5,4,1} + \phi_{6,4,1}$
7	$\phi_{2,1,4} - \phi_{3,1,4} + \phi_{5,4,1} - \phi_{6,4,1}$
8	$\phi_{2,1,4} - \phi_{3,1,4} - \phi_{5,4,1} + \phi_{6,4,1}$
9	$\phi_{2,1,4} + \phi_{3,1,4} - \phi_{5,4,1} - \phi_{6,4,1}$
10	$\tau_{2,1,4,5} + \tau_{3,1,4,6}$
11	$\gamma_{1,4,5,6} + \gamma_{4,1,2,3}$
12	$\gamma_{1,4,5,6} - \gamma_{4,1,2,3}$

Frequencies

Table S84: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	201.37	204.23	201.37	201.37	0
2	210.88	210.73	210.88	210.88	0
3	401.04	401.72	401.04	401.04	0
4	418.44	429.82	418.44	418.44	0
5	511.82	544.36	511.82	511.82	0
6	556.41	557.57	556.41	556.41	0
7	559.79	560.96	559.79	559.79	0
8	797.32	798.26	797.32	797.32	0
9	1208.55	1209.09	1208.55	1208.55	0
10	1376.54	1370.04	1376.54	1376.54	0
11	1385.81	1374.39	1385.81	1385.81	0
12	1921.15	1919.42	1921.15	1921.15	0

S1.29 Tetrachloroethylene

Geometries

Table S85: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	1.27393262	0.00000000	0.00000000
2	Cl	3.00539606	−2.74614238	0.00000000
3	Cl	3.00539606	2.74614238	0.00000000
4	C	−1.27393262	0.00000000	0.00000000
5	Cl	−3.00539606	−2.74614238	0.00000000
6	Cl	−3.00539606	2.74614238	0.00000000

Natural Internal Coordinates

Table S86: Symmetrized, unnormalized natural internal coordinates for Tetrachloroethylene.

1	$r_{1,4}$
2	$r_{1,2} + r_{1,3} + r_{4,5} + r_{4,6}$
3	$r_{1,2} + r_{1,3} - r_{4,5} - r_{4,6}$
4	$r_{1,2} - r_{1,3} + r_{4,5} - r_{4,6}$
5	$r_{1,2} - r_{1,3} - r_{4,5} + r_{4,6}$
6	$\phi_{2,1,4} + \phi_{3,1,4} + \phi_{5,4,1} + \phi_{6,4,1}$
7	$\phi_{2,1,4} - \phi_{3,1,4} + \phi_{5,4,1} - \phi_{6,4,1}$
8	$\phi_{2,1,4} - \phi_{3,1,4} - \phi_{5,4,1} + \phi_{6,4,1}$
9	$\phi_{2,1,4} + \phi_{3,1,4} - \phi_{5,4,1} - \phi_{6,4,1}$
10	$\tau_{2,1,4,5} + \tau_{3,1,4,6}$
11	$\gamma_{1,4,5,6} + \gamma_{4,1,2,3}$
12	$\gamma_{1,4,5,6} - \gamma_{4,1,2,3}$

Frequencies

Table S87: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	99.15	101.09	99.15	99.15	0
2	176.42	173.07	176.42	176.42	0
3	236.38	234.26	236.39	236.39	0
4	288.16	289.29	288.16	288.16	0
5	312.17	311.43	312.17	312.17	0
6	348.10	347.47	348.10	348.10	0
7	452.08	450.75	452.08	452.08	0
8	517.55	523.90	517.55	517.55	0
9	785.28	780.62	785.28	785.28	0
10	928.96	919.10	928.96	928.96	0
11	1009.16	988.51	1009.16	1009.16	0
12	1614.67	1601.17	1614.67	1614.67	0

S1.30 Acetylene

Geometries

Table S88: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	X	1.00000000	0.00000000	1.14300021
2	C	−0.00000000	0.00000000	1.14300021
3	X	−0.00000000	1.00000000	1.14300021
4	X	1.00000000	0.00000000	−1.14300021
5	C	−0.00000000	0.00000000	−1.14300021
6	X	−0.00000000	1.00000000	−1.14300021
7	H	−0.00000000	0.00000000	3.15309138
8	H	−0.00000000	−0.00000000	−3.15309138

Natural Internal Coordinates

Table S89: Symmetrized, unnormalized natural internal coordinates for Acetylene.

1	$r_{2,5}$
2	$r_{2,7} + r_{5,8}$
3	$r_{2,7} - r_{5,8}$
4	$\theta_{7,2,5,1} + \theta_{7,2,5,3}$
5	$\theta_{7,2,5,1} - \theta_{7,2,5,3}$
6	$\theta_{8,5,2,4} + \theta_{8,5,2,6}$
7	$\theta_{8,5,2,4} - \theta_{8,5,2,6}$

Frequencies

Table S90: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	577.56	591.03	577.56	577.56	0
2	577.56	591.11	577.56	577.56	0
3	746.28	752.04	746.28	746.28	0
4	746.28	752.11	746.28	746.28	0
5	2000.86	1983.61	2000.91	2000.91	0
6	3409.95	3424.96	3409.95	3409.95	0
7	3510.94	3522.34	3510.91	3510.91	0

S1.31 Glycoxal

Geometries

Table S91: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	1.21889603	−0.76024287	−0.00000000
2	H	0.96585913	−2.82956991	−0.00000000
3	O	3.26409381	0.26574464	−0.00000000
4	C	−1.21889603	0.76024286	0.00000000
5	H	−0.96585912	2.82956990	0.00000000
6	O	−3.26409381	−0.26574463	0.00000000

Natural Internal Coordinates

Table S92: Symmetrized, unnormalized natural internal coordinates for Glycoxal.

1	$r_{1,4}$
2	$r_{1,2} + r_{4,5}$
3	$r_{1,2} - r_{4,5}$
4	$r_{1,3} + r_{4,6}$
5	$r_{1,3} - r_{4,6}$
6	$\phi_{2,1,4} - \phi_{2,1,3} + \phi_{5,4,6} - \phi_{5,4,1}$
7	$\phi_{2,1,4} - \phi_{2,1,3} - \phi_{5,4,6} + \phi_{5,4,1}$
8	$-\phi_{2,1,4} - \phi_{2,1,3} + 2\phi_{4,1,3} - \phi_{5,4,6} - \phi_{5,4,1} + 2\phi_{1,4,6}$
9	$-\phi_{2,1,4} - \phi_{2,1,3} + 2\phi_{4,1,3} + \phi_{5,4,6} + \phi_{5,4,1} - 2\phi_{1,4,6}$
10	$\tau_{6,4,1,3}$
11	$\gamma_{5,4,6,1} + \gamma_{2,1,3,4}$
12	$\gamma_{5,4,6,1} - \gamma_{2,1,3,4}$

Frequencies

Table S93: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	136.26	135.79	136.32	136.26	1
2	330.98	329.78	330.98	330.98	0
3	560.06	557.98	560.08	560.08	0
4	823.86	832.67	823.85	823.86	1
5	1068.80	1079.34	1068.80	1068.80	0
6	1095.40	1095.62	1095.49	1095.49	0
7	1342.00	1343.96	1342.01	1342.01	0
8	1384.84	1387.70	1384.84	1384.84	0
9	1757.89	1750.67	1757.88	1757.88	0
10	1779.77	1763.00	1779.71	1779.71	0
11	2982.13	2998.21	2982.14	2982.14	0
12	2987.10	3002.93	2987.09	2987.09	0

S1.32 Ketene

Geometries

Table S94: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.00000000	0.00000000	−2.45258708
2	C	−0.00000000	0.00000000	0.03916157
3	H	1.77986810	0.00000000	−3.44221703
4	H	−1.77986810	−0.00000000	−3.44221703
5	O	0.00000000	−0.00000000	2.24442655

Natural Internal Coordinates

Table S95: Symmetrized, unnormalized natural internal coordinates for Ketene.

1	$r_{1,2}$
2	$r_{2,5}$
3	$r_{1,3} + r_{1,4}$
4	$r_{1,3} - r_{1,4}$
5	$2\phi_{3,1,4} - \phi_{3,1,2} - \phi_{4,1,2}$
6	$\phi_{3,1,2} - \phi_{4,1,2}$
7	$\gamma_{2,1,3,4}$
8	$\alpha^x_{3,1,2,5} - \alpha^x_{4,1,2,5}$
9	$\alpha^y_{3,1,2,5} - \alpha^y_{4,1,2,5}$

Frequencies

Table S96: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	434.17	432.90	434.38	434.38	0
2	514.86	504.86	521.98	514.86	1
3	590.76	583.94	584.48	590.76	1
4	993.60	986.64	993.51	993.51	0
5	1151.97	1152.32	1151.98	1151.98	0
6	1419.96	1412.28	1419.97	1419.97	0
7	2196.66	2215.50	2196.65	2196.65	0
8	3201.09	3215.62	3201.09	3201.09	0
9	3305.76	3323.30	3305.76	3305.76	0

S1.33 Vinyl Fluoride

Geometries

Table S97: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.23062727	0.84927217	0.00000000
2	F	2.01489057	−0.33348284	−0.00000000
3	H	−0.03883537	2.88455505	0.00000000
4	C	−2.40187281	−0.41086779	−0.00000000
5	H	−2.44489109	−2.45275480	−0.00000000
6	H	−4.15403542	0.63464361	−0.00000000

Natural Internal Coordinates

Table S98: Symmetrized, unnormalized natural internal coordinates for Vinyl Fluoride.

1	$r_{1,4}$
2	$r_{1,2}$
3	$r_{1,3}$
4	$r_{4,5} + r_{4,6}$
5	$r_{4,5} - r_{4,6}$
6	$2\phi_{2,1,4} - \phi_{2,1,3} - \phi_{4,1,3}$
7	$\phi_{2,1,3} - \phi_{4,1,3}$
8	$2\phi_{5,4,6} - \phi_{5,4,1} - \phi_{6,4,1}$
9	$\phi_{5,4,1} - \phi_{6,4,1}$
10	$\tau_{6,4,1,2} + \tau_{5,4,1,2}$
11	$\gamma_{1,4,5,6}$
12	$\gamma_{3,1,2,4}$

Frequencies

Table S99: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	481.38	481.34	481.41	481.41	0
2	725.01	738.02	725.10	725.10	0
3	871.03	871.03	871.09	871.09	0
4	945.55	942.22	945.59	945.56	1
5	956.17	973.16	956.06	956.06	0
6	1186.16	1183.93	1186.17	1186.20	1
7	1335.38	1337.10	1335.38	1335.38	0
8	1424.87	1422.87	1424.85	1424.85	0
9	1703.22	1696.19	1703.21	1703.21	0
10	3178.28	3194.10	3178.29	3178.29	0
11	3216.73	3235.18	3216.71	3216.71	0
12	3280.45	3301.10	3280.45	3280.45	0

S1.34 Vinyl Chloride

Geometries

Table S100: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−1.25457203	0.96043344	0.00000000
2	Cl	1.82672009	−0.15681495	0.00000000
3	H	−1.37832434	2.99846821	0.00000000
4	C	−3.26305888	−0.55916494	0.00000000
5	H	−3.07637332	−2.59407651	0.00000000
6	H	−5.13698193	0.25883536	0.00000000

Natural Internal Coordinates

Table S101: Symmetrized, unnormalized natural internal coordinates for Vinyl Chloride.

1	$r_{1,4}$
2	$r_{1,2}$
3	$r_{1,3}$
4	$r_{4,5} + r_{4,6}$
5	$r_{4,5} - r_{4,6}$
6	$-\phi_{2,1,3} + 2\phi_{2,1,4} - \phi_{3,1,4}$
7	$\phi_{2,1,3} - \phi_{3,1,4}$
8	$2\phi_{5,4,6} - \phi_{5,4,1} - \phi_{6,4,1}$
9	$\phi_{5,4,1} - \phi_{6,4,1}$
10	$\tau_{2,1,4,6} + \tau_{3,1,4,5}$
11	$\gamma_{1,4,5,6}$
12	$\gamma_{4,1,2,3}$

Frequencies

Table S102: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	393.16	392.78	393.17	393.17	0
2	624.92	635.79	624.94	624.94	0
3	728.91	728.17	728.92	728.92	0
4	906.85	907.59	906.93	906.93	0
5	967.57	982.20	967.48	967.48	0
6	1043.79	1038.88	1043.83	1043.83	0
7	1303.91	1302.52	1303.94	1303.94	0
8	1409.03	1407.89	1408.98	1408.98	0
9	1648.92	1640.61	1648.90	1648.90	0
10	3163.14	3178.41	3163.14	3163.14	0
11	3219.69	3237.30	3219.69	3219.69	0
12	3261.58	3282.15	3261.58	3261.58	0

S1.35 Acetyl Chloride

Geometries

Table S103: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	2.37756991	2.26850483	−0.00055361
2	C	1.05905955	−0.24683567	0.00014473
3	O	2.00061832	−2.28726397	0.00084009
4	Cl	−2.32530065	0.10341395	−0.00018125
5	H	4.41124345	1.96733004	−0.00032789
6	H	1.80005376	3.33615707	−1.66508115
7	H	1.79983852	3.33719391	1.66323370

Natural Internal Coordinates

Table S104: Symmetrized, unnormalized natural internal coordinates for Acetyl Chloride.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{2,4}$
4	$r_{1,5} + r_{1,6} + r_{1,7}$
5	$2r_{1,5} - r_{1,6} - r_{1,7}$
6	$r_{1,6} - r_{1,7}$
7	$2\phi_{3,2,4} - \phi_{1,2,3} - \phi_{1,2,4}$
8	$\phi_{1,2,3} - \phi_{1,2,4}$
9	$\phi_{2,1,5} + \phi_{2,1,7} + \phi_{2,1,6} - \phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
10	$2\phi_{2,1,5} - \phi_{2,1,7} - \phi_{2,1,6}$
11	$\phi_{2,1,7} - \phi_{2,1,6}$
12	$2\phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
13	$\phi_{5,1,6} - \phi_{5,1,7}$
14	$\tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{7,1,2,3} + \tau_{5,1,2,4} + \tau_{6,1,2,4} + \tau_{7,1,2,4}$
15	$\gamma_{4,2,3,1}$

Frequencies

Table S105: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	143.29	141.31	143.38	143.38	0
2	343.07	343.02	343.09	343.09	0
3	448.70	445.39	449.01	449.01	0
4	518.05	518.31	518.07	518.07	0
5	613.58	607.92	613.53	613.53	0
6	969.93	964.69	969.97	969.97	0
7	1047.49	1043.56	1047.49	1047.49	0
8	1127.04	1119.34	1126.99	1126.99	0
9	1394.09	1384.66	1394.11	1394.11	0
10	1472.26	1473.36	1472.23	1472.23	0
11	1478.20	1479.88	1478.19	1478.19	0
12	1859.03	1851.75	1859.00	1859.00	0
13	3062.21	3073.63	3062.22	3062.22	0
14	3142.85	3165.10	3142.85	3142.85	0
15	3169.14	3190.52	3169.13	3169.13	0

S1.36 Acetyl Fluoride

Geometries

Table S106: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	2.76454271	0.01457545	0.00000000
2	C	−0.04920230	−0.29403538	−0.00000002
3	O	−1.26541246	−2.18009943	0.00000001
4	F	−1.19736497	1.99333285	0.00000000
5	H	3.66400828	−1.82995283	0.00000007
6	H	3.32965655	1.09054359	−1.66356692
7	H	3.32965649	1.09054368	1.66356688

Natural Internal Coordinates

Table S107: Symmetrized, unnormalized natural internal coordinates for Acetyl Fluoride.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{2,4}$
4	$r_{1,5} + r_{1,6} + r_{1,7}$
5	$2r_{1,5} - r_{1,6} - r_{1,7}$
6	$r_{1,6} - r_{1,7}$
7	$2\phi_{3,2,4} - \phi_{1,2,3} - \phi_{1,2,4}$
8	$\phi_{1,2,3} - \phi_{1,2,4}$
9	$\phi_{2,1,5} + \phi_{2,1,7} + \phi_{2,1,6} - \phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
10	$2\phi_{2,1,5} - \phi_{2,1,7} - \phi_{2,1,6}$
11	$\phi_{2,1,7} - \phi_{2,1,6}$
12	$2\phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
13	$\phi_{5,1,6} - \phi_{5,1,7}$
14	$\tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{7,1,2,3} + \tau_{5,1,2,4} + \tau_{6,1,2,4} + \tau_{7,1,2,4}$
15	$\gamma_{4,2,3,1}$

Frequencies

Table S108: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	135.38	132.54	135.45	135.45	0
2	412.95	414.29	412.96	412.96	0
3	572.45	574.75	572.47	572.47	0
4	605.07	605.58	605.08	605.08	0
5	854.81	852.71	854.85	854.85	0
6	1017.14	1013.96	1017.18	1017.18	0
7	1073.07	1071.02	1073.06	1073.06	0
8	1229.96	1221.96	1229.93	1229.93	0
9	1409.07	1402.51	1409.08	1409.08	0
10	1478.05	1480.42	1478.01	1478.01	0
11	1486.58	1489.92	1486.58	1486.58	0
12	1905.64	1901.44	1905.63	1905.63	0
13	3067.89	3079.93	3067.88	3067.88	0
14	3141.37	3163.75	3141.39	3141.39	0
15	3183.94	3205.21	3183.91	3183.91	0

S1.37 Acetic Acid

Geometries

Table S109: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.75458669	−0.07584462	0.00000006
2	C	0.07515133	0.19163584	0.00000005
3	O	1.24072442	2.15236111	0.00000001
4	O	1.22880289	−2.09877025	−0.00000003
5	H	−3.61644252	1.78677173	0.00000005
6	H	−3.34756391	−1.13717476	−1.66377116
7	H	−3.34756393	−1.13717626	1.66377031
8	H	3.02195767	−1.74165265	−0.00000015

Natural Internal Coordinates

Table S110: Symmetrized, unnormalized natural internal coordinates for Acetic Acid.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{2,4}$
4	$r_{4,8}$
5	$r_{1,5} + r_{1,6} + r_{1,7}$
6	$2r_{1,5} - r_{1,6} - r_{1,7}$
7	$r_{1,6} - r_{1,7}$
8	$\phi_{1,2,3} - \phi_{3,2,4}$
9	$-\phi_{1,2,3} - \phi_{3,2,4} + 2\phi_{4,2,1}$
10	$\phi_{2,4,8}$
11	$\phi_{5,1,2} + \phi_{6,1,2} + \phi_{7,1,2} - \phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
12	$2\phi_{5,1,2} - \phi_{6,1,2} - \phi_{7,1,2}$
13	$\phi_{6,1,2} - \phi_{7,1,2}$
14	$2\phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
15	$\phi_{5,1,6} - \phi_{5,1,7}$
16	$\tau_{1,2,4,8} + \tau_{3,2,4,8}$
17	$\tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{7,1,2,3} + \tau_{5,1,2,4} + \tau_{6,1,2,4} + \tau_{7,1,2,4}$
18	$\gamma_{3,2,1,4}$

Frequencies

Table S111: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	78.18	74.63	78.24	78.24	0
2	418.78	418.93	418.79	418.79	0
3	545.73	550.36	545.87	545.73	1
4	584.13	584.54	584.13	584.13	0
5	664.47	669.23	664.36	664.47	1
6	869.68	868.69	869.70	869.70	0
7	1005.01	1001.34	1005.10	1005.10	0
8	1071.35	1068.94	1071.36	1071.36	0
9	1220.34	1207.39	1220.48	1220.48	0
10	1355.18	1345.92	1355.10	1355.10	0
11	1422.27	1414.33	1422.33	1422.33	0
12	1481.23	1482.91	1481.15	1481.15	0
13	1487.62	1490.52	1487.61	1487.61	0
14	1837.11	1834.76	1837.05	1837.05	0
15	3064.96	3077.09	3064.96	3064.96	0
16	3137.39	3160.27	3137.42	3137.42	0
17	3180.57	3202.28	3180.54	3180.54	0
18	3776.29	3786.74	3776.29	3776.29	0

S1.38 Methyl Formate

Geometries

Table S112: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.56474627	1.03805801	−0.00000001
2	O	−1.13832898	−1.27719414	0.00000001
3	C	1.37333384	−0.93569129	−0.00000000
4	O	2.44023024	1.07500163	0.00000000
5	H	−2.12605991	2.14890436	−1.67647724
6	H	−4.53723889	0.47158333	0.00000002
7	H	−2.12605989	2.14890440	1.67647720
8	H	2.31318467	−2.77931310	−0.00000007

Natural Internal Coordinates

Table S113: Symmetrized, unnormalized natural internal coordinates for Methyl Formate.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{3,4}$
4	$r_{3,8}$
5	$r_{1,6} + r_{1,5} + r_{1,7}$
6	$2r_{1,6} - r_{1,5} - r_{1,7}$
7	$r_{1,5} - r_{1,7}$
8	$\phi_{1,2,3}$
9	$2\phi_{2,3,4} - \phi_{4,3,8} - \phi_{2,3,8}$
10	$\phi_{4,3,8} - \phi_{2,3,8}$
11	$\phi_{5,1,7} + \phi_{6,1,5} + \phi_{6,1,7} - \phi_{6,1,2} - \phi_{5,1,2} - \phi_{7,1,2}$
12	$2\phi_{5,1,7} - \phi_{6,1,5} - \phi_{6,1,7}$
13	$\phi_{6,1,5} - \phi_{6,1,7}$
14	$2\phi_{6,1,2} - \phi_{5,1,2} - \phi_{7,1,2}$
15	$\phi_{5,1,2} - \phi_{7,1,2}$
16	$\tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{7,1,2,3}$
17	$\tau_{1,2,3,4} + \tau_{1,2,3,8}$
18	$\gamma_{8,3,2,4}$

Frequencies

Table S114: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	144.91	146.02	144.93	144.92	1
2	310.98	307.68	311.00	311.00	0
3	339.98	345.55	339.98	339.98	2
4	776.79	775.66	776.84	776.84	0
5	957.60	956.35	957.66	957.66	0
6	1049.47	1051.93	1049.50	1049.50	0
7	1185.12	1186.88	1185.11	1185.11	1
8	1195.91	1192.67	1195.90	1195.89	1
9	1243.84	1244.63	1243.95	1243.95	1
10	1404.55	1405.23	1404.51	1404.51	0
11	1472.50	1472.53	1472.54	1472.54	0
12	1495.32	1501.54	1495.32	1495.32	0
13	1509.79	1514.42	1509.73	1509.73	0
14	1799.60	1796.87	1799.54	1799.54	0
15	3063.30	3075.57	3063.31	3063.31	0
16	3078.26	3094.68	3078.25	3078.25	0
17	3143.88	3167.12	3143.90	3143.90	0
18	3176.95	3200.92	3176.94	3176.94	0

S1.39 Acetaldehyde

Geometries

Table S115: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.38336780	0.31344831	−0.00000000
2	C	0.23682939	−0.79607621	0.00000000
3	O	2.16461069	0.43923199	−0.00000000
4	H	0.32309962	−2.88723239	0.00000000
5	H	−2.29051382	2.36809272	−0.00000000
6	H	−3.41403157	−0.35261154	1.66196703
7	H	−3.41403157	−0.35261154	−1.66196703

Natural Internal Coordinates

Table S116: Symmetrized, unnormalized natural internal coordinates for Acetaldehyde.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{2,4}$
4	$r_{1,5} + r_{1,6} + r_{1,7}$
5	$2r_{1,5} - r_{1,6} - r_{1,7}$
6	$r_{1,6} - r_{1,7}$
7	$2\phi_{3,2,4} - \phi_{1,2,3} - \phi_{1,2,4}$
8	$\phi_{1,2,3} - \phi_{1,2,4}$
9	$\phi_{2,1,5} + \phi_{2,1,7} + \phi_{2,1,6} - \phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
10	$2\phi_{2,1,5} - \phi_{2,1,7} - \phi_{2,1,6}$
11	$\phi_{2,1,7} - \phi_{2,1,6}$
12	$2\phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
13	$\phi_{5,1,6} - \phi_{5,1,7}$
14	$\tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{7,1,2,3} + \tau_{5,1,2,4} + \tau_{6,1,2,4} + \tau_{7,1,2,4}$
15	$\gamma_{4,2,3,1}$

Frequencies

Table S117: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	156.12	156.62	156.22	156.22	0
2	503.56	504.01	503.57	503.57	0
3	777.41	776.76	777.53	777.53	0
4	895.54	892.86	895.58	895.58	0
5	1132.41	1132.22	1132.34	1132.34	0
6	1134.44	1134.44	1134.47	1134.47	0
7	1383.16	1376.14	1383.33	1383.33	0
8	1431.32	1433.07	1431.24	1431.24	0
9	1469.93	1471.25	1469.88	1469.88	0
10	1481.19	1483.82	1481.18	1481.18	0
11	1793.14	1785.54	1793.10	1793.10	0
12	2918.88	2935.71	2918.89	2918.89	0
13	3037.72	3050.23	3037.74	3037.74	0
14	3105.97	3130.03	3105.96	3105.96	0
15	3156.22	3178.16	3156.18	3156.18	0

S1.40 Ethyl Chloride

Geometries

Table S118: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−3.24283313	−0.71079689	0.00001780
2	C	−1.15424910	1.25364339	0.00001865
3	H	−3.11757518	−1.90843903	1.67184314
4	H	−5.08083649	0.23136791	−0.00001805
5	H	−3.11753003	−1.90846919	−1.67178078
6	H	−1.22483776	2.44525634	1.67392859
7	H	−1.22486361	2.44528373	−1.67387166
8	Cl	1.90564864	−0.22389552	−0.00001543

Natural Internal Coordinates

Table S119: Symmetrized, unnormalized natural internal coordinates for Ethyl Chloride.

1	$r_{1,2}$
2	$r_{2,8}$
3	$r_{1,4} + r_{1,3} + r_{1,5}$
4	$2r_{1,4} - r_{1,3} - r_{1,5}$
5	$r_{1,3} - r_{1,5}$
6	$r_{2,6} + r_{2,7}$
7	$r_{2,6} - r_{2,7}$
8	$\phi_{1,2,8}$
9	$\phi_{6,2,1} + \phi_{6,2,8} - \phi_{7,2,1} - \phi_{7,2,8}$
10	$\phi_{6,2,1} - \phi_{6,2,8} + \phi_{7,2,1} - \phi_{7,2,8}$
11	$\phi_{6,2,1} - \phi_{6,2,8} - \phi_{7,2,1} + \phi_{7,2,8}$
12	$-\phi_{6,2,1} - \phi_{6,2,8} - \phi_{7,2,1} - \phi_{7,2,8} + 4\phi_{6,2,7}$
13	$\phi_{4,1,2} + \phi_{3,1,2} + \phi_{5,1,2} - \phi_{3,1,5} - \phi_{4,1,3} - \phi_{4,1,5}$
14	$2\phi_{4,1,2} - \phi_{3,1,2} - \phi_{5,1,2}$
15	$\phi_{3,1,2} - \phi_{5,1,2}$
16	$2\phi_{3,1,5} - \phi_{4,1,3} - \phi_{4,1,5}$
17	$\phi_{4,1,3} - \phi_{4,1,5}$
18	$\tau_{3,1,2,8} + \tau_{4,1,2,8} + \tau_{5,1,2,8}$

Frequencies

Table S120: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	261.87	265.79	261.89	261.89	0
2	331.54	330.18	331.55	331.55	0
3	688.50	691.87	688.51	688.51	0
4	787.64	788.34	787.64	787.64	0
5	993.23	991.27	993.27	993.27	0
6	1080.78	1081.09	1080.85	1080.85	0
7	1094.08	1092.66	1094.11	1094.11	0
8	1280.40	1281.03	1280.35	1280.35	0
9	1321.69	1318.36	1321.70	1321.70	0
10	1414.25	1406.60	1414.25	1414.25	0
11	1492.91	1495.20	1492.90	1492.90	0
12	1498.26	1499.58	1498.25	1498.25	0
13	1507.54	1510.15	1507.49	1507.49	0
14	3042.95	3055.65	3042.99	3042.99	0
15	3091.31	3107.38	3091.34	3091.34	0
16	3119.73	3143.55	3119.60	3119.60	0
17	3127.71	3152.19	3127.75	3127.75	0
18	3154.38	3177.69	3154.39	3154.39	0

S1.41 Ethane

Geometries

Table S121: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−1.44464665	−0.00000002	0.00000001
2	C	1.44464665	0.00000008	−0.00000008
3	H	−2.19072560	−1.85534039	0.50798051
4	H	−2.19072568	1.36759417	1.35278165
5	H	−2.19072574	0.48774615	−1.86076207
6	H	2.19072576	−0.48774633	1.86076194
7	H	2.19072558	1.85534053	−0.50798031
8	H	2.19072568	−1.36759487	−1.35278094

Natural Internal Coordinates

Table S122: Symmetrized, unnormalized natural internal coordinates for Ethane.

1	$r_{1,2}$
2	$r_{1,3} + r_{1,4} + r_{1,5} + r_{2,7} + r_{2,6} + r_{2,8}$
3	$r_{1,3} + r_{1,4} + r_{1,5} - r_{2,7} - r_{2,6} - r_{2,8}$
4	$2r_{1,3} - r_{1,4} - r_{1,5} + 2r_{2,7} - r_{2,6} - r_{2,8}$
5	$2r_{1,3} - r_{1,4} - r_{1,5} - 2r_{2,7} + r_{2,6} + r_{2,8}$
6	$r_{1,4} - r_{1,5} + r_{2,6} - r_{2,8}$
7	$r_{1,4} - r_{1,5} - r_{2,6} + r_{2,8}$
8	$\phi_{4,1,5} + \phi_{3,1,4} + \phi_{3,1,5} - \phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2} + \phi_{6,2,8} + \phi_{7,2,6} + \phi_{7,2,8} - \phi_{7,2,1} - \phi_{6,2,1} - \phi_{8,2,1}$
9	$\phi_{4,1,5} + \phi_{3,1,4} + \phi_{3,1,5} - \phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2} - \phi_{6,2,8} - \phi_{7,2,6} - \phi_{7,2,8} + \phi_{7,2,1} + \phi_{6,2,1} + \phi_{8,2,1}$
10	$2\phi_{4,1,5} - \phi_{3,1,4} - \phi_{3,1,5} + 2\phi_{6,2,8} - \phi_{7,2,6} - \phi_{7,2,8}$
11	$2\phi_{4,1,5} - \phi_{3,1,4} - \phi_{3,1,5} - 2\phi_{6,2,8} + \phi_{7,2,6} + \phi_{7,2,8}$
12	$\phi_{3,1,4} - \phi_{3,1,5} + \phi_{7,2,6} - \phi_{7,2,8}$
13	$\phi_{3,1,4} - \phi_{3,1,5} - \phi_{7,2,6} + \phi_{7,2,8}$
14	$2\phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2} + 2\phi_{7,2,1} - \phi_{6,2,1} - \phi_{8,2,1}$
15	$2\phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2} - 2\phi_{7,2,1} + \phi_{6,2,1} + \phi_{8,2,1}$
16	$\phi_{4,1,2} - \phi_{5,1,2} + \phi_{6,2,1} - \phi_{8,2,1}$
17	$\phi_{4,1,2} - \phi_{5,1,2} - \phi_{6,2,1} + \phi_{8,2,1}$
18	$\tau_{3,1,2,7} + \tau_{7,2,1,3} + \tau_{4,1,2,8} + \tau_{8,2,1,4} + \tau_{5,1,2,6} + \tau_{6,2,1,5}$

Frequencies

Table S123: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	310.01	314.19	310.01	310.01	0
2	820.85	821.76	820.87	820.87	0
3	820.85	821.77	820.87	820.87	0
4	1013.93	1015.05	1013.95	1013.95	0
5	1224.79	1222.44	1224.82	1224.82	0
6	1224.79	1222.45	1224.82	1224.82	0
7	1406.53	1402.28	1406.53	1406.53	0
8	1427.46	1421.32	1427.46	1427.46	0
9	1510.83	1515.39	1510.81	1510.81	0
10	1510.83	1515.40	1510.82	1510.82	0
11	1512.52	1515.61	1512.51	1512.51	0
12	1512.52	1515.62	1512.52	1512.52	0
13	3038.00	3051.30	3037.91	3037.91	0
14	3039.53	3052.91	3039.49	3039.49	0
15	3096.88	3123.44	3096.90	3096.90	0
16	3096.88	3123.50	3096.95	3096.95	0
17	3120.06	3145.54	3120.06	3120.06	0
18	3120.06	3145.60	3120.11	3120.11	0

S1.42 Dimethyl Ether

Geometries

Table S124: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.19409540	0.47534797	−0.00000000
2	O	0.00000000	−1.03943917	0.00000000
3	C	2.19409540	0.47534797	−0.00000000
4	H	−3.82041225	−0.78516753	0.00000000
5	H	−2.27639290	1.68680381	−1.68214609
6	H	−2.27639290	1.68680381	1.68214609
7	H	2.27639289	1.68680383	1.68214608
8	H	2.27639289	1.68680383	−1.68214608
9	H	3.82041225	−0.78516754	0.00000000

Natural Internal Coordinates

Table S125: Symmetrized, unnormalized natural internal coordinates for Dimethyl Ether.

1	$r_{1,2} + r_{2,3}$
2	$r_{1,2} - r_{2,3}$
3	$r_{1,4} + r_{1,5} + r_{1,6} + r_{3,9} + r_{3,7} + r_{3,8}$
4	$r_{1,4} + r_{1,5} + r_{1,6} - r_{3,9} - r_{3,7} - r_{3,8}$
5	$2r_{1,4} - r_{1,5} - r_{1,6} + 2r_{3,9} - r_{3,7} - r_{3,8}$
6	$2r_{1,4} - r_{1,5} - r_{1,6} - 2r_{3,9} + r_{3,7} + r_{3,8}$
7	$r_{1,5} - r_{1,6} + r_{3,7} - r_{3,8}$
8	$r_{1,5} - r_{1,6} - r_{3,7} + r_{3,8}$
9	$\phi_{1,2,3}$
10	$\phi_{4,1,2} + \phi_{5,1,2} + \phi_{6,1,2} - \phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} + \phi_{9,3,2} + \phi_{7,3,2} + \phi_{8,3,2} - \phi_{7,3,8} - \phi_{9,3,7} - \phi_{9,3,8}$
11	$\phi_{4,1,2} + \phi_{5,1,2} + \phi_{6,1,2} - \phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} - \phi_{9,3,2} - \phi_{7,3,2} - \phi_{8,3,2} + \phi_{7,3,8} + \phi_{9,3,7} + \phi_{9,3,8}$
12	$2\phi_{4,1,2} - \phi_{5,1,2} - \phi_{6,1,2} + 2\phi_{9,3,2} - \phi_{7,3,2} - \phi_{8,3,2}$
13	$2\phi_{4,1,2} - \phi_{5,1,2} - \phi_{6,1,2} - 2\phi_{9,3,2} + \phi_{7,3,2} + \phi_{8,3,2}$
14	$\phi_{5,1,2} - \phi_{6,1,2} + \phi_{7,3,2} - \phi_{8,3,2}$
15	$\phi_{5,1,2} - \phi_{6,1,2} - \phi_{7,3,2} + \phi_{8,3,2}$
16	$2\phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} + 2\phi_{7,3,8} - \phi_{9,3,7} - \phi_{9,3,8}$
17	$2\phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} - 2\phi_{7,3,8} + \phi_{9,3,7} + \phi_{9,3,8}$
18	$\phi_{4,1,5} - \phi_{4,1,6} + \phi_{9,3,7} - \phi_{9,3,8}$
19	$\phi_{4,1,5} - \phi_{4,1,6} - \phi_{9,3,7} + \phi_{9,3,8}$
20	$\tau_{4,1,2,3} + \tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{7,3,2,1} + \tau_{8,3,2,1} + \tau_{9,3,2,1}$
21	$\tau_{4,1,2,3} + \tau_{5,1,2,3} + \tau_{6,1,2,3} - \tau_{7,3,2,1} - \tau_{8,3,2,1} - \tau_{9,3,2,1}$

Frequencies

Table S126: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	203.09	207.76	203.10	203.10	0
2	255.06	258.31	255.06	255.06	1
3	418.84	414.76	418.85	418.85	0
4	964.06	961.48	964.15	964.15	0
5	1128.79	1130.96	1128.83	1128.83	1
6	1169.37	1171.81	1169.38	1169.38	0
7	1202.41	1202.56	1202.42	1202.42	1
8	1212.11	1211.19	1212.15	1212.15	1
9	1277.41	1272.64	1277.38	1277.38	0
10	1460.11	1459.71	1460.07	1460.07	0
11	1490.45	1494.21	1490.45	1490.45	0
12	1494.98	1495.83	1495.12	1495.12	0
13	1500.07	1505.74	1500.07	1500.07	0
14	1508.70	1513.11	1508.68	1508.68	0
15	1526.82	1530.65	1526.67	1526.67	0
16	2978.19	2992.86	2978.26	2978.26	0
17	2987.43	2999.99	2987.54	2987.54	0
18	3030.84	3055.53	3030.84	3030.84	0
19	3036.25	3062.58	3036.25	3036.25	0
20	3129.14	3153.25	3129.08	3129.08	0
21	3130.94	3154.27	3130.84	3130.84	0

S1.43 Ethanol

Geometries

Table S127: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.38160558	0.47396349	0.00000002
2	C	0.01654024	−1.09258611	−0.00000002
3	H	−2.44560526	1.67800747	1.67220551
4	H	−2.44560533	1.67800746	−1.67220550
5	H	−4.04445451	−0.74741713	0.00000006
6	H	0.06559877	−2.31232195	1.67426817
7	H	0.06559875	−2.31232193	−1.67426821
8	O	2.10079664	0.61455797	−0.00000002
9	H	3.62372825	−0.37160124	0.00000035

Natural Internal Coordinates

Table S128: Symmetrized, unnormalized natural internal coordinates for Ethanol.

1	$r_{1,2}$
2	$r_{2,8}$
3	$r_{8,9}$
4	$r_{1,5} + r_{1,3} + r_{1,4}$
5	$2r_{1,5} - r_{1,3} - r_{1,4}$
6	$r_{1,3} - r_{1,4}$
7	$r_{2,6} + r_{2,7}$
8	$r_{2,6} - r_{2,7}$
9	$\phi_{1,2,8}$
10	$\phi_{2,8,9}$
11	$\phi_{5,1,2} + \phi_{3,1,2} + \phi_{4,1,2} - \phi_{3,1,4} - \phi_{5,1,3} - \phi_{5,1,4}$
12	$2\phi_{5,1,2} - \phi_{3,1,2} - \phi_{4,1,2}$
13	$\phi_{3,1,2} - \phi_{4,1,2}$
14	$2\phi_{3,1,4} - \phi_{5,1,3} - \phi_{5,1,4}$
15	$\phi_{5,1,3} - \phi_{5,1,4}$
16	$2\phi_{6,2,7} - \phi_{6,2,1} - \phi_{6,2,8} - \phi_{7,2,1} - \phi_{7,2,8}$
17	$\phi_{6,2,1} + \phi_{6,2,8} - \phi_{7,2,1} - \phi_{7,2,8}$
18	$\phi_{6,2,1} - \phi_{6,2,8} + \phi_{7,2,1} - \phi_{7,2,8}$
19	$\phi_{6,2,1} - \phi_{6,2,8} - \phi_{7,2,1} + \phi_{7,2,8}$
20	$\tau_{5,1,2,8} + \tau_{3,1,2,8} + \tau_{4,1,2,8}$
21	$\tau_{9,8,2,1}$

Frequencies

Table S129: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	235.41	239.15	235.45	235.45	0
2	280.63	285.48	280.63	280.63	0
3	413.74	412.37	413.75	413.75	0
4	818.70	819.61	818.71	818.71	0
5	909.14	908.42	909.19	909.19	0
6	1050.78	1047.15	1050.93	1050.93	0
7	1121.48	1120.55	1121.59	1121.59	0
8	1187.04	1185.90	1187.09	1187.09	0
9	1285.13	1276.07	1285.06	1285.06	0
10	1306.08	1308.60	1306.06	1306.06	0
11	1403.22	1397.50	1403.22	1403.22	0
12	1468.04	1460.93	1467.98	1467.98	0
13	1489.67	1492.61	1489.65	1489.65	0
14	1508.41	1511.49	1508.33	1508.33	0
15	1538.40	1541.12	1538.39	1538.39	0
16	3000.32	3016.78	3000.34	3000.34	0
17	3032.33	3057.80	3032.32	3032.32	0
18	3045.11	3058.83	3045.06	3045.06	0
19	3123.33	3148.58	3123.33	3123.33	0
20	3128.35	3153.32	3128.39	3128.39	0
21	3857.30	3874.39	3857.30	3857.30	0

S1.44 Acetonitrile

Geometries

Table S130: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	N	2.51255949	−0.00000000	0.00000000
2	C	0.31660733	−0.00000000	0.00000000
3	C	−2.45420572	0.00000000	−0.00000000
4	H	−3.15278789	0.96811431	−1.67682317
5	H	−3.15278789	−1.93622862	−0.00000000
6	H	−3.15278789	0.96811431	1.67682317

Natural Internal Coordinates

Table S131: Symmetrized, unnormalized natural internal coordinates for Acetonitrile.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{3,4} + r_{3,5} + r_{3,6}$
4	$2r_{3,4} - r_{3,5} - r_{3,6}$
5	$r_{3,5} - r_{3,6}$
6	$\phi_{4,3,2} + \phi_{5,3,2} + \phi_{6,3,2} - \phi_{5,3,6} - \phi_{4,3,5} - \phi_{4,3,6}$
7	$2\phi_{4,3,2} - \phi_{5,3,2} - \phi_{6,3,2}$
8	$\phi_{5,3,2} - \phi_{6,3,2}$
9	$2\phi_{5,3,6} - \phi_{4,3,5} - \phi_{4,3,6}$
10	$\phi_{4,3,5} - \phi_{4,3,6}$
11	$2\alpha^x_{4,3,2,1} - \alpha^x_{5,3,2,1} - \alpha^x_{6,3,2,1}$
12	$2\alpha^y_{4,3,2,1} - \alpha^y_{5,3,2,1} - \alpha^y_{6,3,2,1}$

Frequencies

Table S132: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	361.14	362.27	361.14	361.14	0
2	361.14	362.28	361.14	361.14	0
3	921.28	919.61	921.35	921.35	0
4	1062.13	1062.25	1062.14	1062.14	0
5	1062.13	1062.26	1062.14	1062.14	0
6	1414.02	1409.05	1414.03	1414.03	0
7	1487.57	1490.60	1487.56	1487.56	0
8	1487.57	1490.61	1487.56	1487.56	0
9	2298.73	2261.22	2298.70	2298.70	0
10	3066.03	3078.30	3066.02	3066.02	0
11	3149.91	3171.86	3149.91	3149.91	0
12	3149.91	3171.98	3149.92	3149.92	0

S1.45 Propyene

Geometries

Table S133: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	H	4.59758364	−0.00000001	0.00000000
2	C	2.58924928	−0.00000000	−0.00000000
3	C	0.30051907	0.00000001	−0.00000000
4	C	−2.47081506	−0.00000000	−0.00000000
5	H	−3.19532958	1.92992565	0.00000000
6	H	−3.19532957	−0.96496284	−1.67136465
7	H	−3.19532957	−0.96496284	1.67136465

Natural Internal Coordinates

Table S134: Symmetrized, unnormalized natural internal coordinates for Propyene.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{3,4}$
4	$r_{4,5} + r_{4,6} + r_{4,7}$
5	$2r_{4,5} - r_{4,6} - r_{4,7}$
6	$r_{4,6} - r_{4,7}$
7	$\phi_{6,4,7} + \phi_{5,4,6} + \phi_{5,4,7} - \phi_{5,4,3} - \phi_{6,4,3} - \phi_{7,4,3}$
8	$2\phi_{6,4,7} - \phi_{5,4,6} - \phi_{5,4,7}$
9	$\phi_{5,4,6} - \phi_{5,4,7}$
10	$2\phi_{5,4,3} - \phi_{6,4,3} - \phi_{7,4,3}$
11	$\phi_{6,4,3} - \phi_{7,4,3}$
12	$2\alpha^x_{5,4,3,2} - \alpha^x_{6,4,3,2} - \alpha^x_{7,4,3,2}$
13	$\alpha^x_{6,4,3,2} - \alpha^x_{7,4,3,2}$
14	$2\alpha^x_{5,4,2,1} - \alpha^x_{6,4,2,1} - \alpha^x_{7,4,2,1}$
15	$\alpha^x_{6,4,2,1} - \alpha^x_{7,4,2,1}$

Frequencies

Table S135: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	322.43	325.90	322.49	322.44	1
2	322.43	325.91	322.49	322.44	1
3	619.78	627.58	619.76	619.78	1
4	619.78	627.61	619.76	619.78	1
5	935.50	934.18	935.51	935.51	0
6	1059.94	1059.06	1059.95	1059.95	0
7	1059.94	1059.07	1059.96	1059.96	0
8	1417.12	1410.48	1417.13	1417.13	0
9	1491.36	1493.71	1491.35	1491.35	0
10	1491.36	1493.73	1491.35	1491.35	0
11	2177.61	2158.84	2177.64	2177.64	0
12	3048.35	3060.93	3048.33	3048.33	0
13	3122.33	3145.88	3122.33	3122.33	0
14	3122.33	3145.99	3122.33	3122.33	0
15	3470.25	3483.45	3470.23	3470.23	0

S1.46 Trifluoroacetonitrile

Geometries

Table S136: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	N	4.43122755	−0.00000000	0.00000000
2	C	2.23806724	−0.00000000	0.00000000
3	C	−0.57616305	−0.00000000	0.00000000
4	F	−1.43860612	1.17812158	−2.04056644
5	F	−1.43860612	−2.35624316	−0.00000000
6	F	−1.43860612	1.17812158	2.04056644

Natural Internal Coordinates

Table S137: Symmetrized, unnormalized natural internal coordinates for Trifluoroacetonitrile.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{3,4} + r_{3,5} + r_{3,6}$
4	$2r_{3,4} - r_{3,5} - r_{3,6}$
5	$r_{3,5} - r_{3,6}$
6	$\phi_{4,3,2} + \phi_{5,3,2} + \phi_{6,3,2} - \phi_{5,3,6} - \phi_{4,3,5} - \phi_{4,3,6}$
7	$2\phi_{4,3,2} - \phi_{5,3,2} - \phi_{6,3,2}$
8	$\phi_{5,3,2} - \phi_{6,3,2}$
9	$2\phi_{5,3,6} - \phi_{4,3,5} - \phi_{4,3,6}$
10	$\phi_{4,3,5} - \phi_{4,3,6}$
11	$2\alpha^x_{4,3,2,1} - \alpha^x_{5,3,2,1} - \alpha^x_{6,3,2,1}$
12	$2\alpha^y_{4,3,2,1} - \alpha^y_{5,3,2,1} - \alpha^y_{6,3,2,1}$

Frequencies

Table S138: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	189.86	190.44	189.88	189.88	0
2	189.86	190.44	189.88	189.88	0
3	469.33	470.41	469.34	469.33	1
4	469.33	470.42	469.34	469.33	1
5	527.15	526.30	527.20	527.20	0
6	629.30	631.92	629.30	629.30	1
7	629.30	631.93	629.30	629.30	1
8	821.09	821.56	821.11	821.11	0
9	1258.53	1246.94	1258.38	1258.38	0
10	1258.53	1246.99	1258.53	1258.53	0
11	1258.85	1254.44	1259.00	1259.00	0
12	2304.40	2254.12	2304.38	2304.38	0

S1.47 Silicon Tetrachloride

Geometries

Table S139: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	Si	0.00000000	0.00000000	−0.00000000
2	Cl	0.00000000	−3.13063739	2.21369401
3	Cl	0.00000000	3.13063739	2.21369401
4	Cl	3.13063738	0.00000000	−2.21369401
5	Cl	−3.13063738	0.00000000	−2.21369401

Natural Internal Coordinates

Table S140: Symmetrized, unnormalized natural internal coordinates for Silicon Tetrachloride.

1	$r_{1,2} + r_{1,3} + r_{1,4} + r_{1,5}$
2	$r_{1,2} + r_{1,3} - r_{1,4} - r_{1,5}$
3	$r_{1,2} - r_{1,3}$
4	$r_{1,4} - r_{1,5}$
5	$\phi_{2,1,3} + \phi_{4,1,5}$
6	$\phi_{2,1,3} - \phi_{4,1,5}$
7	$\phi_{2,1,4} - \phi_{2,1,5} + \phi_{3,1,4} - \phi_{3,1,5}$
8	$\phi_{2,1,4} + \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5}$
9	$\phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} + \phi_{3,1,5}$

Frequencies

Table S141: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	146.56	145.92	146.56	146.56	0
2	146.57	145.92	146.57	146.57	0
3	221.54	220.44	221.58	221.58	0
4	221.56	220.44	221.63	221.63	0
5	221.78	220.46	221.65	221.65	0
6	424.70	424.37	424.70	424.70	0
7	627.16	625.14	627.19	627.19	0
8	627.19	625.16	627.19	627.19	0
9	627.23	625.18	627.19	627.19	0

S1.48 Silicon Tetrafluoride

Geometries

Table S142: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	Si	0.00000000	0.00000000	−0.00000003
2	F	0.00000000	−2.40960515	1.70384729
3	F	0.00000000	2.40960515	1.70384729
4	F	2.40960519	0.00000000	−1.70384727
5	F	−2.40960519	0.00000000	−1.70384727

Natural Internal Coordinates

Table S143: Symmetrized, unnormalized natural internal coordinates for Silicon Tetrafluoride.

1	$r_{1,2} + r_{1,3} + r_{1,4} + r_{1,5}$
2	$r_{1,2} + r_{1,3} - r_{1,4} - r_{1,5}$
3	$r_{1,2} - r_{1,3}$
4	$r_{1,4} - r_{1,5}$
5	$\phi_{2,1,3} + \phi_{4,1,5}$
6	$\phi_{2,1,3} - \phi_{4,1,5}$
7	$\phi_{2,1,4} - \phi_{2,1,5} + \phi_{3,1,4} - \phi_{3,1,5}$
8	$\phi_{2,1,4} + \phi_{2,1,5} - \phi_{3,1,4} - \phi_{3,1,5}$
9	$\phi_{2,1,4} - \phi_{2,1,5} - \phi_{3,1,4} + \phi_{3,1,5}$

Frequencies

Table S144: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	263.22	263.81	263.24	263.24	0
2	263.27	263.82	263.25	263.25	0
3	387.72	388.18	387.73	387.73	0
4	387.76	388.19	387.76	387.76	0
5	387.78	388.21	387.77	387.77	0
6	798.06	799.38	798.06	798.06	0
7	1038.05	1040.66	1038.04	1038.04	0
8	1038.06	1040.71	1038.06	1038.06	0
9	1038.07	1040.75	1038.07	1038.07	0

S1.49 Disilane

Geometries

Table S145: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	Si	0.00000209	2.21895084	0.00000000
2	Si	−0.00000209	−2.21895084	0.00000000
3	H	−1.31404950	3.19278368	−2.27600840
4	H	−1.31404950	3.19278368	2.27600840
5	H	2.62810651	3.19279459	0.00000000
6	H	−2.62810651	−3.19279459	0.00000000
7	H	1.31404950	−3.19278368	2.27600840
8	H	1.31404950	−3.19278368	−2.27600840

Natural Internal Coordinates

Table S146: Symmetrized, unnormalized natural internal coordinates for Disilane.

1	$r_{1,2}$
2	$r_{1,3} + r_{1,4} + r_{1,5} + r_{2,7} + r_{2,6} + r_{2,8}$
3	$r_{1,3} + r_{1,4} + r_{1,5} - r_{2,7} - r_{2,6} - r_{2,8}$
4	$2r_{1,3} - r_{1,4} - r_{1,5} + 2r_{2,7} - r_{2,6} - r_{2,8}$
5	$2r_{1,3} - r_{1,4} - r_{1,5} - 2r_{2,7} + r_{2,6} + r_{2,8}$
6	$r_{1,4} - r_{1,5} + r_{2,6} - r_{2,8}$
7	$r_{1,4} - r_{1,5} - r_{2,6} + r_{2,8}$
8	$\phi_{4,1,5} + \phi_{3,1,4} + \phi_{3,1,5} - \phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2} + \phi_{6,2,8} + \phi_{7,2,6} + \phi_{7,2,8} - \phi_{7,2,1} - \phi_{6,2,1} - \phi_{8,2,1}$
9	$\phi_{4,1,5} + \phi_{3,1,4} + \phi_{3,1,5} - \phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2} - \phi_{6,2,8} - \phi_{7,2,6} - \phi_{7,2,8} + \phi_{7,2,1} + \phi_{6,2,1} + \phi_{8,2,1}$
10	$2\phi_{4,1,5} - \phi_{3,1,4} - \phi_{3,1,5} + 2\phi_{6,2,8} - \phi_{7,2,6} - \phi_{7,2,8}$
11	$2\phi_{4,1,5} - \phi_{3,1,4} - \phi_{3,1,5} - 2\phi_{6,2,8} + \phi_{7,2,6} + \phi_{7,2,8}$
12	$\phi_{3,1,4} - \phi_{3,1,5} + \phi_{7,2,6} - \phi_{7,2,8}$
13	$\phi_{3,1,4} - \phi_{3,1,5} - \phi_{7,2,6} + \phi_{7,2,8}$
14	$2\phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2} + 2\phi_{7,2,1} - \phi_{6,2,1} - \phi_{8,2,1}$
15	$2\phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2} - 2\phi_{7,2,1} + \phi_{6,2,1} + \phi_{8,2,1}$
16	$\phi_{4,1,2} - \phi_{5,1,2} + \phi_{6,2,1} - \phi_{8,2,1}$
17	$\phi_{4,1,2} - \phi_{5,1,2} - \phi_{6,2,1} + \phi_{8,2,1}$
18	$\tau_{3,1,2,7} + \tau_{7,2,1,3} + \tau_{4,1,2,8} + \tau_{8,2,1,4} + \tau_{5,1,2,6} + \tau_{6,2,1,5}$

Frequencies

Table S147: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	137.39	140.45	137.39	137.39	0
2	371.94	372.11	371.94	371.94	0
3	371.94	372.11	371.94	371.94	0
4	437.94	440.91	437.95	437.95	0
5	636.90	642.79	636.91	636.91	0
6	636.90	642.79	636.91	636.91	0
7	860.79	869.97	860.79	860.79	0
8	935.18	946.79	935.18	935.18	0
9	952.27	966.05	952.27	952.27	0
10	952.28	966.06	952.28	952.28	0
11	966.37	980.57	966.38	966.38	0
12	966.39	980.58	966.38	966.38	0
13	2221.82	2241.56	2221.81	2221.81	0
14	2229.68	2249.06	2229.68	2229.68	0
15	2229.68	2249.08	2229.68	2229.68	0
16	2230.82	2249.93	2230.82	2230.82	0
17	2238.14	2257.81	2238.14	2238.14	0
18	2238.14	2257.83	2238.15	2238.15	0

S1.50 Methyl Silane

Geometries

Table S148: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	Si	1.14265735	−0.00000106	0.00000000
2	C	−2.40853504	0.00000395	0.00000000
3	H	2.12904008	−1.31148904	−2.27156471
4	H	2.12905165	2.62297024	0.00000000
5	H	2.12904008	−1.31148904	2.27156471
6	H	−3.14298917	0.96423858	−1.67011742
7	H	−3.14298917	0.96423858	1.67011742
8	H	−3.14297141	−1.92848698	0.00000000

Natural Internal Coordinates

Table S149: Symmetrized, unnormalized natural internal coordinates for Methyl Silane.

1	$r_{1,2}$
2	$r_{1,4} + r_{1,3} + r_{1,5}$
3	$2r_{1,4} - r_{1,3} - r_{1,5}$
4	$r_{1,3} - r_{1,5}$
5	$r_{2,8} + r_{2,6} + r_{2,7}$
6	$2r_{2,8} - r_{2,6} - r_{2,7}$
7	$r_{2,6} - r_{2,7}$
8	$\phi_{4,1,2} + \phi_{3,1,2} + \phi_{5,1,2} - \phi_{3,1,5} - \phi_{4,1,3} - \phi_{4,1,5}$
9	$2\phi_{4,1,2} - \phi_{3,1,2} - \phi_{5,1,2}$
10	$\phi_{3,1,2} - \phi_{5,1,2}$
11	$2\phi_{3,1,5} - \phi_{4,1,3} - \phi_{4,1,5}$
12	$\phi_{4,1,3} - \phi_{4,1,5}$
13	$\phi_{8,2,1} + \phi_{6,2,1} + \phi_{7,2,1} - \phi_{6,2,7} - \phi_{8,2,6} - \phi_{8,2,7}$
14	$2\phi_{8,2,1} - \phi_{6,2,1} - \phi_{7,2,1}$
15	$\phi_{6,2,1} - \phi_{7,2,1}$
16	$2\phi_{6,2,7} - \phi_{8,2,6} - \phi_{8,2,7}$
17	$\phi_{8,2,6} - \phi_{8,2,7}$
18	$\tau_{8,2,1,4} + \tau_{6,2,1,5} + \tau_{7,2,1,3}$

Frequencies

Table S150: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	204.58	206.93	204.58	204.58	0
2	517.82	519.12	517.88	517.88	0
3	517.82	519.13	517.88	517.88	0
4	705.49	706.73	705.52	705.52	0
5	887.60	888.31	887.59	887.59	0
6	887.60	888.31	887.59	887.59	0
7	957.95	969.03	957.94	957.94	0
8	973.68	986.96	973.68	973.68	0
9	973.70	986.97	973.69	973.69	0
10	1294.07	1286.33	1294.07	1294.07	0
11	1469.42	1470.26	1469.41	1469.41	0
12	1469.44	1470.27	1469.43	1469.43	0
13	2233.65	2251.79	2233.65	2233.65	0
14	2233.66	2251.83	2233.66	2233.66	0
15	2235.39	2253.80	2235.38	2235.38	0
16	3038.03	3051.79	3038.02	3038.02	0
17	3122.33	3147.19	3122.34	3122.34	0
18	3122.34	3147.30	3122.34	3122.34	0

S1.51 Phosphane

Geometries

Table S151: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	P	0.12868063	0.00000031	0.00000000
2	H	−1.31825839	1.12497772	−1.94852696
3	H	−1.31826007	−2.24996482	0.00000000
4	H	−1.31825839	1.12497772	1.94852696

Natural Internal Coordinates

Table S152: Symmetrized, unnormalized natural internal coordinates for Phosphane.

1	$r_{1,2} + r_{1,3} + r_{1,4}$
2	$2r_{1,2} - r_{1,3} - r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{3,1,4}$
5	$\phi_{2,1,4} - \phi_{3,1,4}$
6	$\gamma_{2,1,3,4} + \gamma_{3,1,4,2} + \gamma_{4,1,2,3}$

Frequencies

Table S153: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1021.69	1019.60	1021.71	1021.71	0
2	1145.25	1158.76	1145.24	1145.24	0
3	1145.25	1159.76	1145.25	1145.25	0
4	2415.52	2439.27	2415.52	2415.52	0
5	2422.82	2450.00	2422.82	2422.82	0
6	2422.82	2450.06	2422.82	2422.82	0

S1.52 Phosphorus Trifluoride

Geometries

Table S154: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	P	−0.00000092	0.94258107	0.00000000
2	F	−1.28867646	−0.51224165	2.23205457
3	F	−1.28867646	−0.51224165	−2.23205457
4	F	2.57735441	−0.51223963	0.00000000

Natural Internal Coordinates

Table S155: Symmetrized, unnormalized natural internal coordinates for Phosphorus Trifluoride.

1	$r_{1,2} + r_{1,3} + r_{1,4}$
2	$2r_{1,2} - r_{1,3} - r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{3,1,4}$
5	$\phi_{2,1,4} - \phi_{3,1,4}$
6	$\gamma_{2,1,3,4} + \gamma_{3,1,4,2} + \gamma_{4,1,2,3}$

Frequencies

Table S156: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	359.12	348.74	359.13	359.13	0
2	359.14	348.88	359.13	359.13	0
3	501.47	491.44	501.48	501.48	0
4	897.80	887.57	897.80	897.80	0
5	897.81	887.61	897.81	897.81	0
6	915.76	913.41	915.76	915.76	0

S1.53 Hypochlorous Acide

Geometries

Table S157: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	H	−2.59688895	1.66013000	0.00000000
2	O	−2.15400490	−0.10905861	0.00000000
3	Cl	1.06009581	0.00203789	0.00000000

Natural Internal Coordinates

Table S158: Symmetrized, unnormalized natural internal coordinates for Hypochlorous Acide.

1	$r_{1,2}$
2	$r_{2,3}$
3	$\phi_{1,2,3}$

Frequencies

Table S159: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	732.53	746.75	732.59	732.59	0
2	1281.33	1271.95	1281.35	1281.35	0
3	3809.62	3822.52	3809.60	3809.60	0

S1.54 Nitrosyl Chloride

Geometries

Table S160: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	O	−2.97939346	0.63940304	0.00000000
2	N	−1.57525854	−0.99888693	0.00000000
3	Cl	1.99359145	0.10753257	0.00000000

Natural Internal Coordinates

Table S161: Symmetrized, unnormalized natural internal coordinates for Nitrosyl Chloride.

1	$r_{1,2}$
2	$r_{2,3}$
3	$\phi_{1,2,3}$

Frequencies

Table S162: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	342.84	347.69	342.99	342.84	2
2	609.86	615.76	609.88	609.86	2
3	1828.88	1827.82	1828.85	1828.88	2

S1.55 Ozone

Geometries

Table S163: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	O	0.00000000	−2.05457709	0.42011174
2	O	0.00000000	0.00000000	−0.84022349
3	O	0.00000000	2.05457709	0.42011174

Natural Internal Coordinates

Table S164: Symmetrized, unnormalized natural internal coordinates for Ozone.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$\phi_{2,1,3}$

Frequencies

Table S165: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	715.68	747.86	716.31	715.68	2
2	1054.32	1186.64	1054.32	1054.32	1
3	1153.11	2202.81	1152.72	1153.11	1

S1.56 Oxygen Difluroide

Geometries

Table S166: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	O	0.00000000	0.00000000	1.16502871
2	F	0.00000000	−2.08708826	−0.49042371
3	F	0.00000000	2.08708826	−0.49042371

Natural Internal Coordinates

Table S167: Symmetrized, unnormalized natural internal coordinates for Oxygen Difluroide.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$\phi_{2,1,3}$

Frequencies

Table S168: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	469.29	474.29	469.34	469.34	0
2	867.42	888.05	867.42	867.42	0
3	950.11	959.11	950.08	950.08	0

S1.57 Water

Geometries

Table S169: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	O	0.00000000	0.00000000	0.12550454
2	H	0.00000000	−1.42462540	−0.99592409
3	H	0.00000000	1.42462540	−0.99592409

Natural Internal Coordinates

Table S170: Symmetrized, unnormalized natural internal coordinates for Water.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$\phi_{2,1,3}$

Frequencies

Table S171: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1668.87	1650.39	1668.88	1668.88	0
2	3840.92	3850.50	3840.92	3840.92	0
3	3945.53	3971.33	3945.53	3945.53	0

S1.58 Trifluoroamine

Geometries

Table S172: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	N	0.92019321	0.00000000	−0.00000000
2	F	−0.22608099	1.16249337	−2.01349759
3	F	−0.22608099	−2.32498675	0.00000000
4	F	−0.22608099	1.16249337	2.01349759

Natural Internal Coordinates

Table S173: Symmetrized, unnormalized natural internal coordinates for Trifluoroamine.

1	$r_{1,2} + r_{1,3} + r_{1,4}$
2	$2r_{1,2} - r_{1,3} - r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{3,1,4}$
5	$\phi_{2,1,4} - \phi_{3,1,4}$
6	$\gamma_{2,1,3,4} + \gamma_{3,1,4,2} + \gamma_{4,1,2,3}$

Frequencies

Table S174: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	502.48	503.59	502.53	502.53	0
2	502.48	503.66	502.53	502.53	0
3	659.91	666.00	659.91	659.91	0
4	949.20	933.31	949.17	949.17	0
5	949.20	933.38	949.17	949.17	0
6	1058.35	1059.49	1058.35	1058.35	0

S1.59 Chlorine Trifluoride

Geometries

Table S175: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	Cl	0.00000000	0.00000000	0.69252140
2	F	0.00000000	0.00000000	−2.33980384
3	F	0.00000000	3.20469409	0.53256734
4	F	0.00000000	−3.20469409	0.53256734

Natural Internal Coordinates

Table S176: Symmetrized, unnormalized natural internal coordinates for Chlorine Trifluoride.

1	$r_{1,2}$
2	$r_{1,3} + r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$\phi_{3,1,2} + \phi_{4,1,2}$
5	$\phi_{3,1,2} - \phi_{4,1,2}$
6	$\gamma_{2,1,3,4}$

Frequencies

Table S177: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	336.96	337.43	337.00	337.00	0
2	338.43	338.07	338.44	338.44	0
3	441.96	444.95	441.96	441.96	0
4	543.99	542.82	544.21	544.21	0
5	735.59	752.25	735.59	735.59	0
6	765.58	772.22	765.40	765.40	0

S1.60 Hydrogen Peroxide

Geometries

Table S178: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	H	−1.79701451	1.36358961	0.92174870
2	O	−1.37290862	−0.11245968	−0.05807855
3	O	1.37290862	0.11245968	−0.05807855
4	H	1.79701451	−1.36358961	0.92174870

Natural Internal Coordinates

Table S179: Symmetrized, unnormalized natural internal coordinates for Hydrogen Peroxide.

1	$r_{2,3}$
2	$r_{1,2} + r_{3,4}$
3	$r_{1,2} - r_{3,4}$
4	$\phi_{1,2,3} + \phi_{2,3,4}$
5	$\phi_{1,2,3} - \phi_{2,3,4}$
6	$\tau_{1,2,3,4}$

Frequencies

Table S180: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	372.17	370.94	372.26	372.18	1
2	911.79	924.21	912.43	911.93	1
3	1323.64	1319.01	1323.64	1323.64	0
4	1435.98	1426.62	1435.66	1436.00	2
5	3807.91	3825.40	3807.97	3807.97	0
6	3809.29	3826.79	3809.18	3809.18	0

S1.61 Carbonyl Fluoride

Geometries

Table S181: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.30295787	−0.00000001	0.00000000
2	F	1.15873701	−2.00577068	0.00000000
3	F	1.15873683	2.00577078	0.00000000
4	O	−2.52535314	−0.00000011	−0.00000000

Natural Internal Coordinates

Table S182: Symmetrized, unnormalized natural internal coordinates for Carbonyl Fluoride.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$r_{1,4}$
4	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{3,1,4}$
5	$\phi_{2,1,4} - \phi_{3,1,4}$
6	$\gamma_{4,1,2,3}$

Frequencies

Table S183: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	588.74	590.42	588.74	588.74	0
2	626.11	626.93	626.11	626.11	0
3	786.02	791.18	786.02	786.02	0
4	983.53	982.88	983.52	983.52	0
5	1293.99	1281.37	1293.99	1293.99	0
6	1978.03	1979.81	1978.03	1978.03	0

S1.62 Singlet Silylene

Geometries

Table S184: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	Si	0.00000000	0.00000000	0.13352287
2	H	0.00000000	−2.07118886	−1.85327784
3	H	0.00000000	2.07118886	−1.85327784

Natural Internal Coordinates

Table S185: Symmetrized, unnormalized natural internal coordinates for Singlet Silylene.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$\phi_{2,1,3}$

Frequencies

Table S186: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1025.33	1043.37	1025.33	1025.33	0
2	2060.52	2083.23	2060.52	2060.52	0
3	2063.17	2085.73	2063.16	2063.16	0

S1.63 Nitrous Oxide

Geometries

Table S187: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	N	−0.00000000	−0.00000000	−2.27661556
2	X	1.00000000	−0.00000000	−0.13588985
3	N	−0.00000000	−0.00000000	−0.13588985
4	X	−0.00000000	1.00000000	−0.13588985
5	O	0.00000000	0.00000000	2.11207702

Natural Internal Coordinates

Table S188: Symmetrized, unnormalized natural internal coordinates for Nitrous Oxide.

1	$r_{1,3}$
2	$r_{3,5}$
3	$\theta_{1,3,5,2}$
4	$\theta_{1,3,5,4}$

Frequencies

Table S189: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	601.18	607.30	601.18	601.18	0
2	601.18	607.31	601.18	601.18	0
3	1297.09	1322.29	1306.43	1297.09	1
4	2282.57	2307.73	2277.23	2282.57	1

S1.64 Hydrazine

Geometries

Table S190: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	N	−0.17939083	−1.39259049	0.00000000
2	N	0.17939083	1.39259049	0.00000000
3	H	0.87854704	−1.97545387	−1.49671921
4	H	0.87854704	−1.97545387	1.49671921
5	H	−0.87854704	1.97545387	−1.49671921
6	H	−0.87854704	1.97545387	1.49671921

Natural Internal Coordinates

Table S191: Symmetrized, unnormalized natural internal coordinates for Hydrazine.

1	$r_{1,2}$
2	$r_{1,3} + r_{1,4} + r_{2,5} + r_{2,6}$
3	$r_{1,3} + r_{1,4} - r_{2,5} - r_{2,6}$
4	$r_{1,3} - r_{1,4} + r_{2,5} - r_{2,6}$
5	$r_{1,3} - r_{1,4} - r_{2,5} + r_{2,6}$
6	$2\phi_{3,1,4} - \phi_{3,1,2} - \phi_{4,1,2} + 2\phi_{5,2,6} - \phi_{5,2,1} - \phi_{6,2,1}$
7	$2\phi_{3,1,4} - \phi_{3,1,2} - \phi_{4,1,2} - 2\phi_{5,2,6} + \phi_{5,2,1} + \phi_{6,2,1}$
8	$\phi_{3,1,2} - \phi_{4,1,2} + \phi_{5,2,1} - \phi_{6,2,1}$
9	$\phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,2,1} + \phi_{6,2,1}$
10	$\tau_{3,1,2,5} + \tau_{3,1,2,6} + \tau_{4,1,2,5} + \tau_{4,1,2,6}$
11	$\gamma_{1,2,5,6} + \gamma_{2,1,3,4}$
12	$\gamma_{1,2,5,6} - \gamma_{2,1,3,4}$

Frequencies

Table S192: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	25.68	37.17	26.30	26.30	0
2	943.78	942.12	944.42	943.85	1
3	1068.37	1059.20	1068.40	1068.40	0
4	1108.51	1106.06	1108.50	1108.50	0
5	1256.79	1243.44	1256.37	1256.80	1
6	1487.98	1479.54	1487.98	1487.98	0
7	1638.68	1630.83	1638.66	1638.66	0
8	1690.46	1684.70	1690.44	1690.44	0
9	3437.77	3454.45	3437.77	3437.77	0
10	3455.35	3472.41	3455.35	3455.35	0
11	3512.91	3541.31	3512.91	3512.91	0
12	3533.97	3561.31	3533.97	3533.97	0

S1.65 Cyanogen

Geometries

Table S193: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	X	1.00000000	0.00000000	1.31251829
2	C	−0.00000000	0.00000000	1.31251829
3	X	−0.00000000	1.00000000	1.31251829
4	X	1.00000000	0.00000000	−1.31251829
5	C	0.00000000	0.00000000	−1.31251829
6	X	0.00000000	1.00000000	−1.31251829
7	N	0.00000000	0.00000000	3.51379022
8	N	−0.00000000	0.00000000	−3.51379022

Natural Internal Coordinates

Table S194: Symmetrized, unnormalized natural internal coordinates for Cyanogen.

1	$r_{2,5}$
2	$r_{2,7} + r_{5,8}$
3	$r_{2,7} - r_{5,8}$
4	$\theta_{7,2,5,1} + \theta_{7,2,5,3}$
5	$\theta_{7,2,5,1} - \theta_{7,2,5,3}$
6	$\theta_{8,5,2,4} + \theta_{8,5,2,6}$
7	$\theta_{8,5,2,4} - \theta_{8,5,2,6}$

Frequencies

Table S195: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	236.26	240.68	236.26	236.26	0
2	236.26	240.71	236.26	236.26	0
3	498.61	510.80	498.61	498.61	0
4	498.61	510.88	498.61	498.61	0
5	855.82	848.47	855.89	855.89	0
6	2175.85	2131.38	2175.85	2175.85	0
7	2367.74	2309.29	2367.72	2367.72	0

S1.66 Aziridine

Geometries

Table S196: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	N	1.59582703	0.17617984	0.00000000
2	C	−0.81575373	−0.02639125	1.40146541
3	C	−0.81575373	−0.02639125	−1.40146541
4	H	−1.14815063	−1.78855443	2.38563323
5	H	−1.43745953	1.65562797	2.38563323
6	H	−1.43745953	1.65562797	−2.38563323
7	H	−1.14815063	−1.78855443	−2.38563323
8	H	2.42432052	−1.55357917	0.00000000

Natural Internal Coordinates

Table S197: Symmetrized, unnormalized natural internal coordinates for Aziridine.

1	$r_{1,8}$
2	$r_{2,3} + r_{1,2} + r_{1,3}$
3	$2r_{2,3} - r_{1,2} - r_{1,3}$
4	$r_{1,2} - r_{1,3}$
5	$r_{2,4} + r_{2,5} + r_{3,6} + r_{3,7}$
6	$r_{2,4} + r_{2,5} - r_{3,6} - r_{3,7}$
7	$r_{2,4} - r_{2,5} - r_{3,6} + r_{3,7}$
8	$r_{2,4} - r_{2,5} + r_{3,6} - r_{3,7}$
9	$\phi_{8,1,2} - \phi_{8,1,3}$
10	$4\phi_{4,2,5} - \phi_{4,2,1} - \phi_{4,2,3} - \phi_{5,2,1} - \phi_{5,2,3} + 4\phi_{6,3,7} - \phi_{6,3,1} - \phi_{6,3,2} - \phi_{7,3,1} - \phi_{7,3,2}$
11	$4\phi_{4,2,5} - \phi_{4,2,1} - \phi_{4,2,3} - \phi_{5,2,1} - \phi_{5,2,3} - 4\phi_{6,3,7} + \phi_{6,3,1} + \phi_{6,3,2} + \phi_{7,3,1} + \phi_{7,3,2}$
12	$\phi_{4,2,1} - \phi_{4,2,3} + \phi_{5,2,1} - \phi_{5,2,3} + \phi_{6,3,1} - \phi_{6,3,2} + \phi_{7,3,1} - \phi_{7,3,2}$
13	$\phi_{4,2,1} - \phi_{4,2,3} + \phi_{5,2,1} - \phi_{5,2,3} - \phi_{6,3,1} + \phi_{6,3,2} - \phi_{7,3,1} + \phi_{7,3,2}$
14	$\phi_{4,2,1} + \phi_{4,2,3} - \phi_{5,2,1} - \phi_{5,2,3} + \phi_{6,3,1} + \phi_{6,3,2} - \phi_{7,3,1} - \phi_{7,3,2}$
15	$\phi_{4,2,1} + \phi_{4,2,3} - \phi_{5,2,1} - \phi_{5,2,3} - \phi_{6,3,1} - \phi_{6,3,2} + \phi_{7,3,1} + \phi_{7,3,2}$
16	$\phi_{4,2,1} - \phi_{4,2,3} - \phi_{5,2,1} + \phi_{5,2,3} + \phi_{6,3,1} - \phi_{6,3,2} - \phi_{7,3,1} + \phi_{7,3,2}$
17	$\phi_{4,2,1} - \phi_{4,2,3} - \phi_{5,2,1} + \phi_{5,2,3} - \phi_{6,3,1} + \phi_{6,3,2} + \phi_{7,3,1} - \phi_{7,3,2}$
18	$\gamma_{8,1,2,3}$

Frequencies

Table S198: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	782.13	773.27	783.89	783.89	0
2	840.79	842.61	841.45	841.19	2
3	874.83	876.98	874.10	874.10	0
4	923.43	918.64	924.22	924.22	1
5	1022.46	1025.72	1022.57	1022.57	0
6	1113.59	1101.90	1113.60	1113.60	0
7	1120.20	1108.14	1119.96	1119.96	0
8	1162.60	1164.93	1162.56	1162.56	0
9	1245.94	1244.31	1246.55	1246.55	0
10	1272.26	1260.66	1271.62	1271.79	1
11	1307.58	1302.11	1306.88	1306.88	0
12	1501.76	1503.54	1501.67	1501.67	0
13	1532.65	1530.55	1532.55	1532.55	0
14	3130.26	3146.66	3130.22	3130.22	0
15	3137.27	3152.69	3137.23	3137.23	0
16	3214.74	3238.40	3214.71	3214.71	0
17	3228.03	3250.97	3227.99	3227.99	0
18	3515.02	3536.09	3515.01	3515.01	0

S1.67 Acetamide

Geometries

Table S199: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	2.71257408	0.46659407	−0.00029896
2	C	−0.08279841	−0.16544287	0.00691252
3	O	−0.87869630	−2.32459739	−0.00775877
4	N	−1.66151859	1.89377014	0.05553476
5	H	3.75222131	−1.12020941	0.78819940
6	H	3.33318276	0.75461502	−1.94795633
7	H	3.11796536	2.17773791	1.07525063
8	H	−0.98387343	3.61876868	−0.34837186
9	H	−3.50051514	1.56367391	−0.29435040

Natural Internal Coordinates

Table S200: Symmetrized, unnormalized natural internal coordinates for Acetamide.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{2,4}$
4	$r_{1,5} + r_{1,6} + r_{1,7}$
5	$2r_{1,5} - r_{1,6} - r_{1,7}$
6	$r_{1,6} - r_{1,7}$
7	$r_{4,8} + r_{4,9}$
8	$r_{4,8} - r_{4,9}$
9	$2\phi_{1,2,4} - \phi_{1,2,3} - \phi_{4,2,3}$
10	$\phi_{1,2,3} - \phi_{4,2,3}$
11	$\phi_{5,1,2} + \phi_{6,1,2} + \phi_{7,1,2} - \phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
12	$2\phi_{5,1,2} - \phi_{6,1,2} - \phi_{7,1,2}$
13	$\phi_{6,1,2} - \phi_{7,1,2}$
14	$2\phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
15	$\phi_{5,1,6} - \phi_{5,1,7}$
16	$2\phi_{8,4,9} - \phi_{8,4,2} - \phi_{9,4,2}$
17	$\phi_{8,4,2} - \phi_{9,4,2}$
18	$\tau_{5,1,2,3} + \tau_{5,1,2,4} + \tau_{6,1,2,3} + \tau_{6,1,2,4} + \tau_{7,1,2,3} + \tau_{7,1,2,4}$
19	$\tau_{8,4,2,1} + \tau_{8,4,2,3} + \tau_{9,4,2,1} + \tau_{9,4,2,3}$
20	$\gamma_{3,2,1,4}$
21	$\gamma_{2,4,8,9}$

Frequencies

Table S201: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	56.09	56.97	56.31	56.27	4
2	300.01	321.99	300.20	300.15	2
3	416.23	416.62	416.22	416.22	1
4	508.36	510.84	508.41	508.41	1
5	553.53	554.19	553.53	553.53	0
6	638.47	642.37	638.42	638.42	1
7	854.16	852.39	854.18	854.18	0
8	981.94	978.59	981.96	981.96	1
9	1057.36	1053.87	1057.38	1057.38	0
10	1134.12	1130.72	1134.15	1134.15	0
11	1344.17	1338.81	1344.18	1344.18	0
12	1409.87	1401.90	1409.96	1409.96	0
13	1480.84	1482.47	1480.80	1480.80	0
14	1495.75	1498.58	1495.74	1495.74	0
15	1628.26	1622.06	1628.25	1628.25	0
16	1794.31	1797.06	1794.24	1794.24	2
17	3050.62	3063.10	3050.69	3050.69	0
18	3122.95	3146.22	3122.92	3122.92	0
19	3165.52	3187.23	3165.47	3165.47	0
20	3604.29	3612.64	3604.30	3604.30	0
21	3738.95	3755.73	3738.94	3738.94	0

S1.68 Dimethylamine

Geometries

Table S202: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	N	1.05866364	−0.16314434	0.00000000
2	H	2.32232113	1.27592347	−0.00000000
3	C	−0.48856083	0.03001809	2.27606500
4	C	−0.48856083	0.03001809	−2.27606500
5	H	0.71957620	0.01962878	3.94620566
6	H	−1.73337996	−1.61370927	2.38661331
7	H	−1.68486837	1.73209079	2.33361602
8	H	0.71957620	0.01962878	−3.94620566
9	H	−1.73337996	−1.61370927	−2.38661331
10	H	−1.68486837	1.73209079	−2.33361602

Natural Internal Coordinates

Table S203: Symmetrized, unnormalized natural internal coordinates for Dimethylamine.

1	$r_{1,2}$
2	$r_{1,3} + r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$r_{3,6} + r_{3,5} + r_{3,7} + r_{4,9} + r_{4,8} + r_{4,10}$
5	$r_{3,6} + r_{3,5} + r_{3,7} - r_{4,9} - r_{4,8} - r_{4,10}$
6	$2r_{3,6} - r_{3,5} - r_{3,7} + 2r_{4,9} - r_{4,8} - r_{4,10}$
7	$2r_{3,6} - r_{3,5} - r_{3,7} - 2r_{4,9} + r_{4,8} + r_{4,10}$
8	$r_{3,5} - r_{3,7} + r_{4,8} - r_{4,10}$
9	$r_{3,5} - r_{3,7} - r_{4,8} + r_{4,10}$
10	$\phi_{3,1,4}$
11	$\phi_{2,1,3} + \phi_{2,1,4}$
12	$\phi_{2,1,3} - \phi_{2,1,4}$
13	$\phi_{6,3,1} + \phi_{5,3,1} + \phi_{7,3,1} - \phi_{5,3,7} - \phi_{6,3,7} - \phi_{5,3,6} + \phi_{9,4,1} + \phi_{8,4,1} + \phi_{10,4,1} - \phi_{8,4,10} - \phi_{9,4,10} - \phi_{8,4,9}$
14	$\phi_{6,3,1} + \phi_{5,3,1} + \phi_{7,3,1} - \phi_{5,3,7} - \phi_{6,3,7} - \phi_{5,3,6} - \phi_{9,4,1} - \phi_{8,4,1} - \phi_{10,4,1} + \phi_{8,4,10} + \phi_{9,4,10} + \phi_{8,4,9}$
15	$2\phi_{6,3,1} - \phi_{5,3,1} - \phi_{7,3,1} + 2\phi_{9,4,1} - \phi_{8,4,1} - \phi_{10,4,1}$
16	$2\phi_{6,3,1} - \phi_{5,3,1} - \phi_{7,3,1} - 2\phi_{9,4,1} + \phi_{8,4,1} + \phi_{10,4,1}$
17	$\phi_{5,3,1} - \phi_{7,3,1} + \phi_{8,4,1} - \phi_{10,4,1}$
18	$\phi_{5,3,1} - \phi_{7,3,1} - \phi_{8,4,1} + \phi_{10,4,1}$
19	$2\phi_{5,3,7} - \phi_{6,3,7} - \phi_{5,3,6} + 2\phi_{8,4,10} - \phi_{9,4,10} - \phi_{8,4,9}$
20	$2\phi_{5,3,7} - \phi_{6,3,7} - \phi_{5,3,6} - 2\phi_{8,4,10} + \phi_{9,4,10} + \phi_{8,4,9}$
21	$\phi_{6,3,7} - \phi_{5,3,6} + \phi_{9,4,10} - \phi_{8,4,9}$
22	$\phi_{6,3,7} - \phi_{5,3,6} - \phi_{9,4,10} + \phi_{8,4,9}$
23	$\tau_{5,3,1,4} + \tau_{5,3,1,2} + \tau_{6,3,1,4} + \tau_{6,3,1,2} + \tau_{7,3,1,4} + \tau_{7,3,1,2} + \tau_{8,4,1,3} + \tau_{8,4,1,2} + \tau_{9,4,1,3} + \tau_{9,4,1,2} + \tau_{10,4,1,3} + \tau_{10,4,1,2}$
24	$\tau_{5,3,1,4} + \tau_{5,3,1,2} + \tau_{6,3,1,4} + \tau_{6,3,1,2} + \tau_{7,3,1,4} + \tau_{7,3,1,2} - \tau_{8,4,1,3} - \tau_{8,4,1,2} - \tau_{9,4,1,3} - \tau_{9,4,1,2} - \tau_{10,4,1,3} - \tau_{10,4,1,2}$

Frequencies

Table S204: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	223.19	227.53	223.19	223.19	1
2	268.98	272.35	269.00	269.00	1
3	385.55	382.31	385.57	385.57	0
4	812.70	806.34	812.80	812.80	0
5	953.41	952.91	953.44	953.44	0
6	1028.85	1029.19	1028.87	1028.87	1
7	1100.92	1102.64	1100.95	1100.95	0
8	1177.66	1175.95	1177.77	1177.77	0
9	1198.28	1194.60	1198.24	1198.24	1
10	1273.32	1269.74	1273.33	1273.33	0
11	1438.95	1435.42	1438.91	1438.91	0
12	1467.77	1464.15	1467.82	1467.82	0
13	1478.41	1470.34	1479.09	1479.09	0
14	1492.67	1495.80	1492.45	1492.45	0
15	1504.35	1507.96	1504.27	1504.27	0
16	1522.52	1523.91	1522.02	1522.02	0
17	1524.85	1528.90	1524.84	1524.84	0
18	2958.30	2975.76	2958.58	2958.58	0
19	2959.91	2976.09	2960.34	2960.34	0
20	3065.27	3085.82	3064.95	3064.95	0
21	3066.32	3088.88	3066.03	3066.03	0
22	3112.90	3138.53	3112.93	3112.93	0
23	3113.81	3138.73	3113.70	3113.70	0
24	3524.72	3545.68	3524.71	3524.71	0

S1.69 Ethylamine

Geometries

Table S205: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.41599594	0.50146691	0.00000000
2	C	0.01027304	−1.06763773	−0.00000000
3	N	2.36790056	0.39595653	0.00000000
4	H	−4.09501177	−0.70240098	−0.00000000
5	H	−2.49875000	1.71532507	−1.67014001
6	H	−2.49875000	1.71532507	1.67014001
7	H	0.04170761	−2.30474842	1.65378697
8	H	0.04170761	−2.30474842	−1.65378697
9	H	2.37659366	1.56049390	1.52504554
10	H	2.37659366	1.56049390	−1.52504554

Natural Internal Coordinates

Table S206: Symmetrized, unnormalized natural internal coordinates for Ethylamine.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{1,4} + r_{1,5} + r_{1,6}$
4	$2r_{1,4} - r_{1,5} - r_{1,6}$
5	$r_{1,5} - r_{1,6}$
6	$r_{2,7} + r_{2,8}$
7	$r_{2,7} - r_{2,8}$
8	$r_{3,9} + r_{3,10}$
9	$r_{3,9} - r_{3,10}$
10	$\phi_{1,2,3}$
11	$\phi_{4,1,2} + \phi_{5,1,2} + \phi_{6,1,2} - \phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6}$
12	$2\phi_{4,1,2} - \phi_{5,1,2} - \phi_{6,1,2}$
13	$\phi_{5,1,2} - \phi_{6,1,2}$
14	$2\phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6}$
15	$\phi_{4,1,5} - \phi_{4,1,6}$
16	$2\phi_{7,2,8} - \phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,2,1} - \phi_{8,2,3}$
17	$\phi_{7,2,1} + \phi_{7,2,3} - \phi_{8,2,1} - \phi_{8,2,3}$
18	$\phi_{7,2,1} - \phi_{7,2,3} + \phi_{8,2,1} - \phi_{8,2,3}$
19	$\phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,2,1} + \phi_{8,2,3}$
20	$2\phi_{9,3,10} - \phi_{9,3,2} - \phi_{10,3,2}$
21	$\phi_{9,3,2} - \phi_{10,3,2}$
22	$\tau_{4,1,2,3} + \tau_{5,1,2,3} + \tau_{6,1,2,3}$
23	$\tau_{9,3,2,1} + \tau_{10,3,2,1}$
24	$\gamma_{2,3,9,10}$

Frequencies

Table S207: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	254.09	257.07	254.18	254.18	0
2	288.51	290.76	288.45	288.45	0
3	396.61	396.27	396.61	396.61	0
4	777.12	778.23	777.12	777.12	0
5	877.07	871.99	877.81	877.14	1
6	914.85	909.23	914.29	914.94	1
7	1008.36	1007.33	1008.38	1008.38	0
8	1081.55	1079.91	1081.60	1081.60	0
9	1160.25	1157.59	1160.24	1160.24	0
10	1276.10	1273.23	1276.18	1276.18	0
11	1380.25	1373.99	1380.28	1380.28	0
12	1396.10	1394.03	1396.03	1396.03	0
13	1408.58	1400.43	1408.50	1408.50	0
14	1493.31	1495.53	1493.33	1493.33	0
15	1499.43	1502.18	1499.42	1499.42	0
16	1511.30	1512.65	1511.25	1511.25	0
17	1663.18	1653.07	1663.16	1663.16	0
18	3022.37	3034.86	3022.43	3022.43	0
19	3043.45	3060.46	3043.39	3043.39	0
20	3074.11	3100.85	3074.13	3074.13	0
21	3100.09	3125.35	3100.05	3100.05	0
22	3103.24	3128.83	3103.26	3103.26	0
23	3477.75	3492.65	3477.74	3477.74	0
24	3559.16	3585.79	3559.16	3559.16	0

S1.70 Acetone

Geometries

Table S208: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.00000000	−2.43146449	1.32246298
2	C	−0.00000000	−0.00000000	−0.19161611
3	C	0.00000000	2.43146449	1.32246298
4	H	−0.00000000	−4.04696082	0.05128367
5	H	−1.66203278	−2.50063407	2.54685039
6	H	1.66203278	−2.50063407	2.54685039
7	H	0.00000000	4.04696082	0.05128367
8	H	1.66203278	2.50063407	2.54685039
9	H	−1.66203278	2.50063407	2.54685039
10	O	−0.00000000	0.00000000	−2.48892898

Natural Internal Coordinates

Table S209: Symmetrized, unnormalized natural internal coordinates for Acetone.

1	$r_{2,10}$
2	$r_{1,2} + r_{2,3}$
3	$r_{1,2} - r_{2,3}$
4	$r_{1,4} + r_{1,5} + r_{1,6} + r_{3,7} + r_{3,8} + r_{3,9}$
5	$r_{1,4} + r_{1,5} + r_{1,6} - r_{3,7} - r_{3,8} - r_{3,9}$
6	$2r_{1,4} - r_{1,5} - r_{1,6} + 2r_{3,7} - r_{3,8} - r_{3,9}$
7	$2r_{1,4} - r_{1,5} - r_{1,6} - 2r_{3,7} + r_{3,8} + r_{3,9}$
8	$r_{1,5} - r_{1,6} + r_{3,8} - r_{3,9}$
9	$r_{1,5} - r_{1,6} - r_{3,8} + r_{3,9}$
10	$2\phi_{1,2,3} - \phi_{1,2,10} - \phi_{3,2,10}$
11	$\phi_{1,2,10} - \phi_{3,2,10}$
12	$\phi_{4,1,2} + \phi_{5,1,2} + \phi_{6,1,2} - \phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} + \phi_{7,3,2} + \phi_{8,3,2} + \phi_{9,3,2} - \phi_{8,3,9} - \phi_{7,3,8} - \phi_{7,3,9}$
13	$\phi_{4,1,2} + \phi_{5,1,2} + \phi_{6,1,2} - \phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} - \phi_{7,3,2} - \phi_{8,3,2} - \phi_{9,3,2} + \phi_{8,3,9} + \phi_{7,3,8} + \phi_{7,3,9}$
14	$2\phi_{4,1,2} - \phi_{5,1,2} - \phi_{6,1,2} + 2\phi_{7,3,2} - \phi_{8,3,2} - \phi_{9,3,2}$
15	$2\phi_{4,1,2} - \phi_{5,1,2} - \phi_{6,1,2} - 2\phi_{7,3,2} + \phi_{8,3,2} + \phi_{9,3,2}$
16	$\phi_{5,1,2} - \phi_{6,1,2} + \phi_{8,3,2} - \phi_{9,3,2}$
17	$\phi_{5,1,2} - \phi_{6,1,2} - \phi_{8,3,2} + \phi_{9,3,2}$
18	$2\phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} + 2\phi_{8,3,9} - \phi_{7,3,8} - \phi_{7,3,9}$
19	$2\phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} - 2\phi_{8,3,9} + \phi_{7,3,8} + \phi_{7,3,9}$
20	$\phi_{4,1,5} - \phi_{4,1,6} + \phi_{7,3,8} - \phi_{7,3,9}$
21	$\phi_{4,1,5} - \phi_{4,1,6} - \phi_{7,3,8} + \phi_{7,3,9}$
22	$\tau_{4,1,2,3} + \tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{7,3,2,1} + \tau_{8,3,2,1} + \tau_{9,3,2,1}$
23	$\tau_{4,1,2,3} + \tau_{5,1,2,3} + \tau_{6,1,2,3} - \tau_{7,3,2,1} - \tau_{8,3,2,1} - \tau_{9,3,2,1}$
24	$\gamma_{10,2,1,3}$

Frequencies

Table S210: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	20.78	-10.52	21.35	20.79	2
2	141.09	140.80	141.21	141.21	0
3	371.56	371.71	371.56	371.56	0
4	480.47	481.32	480.48	480.48	0
5	527.58	528.02	527.58	527.58	0
6	794.73	792.57	794.75	794.75	0
7	887.40	881.97	887.40	887.41	1
8	894.52	888.87	894.55	894.55	0
9	1081.17	1078.21	1081.21	1081.21	0
10	1116.27	1112.83	1116.27	1116.27	0
11	1246.46	1240.20	1246.47	1246.47	0
12	1386.96	1377.91	1387.02	1387.02	0
13	1395.11	1385.60	1395.14	1395.14	0
14	1468.80	1469.13	1468.76	1468.76	0
15	1474.27	1475.62	1474.26	1474.27	1
16	1476.54	1477.39	1476.53	1476.53	0
17	1495.93	1498.65	1495.92	1495.92	0
18	1786.22	1778.64	1786.17	1786.17	0
19	3037.08	3049.81	3037.11	3037.11	0
20	3042.41	3054.46	3042.47	3042.47	0
21	3104.03	3128.22	3104.02	3104.02	0
22	3110.28	3134.05	3110.28	3110.28	0
23	3157.81	3179.74	3157.77	3157.77	0
24	3159.26	3180.75	3159.20	3159.20	0

S1.71 1-Chloropropane

Geometries

Table S211: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−4.78185816	0.13547591	0.00000000
2	C	−2.11109876	−0.97139330	0.00000000
3	C	−0.14244981	1.11919067	0.00000000
4	Cl	3.00981998	−0.14144508	0.00000000
5	H	−6.19879779	−1.36232962	0.00000000
6	H	−5.09986073	1.30896986	−1.66945794
7	H	−5.09986073	1.30896986	1.66945794
8	H	−1.82642436	−2.16506020	1.66021781
9	H	−1.82642436	−2.16506020	−1.66021781
10	H	−0.30600557	2.30469630	1.67497536
11	H	−0.30600557	2.30469630	−1.67497536

Natural Internal Coordinates

Table S212: Symmetrized, unnormalized natural internal coordinates for 1-Chloropropane.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{3,4}$
4	$r_{1,5} + r_{1,6} + r_{1,7}$
5	$2r_{1,5} - r_{1,6} - r_{1,7}$
6	$r_{1,6} - r_{1,7}$
7	$r_{2,8} + r_{2,9}$
8	$r_{2,8} - r_{2,9}$
9	$r_{3,10} + r_{3,11}$
10	$r_{3,10} - r_{3,11}$
11	$\phi_{1,2,3}$
12	$\phi_{2,3,4}$
13	$\phi_{5,1,2} + \phi_{6,1,2} + \phi_{7,1,2} - \phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
14	$2\phi_{5,1,2} - \phi_{6,1,2} - \phi_{7,1,2}$
15	$\phi_{6,1,2} - \phi_{7,1,2}$
16	$2\phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
17	$\phi_{5,1,6} - \phi_{5,1,7}$
18	$4\phi_{8,2,9} - \phi_{8,2,1} - \phi_{8,2,3} - \phi_{9,2,1} - \phi_{9,2,3}$
19	$\phi_{8,2,1} + \phi_{8,2,3} - \phi_{9,2,1} - \phi_{9,2,3}$
20	$\phi_{8,2,1} - \phi_{8,2,3} + \phi_{9,2,1} - \phi_{9,2,3}$
21	$\phi_{8,2,1} - \phi_{8,2,3} - \phi_{9,2,1} + \phi_{9,2,3}$
22	$4\phi_{10,3,11} - \phi_{10,3,2} - \phi_{10,3,4} - \phi_{11,3,2} - \phi_{11,3,4}$
23	$\phi_{10,3,2} + \phi_{10,3,4} - \phi_{11,3,2} - \phi_{11,3,4}$
24	$\phi_{10,3,2} - \phi_{10,3,4} + \phi_{11,3,2} - \phi_{11,3,4}$
25	$\phi_{10,3,2} - \phi_{10,3,4} - \phi_{11,3,2} + \phi_{11,3,4}$
26	$\tau_{1,2,3,4}$
27	$\tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{7,1,2,3}$

Frequencies

Table S213: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	117.40	119.31	117.41	117.41	0
2	231.61	231.48	231.62	231.62	0
3	233.16	234.70	233.18	233.18	0
4	363.85	362.94	363.86	363.86	0
5	750.95	752.49	750.96	750.96	0
6	757.78	760.27	757.80	757.80	0
7	870.11	870.09	870.11	870.11	0
8	915.17	913.50	915.21	915.21	0
9	1055.55	1054.26	1055.61	1055.61	0
10	1097.32	1097.60	1097.41	1097.41	0
11	1125.98	1123.80	1126.02	1126.02	0
12	1251.33	1249.66	1251.27	1251.27	0
13	1284.71	1280.89	1284.73	1284.73	0
14	1322.93	1322.45	1322.92	1322.92	0
15	1375.19	1363.53	1375.35	1375.35	0
16	1414.57	1406.73	1414.41	1414.41	0
17	1493.06	1492.70	1493.06	1493.06	0
18	1499.57	1500.06	1499.72	1499.72	0
19	1506.44	1509.11	1506.43	1506.43	0
20	1514.46	1515.22	1514.21	1514.21	0
21	3033.76	3046.21	3033.83	3033.83	0
22	3054.12	3069.68	3054.11	3054.11	0
23	3079.76	3095.29	3079.65	3079.65	0
24	3086.79	3112.35	3086.84	3086.84	0
25	3108.28	3133.25	3108.31	3108.31	0
26	3116.65	3141.29	3116.59	3116.59	0
27	3139.46	3162.47	3139.47	3139.47	0

S1.72 Methoxyethane

Geometries

Table S214: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−3.51555612	0.29044205	−0.00000000
2	C	−0.95458299	−0.99195423	−0.00000000
3	O	0.93589970	0.90095503	−0.00000000
4	C	3.37683746	−0.17280447	0.00000000
5	H	−5.02516284	−1.11599211	−0.00000000
6	H	−3.71909489	1.47840980	−1.67234300
7	H	−3.71909489	1.47840980	1.67234300
8	H	−0.74126596	−2.20420926	1.67415920
9	H	−0.74126596	−2.20420926	−1.67415920
10	H	4.73626773	1.37209229	0.00000000
11	H	3.68698239	−1.34648639	−1.68213636
12	H	3.68698239	−1.34648639	1.68213636

Natural Internal Coordinates

Frequencies

Table S215: Symmetrized, unnormalized natural internal coordinates for Methoxyethane.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{3,4}$
4	$r_{1,5} + r_{1,6} + r_{1,7}$
5	$2r_{1,5} - r_{1,6} - r_{1,7}$
6	$r_{1,6} - r_{1,7}$
7	$r_{2,8} + r_{2,9}$
8	$r_{2,8} - r_{2,9}$
9	$r_{4,10} + r_{4,11} + r_{4,12}$
10	$2r_{4,10} - r_{4,11} - r_{4,12}$
11	$r_{4,11} - r_{4,12}$
12	$\phi_{1,2,3}$
13	$\phi_{2,3,4}$
14	$\phi_{5,1,2} + \phi_{6,1,2} + \phi_{7,1,2} - \phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
15	$2\phi_{5,1,2} - \phi_{6,1,2} - \phi_{7,1,2}$
16	$\phi_{6,1,2} - \phi_{7,1,2}$
17	$2\phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7}$
18	$\phi_{5,1,6} - \phi_{5,1,7}$
19	$4\phi_{8,2,9} - \phi_{8,2,1} - \phi_{8,2,3} - \phi_{9,2,1} - \phi_{9,2,3}$
20	$\phi_{8,2,1} + \phi_{8,2,3} - \phi_{9,2,1} - \phi_{9,2,3}$
21	$\phi_{8,2,1} - \phi_{8,2,3} + \phi_{9,2,1} - \phi_{9,2,3}$
22	$\phi_{8,2,1} - \phi_{8,2,3} - \phi_{9,2,1} + \phi_{9,2,3}$
23	$\phi_{10,4,3} + \phi_{11,4,3} + \phi_{12,4,3} - \phi_{11,4,12} - \phi_{10,4,11} - \phi_{10,4,12}$
24	$2\phi_{10,4,3} - \phi_{11,4,3} - \phi_{12,4,3}$
25	$\phi_{11,4,3} - \phi_{12,4,3}$
26	$2\phi_{11,4,12} - \phi_{10,4,11} - \phi_{10,4,12}$
27	$\phi_{10,4,11} - \phi_{10,4,12}$
28	$\tau_{1,2,3,4}$
29	$\tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{7,1,2,3}$
30	$\tau_{10,4,3,2} + \tau_{11,4,3,2} + \tau_{12,4,3,2}$

Table S216: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	112.85	115.08	112.87	112.86	2
2	209.79	213.20	209.80	209.80	2
3	259.12	262.99	259.13	259.14	3
4	288.79	286.76	288.80	288.80	0
5	468.22	465.34	468.23	468.23	0
6	820.71	821.84	820.73	820.73	0
7	874.88	872.53	874.93	874.93	0
8	1048.43	1045.21	1048.53	1048.53	0
9	1119.09	1117.88	1119.15	1119.15	0
10	1171.74	1172.06	1171.83	1171.83	0
11	1174.17	1172.53	1174.22	1174.22	0
12	1204.65	1203.26	1204.60	1204.60	1
13	1244.73	1239.94	1244.68	1244.68	0
14	1301.19	1302.33	1301.19	1301.19	0
15	1396.67	1391.31	1396.71	1396.71	0
16	1431.74	1424.41	1431.71	1431.71	0
17	1480.96	1479.15	1480.99	1480.99	0
18	1490.30	1493.01	1490.29	1490.29	0
19	1495.37	1500.65	1495.36	1495.36	0
20	1506.90	1509.56	1506.84	1506.84	0
21	1515.64	1519.59	1515.63	1515.63	0
22	1538.29	1539.62	1538.21	1538.21	0
23	2971.39	2987.06	2971.41	2971.41	0
24	2985.25	2998.08	2985.32	2985.32	0
25	3002.00	3027.67	3002.03	3002.03	0
26	3034.72	3058.25	3034.69	3034.69	0
27	3045.76	3060.25	3045.72	3045.72	0
28	3123.74	3148.85	3123.73	3123.73	0
29	3128.05	3152.28	3127.93	3127.93	0
30	3128.68	3153.70	3128.76	3128.76	0

S1.73 Isopropyl Alcohol

Geometries

Table S217: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.38831701	−1.37281068	0.19751772
2	C	−0.00000002	−0.02316624	−0.68077558
3	C	2.38831634	−1.37281178	0.19751772
4	H	−4.06437603	−0.36748732	−0.45670502
5	H	−2.44637430	−1.47961484	2.26098859
6	H	−2.44637460	−3.30273182	−0.54053624
7	H	−0.00000003	0.07560930	−2.74320395
8	O	0.00000063	2.56018606	0.10662450
9	H	0.00000066	2.55954490	1.92575998
10	H	4.06437582	−0.36748919	−0.45670501
11	H	2.44637317	−3.30273286	−0.54053635
12	H	2.44637346	−1.47961611	2.26098862

Natural Internal Coordinates

Frequencies

Table S218: Symmetrized, unnormalized natural internal coordinates for Isopropyl Alcohol.

1	$r_{2,8}$
2	$r_{2,7}$
3	$r_{8,9}$
4	$r_{2,1} + r_{2,3}$
5	$r_{2,1} - r_{2,3}$
6	$r_{1,6} + r_{1,4} + r_{1,5} + r_{3,11} + r_{3,10} + r_{3,12}$
7	$r_{1,6} + r_{1,4} + r_{1,5} - r_{3,11} - r_{3,10} - r_{3,12}$
8	$2r_{1,6} - r_{1,4} - r_{1,5} + 2r_{3,11} - r_{3,10} - r_{3,12}$
9	$2r_{1,6} - r_{1,4} - r_{1,5} - 2r_{3,11} + r_{3,10} + r_{3,12}$
10	$r_{1,4} - r_{1,5} + r_{3,10} - r_{3,12}$
11	$r_{1,4} - r_{1,5} - r_{3,10} + r_{3,12}$
12	$\phi_{2,8,9}$
13	$\phi_{1,2,3}$
14	$\phi_{1,2,7} - \phi_{3,2,7}$
15	$\phi_{1,2,8} - \phi_{3,2,8}$
16	$\phi_{6,1,2} + \phi_{4,1,2} + \phi_{5,1,2} - \phi_{4,1,5} - \phi_{4,1,6} - \phi_{5,1,6} + \phi_{11,3,2} + \phi_{10,3,2} + \phi_{12,3,2} - \phi_{10,3,12} - \phi_{10,3,11} - \phi_{12,3,11}$
17	$\phi_{6,1,2} + \phi_{4,1,2} + \phi_{5,1,2} - \phi_{4,1,5} - \phi_{4,1,6} - \phi_{5,1,6} - \phi_{11,3,2} - \phi_{10,3,2} - \phi_{12,3,2} + \phi_{10,3,12} + \phi_{10,3,11} + \phi_{12,3,11}$
18	$2\phi_{6,1,2} - \phi_{4,1,2} - \phi_{5,1,2} + 2\phi_{11,3,2} - \phi_{10,3,2} - \phi_{12,3,2}$
19	$2\phi_{6,1,2} - \phi_{4,1,2} - \phi_{5,1,2} - 2\phi_{11,3,2} + \phi_{10,3,2} + \phi_{12,3,2}$
20	$\phi_{4,1,2} - \phi_{5,1,2} + \phi_{10,3,2} - \phi_{12,3,2}$
21	$\phi_{4,1,2} - \phi_{5,1,2} - \phi_{10,3,2} + \phi_{12,3,2}$
22	$2\phi_{4,1,5} - \phi_{4,1,6} - \phi_{5,1,6} + 2\phi_{10,3,12} - \phi_{10,3,11} - \phi_{12,3,11}$
23	$2\phi_{4,1,5} - \phi_{4,1,6} - \phi_{5,1,6} - 2\phi_{10,3,12} + \phi_{10,3,11} + \phi_{12,3,11}$
24	$\phi_{4,1,6} - \phi_{5,1,6} - \phi_{10,3,11} + \phi_{12,3,11}$
25	$\phi_{4,1,6} - \phi_{5,1,6} + \phi_{10,3,11} - \phi_{12,3,11}$
26	$\tau_{9,8,2,7}$
27	$\tau_{4,1,2,3} + \tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{10,3,2,1} + \tau_{11,3,2,1} + \tau_{12,3,2,1}$
28	$\tau_{4,1,2,3} + \tau_{5,1,2,3} + \tau_{6,1,2,3} - \tau_{10,3,2,1} - \tau_{11,3,2,1} - \tau_{12,3,2,1}$
29	$\gamma_{7,2,1,3}$
30	$\gamma_{8,2,1,3}$

Table S219: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	224.49	227.33	224.71	224.69	1
2	270.92	272.30	271.02	271.02	1
3	272.99	274.91	273.01	273.04	0
4	357.74	356.46	357.74	357.74	0
5	425.28	423.89	425.26	425.26	0
6	464.61	464.44	464.64	464.64	0
7	825.99	824.93	826.02	826.02	0
8	922.41	920.54	922.43	922.43	0
9	939.40	936.87	939.44	939.44	0
10	983.15	981.53	983.24	983.24	0
11	1092.18	1084.99	1092.36	1092.36	0
12	1159.76	1160.05	1159.84	1159.84	0
13	1196.43	1192.16	1196.56	1196.56	0
14	1315.36	1308.11	1315.50	1315.50	0
15	1367.15	1362.98	1367.12	1367.12	0
16	1403.42	1393.68	1403.39	1403.39	0
17	1410.33	1402.75	1410.35	1410.35	0
18	1427.15	1417.56	1426.84	1426.84	0
19	1487.92	1490.44	1489.26	1489.26	0
20	1491.04	1492.12	1489.63	1489.63	0
21	1503.80	1505.12	1503.90	1503.90	0
22	1511.47	1514.79	1511.25	1511.25	0
23	3024.63	3037.59	3024.58	3024.58	0
24	3028.61	3040.23	3028.65	3028.65	0
25	3060.75	3082.50	3060.77	3060.77	0
26	3092.77	3118.42	3092.86	3092.86	0
27	3103.92	3128.00	3103.90	3103.90	0
28	3121.53	3146.05	3121.50	3121.50	0
29	3124.15	3147.95	3124.10	3124.10	0
30	3819.49	3837.20	3819.49	3819.49	0

S1.74 Propane

Geometries

Table S220: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.39592864	0.51179667	0.00000000
2	C	0.00000000	−1.10217789	0.00000000
3	C	2.39592869	0.51179661	0.00000000
4	H	−4.09939241	−0.65278475	−0.00000000
5	H	−2.45820670	1.73037440	−1.66734556
6	H	−2.45820670	1.73037440	1.66734556
7	H	−0.00000041	−2.34011719	1.65598761
8	H	−0.00000041	−2.34011719	−1.65598761
9	H	4.09939243	−0.65278485	0.00000000
10	H	2.45820678	1.73037434	1.66734556
11	H	2.45820678	1.73037434	−1.66734556

Natural Internal Coordinates

Table S221: Symmetrized, unnormalized natural internal coordinates for Propane.

1	$r_{1,2} + r_{2,3}$
2	$r_{1,2} - r_{2,3}$
3	$r_{1,4} + r_{1,5} + r_{1,6} + r_{3,9} + r_{3,10} + r_{3,11}$
4	$r_{1,4} + r_{1,5} + r_{1,6} - r_{3,9} - r_{3,10} - r_{3,11}$
5	$2r_{1,4} - r_{1,5} - r_{1,6} + 2r_{3,9} - r_{3,10} - r_{3,11}$
6	$2r_{1,4} - r_{1,5} - r_{1,6} - 2r_{3,9} + r_{3,10} + r_{3,11}$
7	$r_{1,5} - r_{1,6} + r_{3,10} - r_{3,11}$
8	$r_{1,5} - r_{1,6} - r_{3,10} + r_{3,11}$
9	$r_{2,7} + r_{2,8}$
10	$r_{2,7} - r_{2,8}$
11	$\phi_{1,2,3}$
12	$\phi_{4,1,2} + \phi_{5,1,2} + \phi_{6,1,2} - \phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} + \phi_{9,3,2} + \phi_{10,3,2} + \phi_{11,3,2} - \phi_{10,3,11} - \phi_{9,3,10} - \phi_{9,3,11}$
13	$\phi_{4,1,2} + \phi_{5,1,2} + \phi_{6,1,2} - \phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} - \phi_{9,3,2} - \phi_{10,3,2} - \phi_{11,3,2} + \phi_{10,3,11} + \phi_{9,3,10} + \phi_{9,3,11}$
14	$2\phi_{4,1,2} - \phi_{5,1,2} - \phi_{6,1,2} + 2\phi_{9,3,2} - \phi_{10,3,2} - \phi_{11,3,2}$
15	$2\phi_{4,1,2} - \phi_{5,1,2} - \phi_{6,1,2} - 2\phi_{9,3,2} + \phi_{10,3,2} + \phi_{11,3,2}$
16	$\phi_{5,1,2} - \phi_{6,1,2} + \phi_{10,3,2} - \phi_{11,3,2}$
17	$\phi_{5,1,2} - \phi_{6,1,2} - \phi_{10,3,2} + \phi_{11,3,2}$
18	$2\phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} + 2\phi_{10,3,11} - \phi_{9,3,10} - \phi_{9,3,11}$
19	$2\phi_{5,1,6} - \phi_{4,1,5} - \phi_{4,1,6} - 2\phi_{10,3,11} + \phi_{9,3,10} + \phi_{9,3,11}$
20	$\phi_{4,1,5} - \phi_{4,1,6} + \phi_{9,3,10} - \phi_{9,3,11}$
21	$\phi_{4,1,5} - \phi_{4,1,6} - \phi_{9,3,10} + \phi_{9,3,11}$
22	$4\phi_{7,2,8} - \phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,2,1} - \phi_{8,2,3}$
23	$\phi_{7,2,1} + \phi_{7,2,3} - \phi_{8,2,1} - \phi_{8,2,3}$
24	$\phi_{7,2,1} - \phi_{7,2,3} + \phi_{8,2,1} - \phi_{8,2,3}$
25	$\phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,2,1} + \phi_{8,2,3}$
26	$\tau_{4,1,2,3} + \tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{9,3,2,1} + \tau_{10,3,2,1} + \tau_{11,3,2,1}$
27	$\tau_{4,1,2,3} + \tau_{5,1,2,3} + \tau_{6,1,2,3} - \tau_{9,3,2,1} - \tau_{10,3,2,1} - \tau_{11,3,2,1}$

Frequencies

Table S222: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	215.56	219.01	215.56	215.56	0
2	273.41	277.19	273.42	273.42	0
3	362.53	360.93	362.54	362.54	0
4	748.63	749.35	748.64	748.64	0
5	885.78	885.83	885.79	885.79	0
6	906.61	906.42	906.63	906.63	0
7	928.98	928.28	929.00	929.00	0
8	1074.04	1074.70	1074.07	1074.07	0
9	1181.29	1178.69	1181.33	1181.33	0
10	1217.54	1213.24	1217.56	1217.56	0
11	1319.32	1319.47	1319.33	1319.33	0
12	1367.14	1359.66	1367.30	1367.30	0
13	1407.52	1398.58	1407.36	1407.36	0
14	1420.81	1414.04	1420.82	1420.82	0
15	1496.33	1497.26	1496.47	1496.47	0
16	1496.59	1499.10	1496.57	1496.57	0
17	1503.87	1506.01	1503.86	1503.86	0
18	1513.81	1517.05	1513.71	1513.71	0
19	1518.58	1519.97	1518.50	1518.50	0
20	3026.70	3040.09	3026.73	3026.73	0
21	3028.77	3040.48	3028.89	3028.89	0
22	3033.74	3051.22	3033.57	3033.57	0
23	3061.46	3088.50	3061.50	3061.50	0
24	3093.71	3120.11	3093.71	3093.71	0
25	3104.68	3129.58	3104.70	3104.70	0
26	3105.03	3130.85	3105.04	3105.04	0
27	3107.75	3132.58	3107.69	3107.69	0

S1.75 Acrylonitrile

Geometries

Table S223: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−3.19156925	0.72327464	−0.00000000
2	C	−1.30268767	−0.96690359	−0.00000000
3	C	1.30844710	−0.21134227	−0.00000000
4	N	3.42266953	0.40043186	0.00000000
5	H	−5.13781563	0.09913705	−0.00000000
6	H	−2.82071717	2.73416350	−0.00000000
7	H	−1.66434467	−2.97977677	0.00000000

Natural Internal Coordinates

Table S224: Symmetrized, unnormalized natural internal coordinates for Acrylonitrile.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{3,4}$
4	$r_{2,7}$
5	$r_{1,5} + r_{1,6}$
6	$r_{1,5} - r_{1,6}$
7	$2\phi_{1,2,3} - \phi_{1,2,7} - \phi_{3,2,7}$
8	$\phi_{1,2,7} - \phi_{3,2,7}$
9	$2\phi_{6,1,5} - \phi_{2,1,6} - \phi_{2,1,5}$
10	$\phi_{2,1,6} - \phi_{2,1,5}$
11	$\tau_{6,1,2,3} + \tau_{5,1,2,3} + \tau_{6,1,2,7} + \tau_{5,1,2,7}$
12	$\gamma_{2,1,6,5}$
13	$\gamma_{7,2,3,1}$
14	$\alpha^{x}_{1,2,3,4}$
15	$\alpha^{y}_{1,2,3,4}$

Frequencies

Table S225: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	227.13	226.78	227.14	227.13	1
2	337.74	336.95	337.76	337.74	1
3	559.50	559.08	559.51	559.52	1
4	688.12	700.45	688.14	688.15	1
5	873.15	871.30	873.21	873.21	0
6	969.04	972.04	969.15	969.15	0
7	993.49	1012.85	993.35	993.35	0
8	1104.14	1101.66	1104.17	1104.17	0
9	1314.40	1313.06	1314.51	1314.51	0
10	1447.12	1447.65	1447.04	1447.04	0
11	1659.64	1653.40	1659.63	1659.63	0
12	2271.92	2235.15	2271.89	2271.89	0
13	3164.32	3178.91	3164.33	3164.33	0
14	3202.58	3219.72	3202.57	3202.57	0
15	3262.58	3282.29	3262.58	3262.58	0

S1.76 Trimethylamine

Geometries

Table S226: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	X	−2.60567339	0.00000000	0.00000000
2	N	−0.71594686	0.00000000	0.00000000
3	C	0.17737959	−1.30146773	−2.25420824
4	C	0.17737959	2.60293546	0.00000000
5	C	0.17737959	−1.30146773	2.25420824
6	H	2.26161442	−1.36371156	−2.36201770
7	H	−0.52888531	−0.34189560	−3.93805529
8	H	−0.52888531	−3.23950812	−2.26511792
9	H	2.26161442	2.72742311	0.00000000
10	H	−0.52888531	3.58140372	1.67293737
11	H	−0.52888531	3.58140372	−1.67293737
12	H	2.26161442	−1.36371156	2.36201770
13	H	−0.52888531	−3.23950812	2.26511792
14	H	−0.52888531	−0.34189560	3.93805529

Natural Internal Coordinates

Frequencies

Table S227: Symmetrized, unnormalized natural internal coordinates for Trimethylamine.

1	$r_{2,3} + r_{2,4} + r_{2,5}$
2	$2r_{2,3} - r_{2,4} - r_{2,5}$
3	$r_{2,4} - r_{2,5}$
4	$r_{3,6} + r_{3,7} + r_{3,8} + r_{4,9} + r_{4,10} + r_{4,11} + r_{5,12} + r_{5,13} + r_{5,14}$
5	$2r_{3,6} + 2r_{3,7} + 2r_{3,8} - r_{4,9} - r_{4,10} - r_{4,11} - r_{5,12} - r_{5,13} - r_{5,14}$
6	$r_{4,9} + r_{4,10} + r_{4,11} - r_{5,12} - r_{5,13} - r_{5,14}$
7	$2r_{3,6} - r_{3,7} - r_{3,8} + 2r_{4,9} - r_{4,10} - r_{4,11} + 2r_{5,12} - r_{5,13} - r_{5,14}$
8	$4r_{3,6} - 2r_{3,7} - 2r_{3,8} - 2r_{4,9} + r_{4,10} + r_{4,11} - 2r_{5,12} + r_{5,13} + r_{5,14}$
9	$2r_{4,9} - r_{4,10} - r_{4,11} - 2r_{5,12} + r_{5,13} + r_{5,14}$
10	$r_{3,7} - r_{3,8} + r_{4,10} - r_{4,11} + r_{5,13} - r_{5,14}$
11	$2r_{3,7} - 2r_{3,8} - r_{4,10} + r_{4,11} - r_{5,13} + r_{5,14}$
12	$r_{4,10} - r_{4,11} - r_{5,13} + r_{5,14}$
13	$2\phi_{4,2,5} - \phi_{3,2,4} - \phi_{3,2,5}$
14	$\phi_{3,2,4} - \phi_{3,2,5}$
15	$\phi_{4,2,5} + \phi_{3,2,4} + \phi_{3,2,5} - \gamma_{3,2,4,5} - \gamma_{4,2,5,3} - \gamma_{5,2,3,4}$
16	$\phi_{6,3,2} + \phi_{7,3,2} + \phi_{8,3,2} - \phi_{7,3,8} - \phi_{6,3,8} - \phi_{6,3,7} + \phi_{9,4,2} + \phi_{10,4,2} + \phi_{11,4,2} - \phi_{10,4,11}$ $-\phi_{9,4,11} - \phi_{9,4,10} + \phi_{12,5,2} + \phi_{13,5,2} + \phi_{14,5,2} - \phi_{13,5,14} - \phi_{12,5,14} - \phi_{12,5,13}$
17	$2\phi_{6,3,2} + 2\phi_{7,3,2} + 2\phi_{8,3,2} - 2\phi_{7,3,8} - 2\phi_{6,3,8} - 2\phi_{6,3,7} - \phi_{9,4,2} - \phi_{10,4,2} - \phi_{11,4,2} + \phi_{10,4,11}$ $+\phi_{9,4,11} + \phi_{9,4,10} - \phi_{12,5,2} - \phi_{13,5,2} - \phi_{14,5,2} + \phi_{13,5,14} + \phi_{12,5,14} + \phi_{12,5,13}$
18	$\phi_{9,4,2} + \phi_{10,4,2} + \phi_{11,4,2} - \phi_{10,4,11} - \phi_{9,4,11} - \phi_{9,4,10} - \phi_{12,5,2} - \phi_{13,5,2} - \phi_{14,5,2} + \phi_{13,5,14}$ $+\phi_{12,5,14} + \phi_{12,5,13}$
19	$2\phi_{6,3,2} - \phi_{7,3,2} - \phi_{8,3,2} + 2\phi_{9,4,2} - \phi_{10,4,2} - \phi_{11,4,2} + 2\phi_{12,5,2} - \phi_{13,5,2} - \phi_{14,5,2}$
20	$4\phi_{6,3,2} - 2\phi_{7,3,2} - 2\phi_{8,3,2} - 2\phi_{9,4,2} + \phi_{10,4,2} + \phi_{11,4,2} - 2\phi_{12,5,2} + \phi_{13,5,2} + \phi_{14,5,2}$
21	$2\phi_{9,4,2} - \phi_{10,4,2} - \phi_{11,4,2} - 2\phi_{12,5,2} + \phi_{13,5,2} + \phi_{14,5,2}$
22	$\phi_{7,3,2} - \phi_{8,3,2} + \phi_{10,4,2} - \phi_{11,4,2} + \phi_{13,5,2} - \phi_{14,5,2}$
23	$2\phi_{7,3,2} - 2\phi_{8,3,2} - \phi_{10,4,2} + \phi_{11,4,2} - \phi_{13,5,2} + \phi_{14,5,2}$
24	$\phi_{10,4,2} - \phi_{11,4,2} - \phi_{13,5,2} + \phi_{14,5,2}$
25	$2\phi_{7,3,8} - \phi_{6,3,8} - \phi_{6,3,7} + 2\phi_{10,4,11} - \phi_{9,4,11} - \phi_{9,4,10} + 2\phi_{13,5,14} - \phi_{12,5,14} - \phi_{12,5,13}$
26	$4\phi_{7,3,8} - 2\phi_{6,3,8} - 2\phi_{6,3,7} - 2\phi_{10,4,11} + \phi_{9,4,11} + \phi_{9,4,10} - 2\phi_{13,5,14} + \phi_{12,5,14} + \phi_{12,5,13}$
27	$2\phi_{10,4,11} - \phi_{9,4,11} - \phi_{9,4,10} - 2\phi_{13,5,14} + \phi_{12,5,14} + \phi_{12,5,13}$
28	$\phi_{6,3,8} - \phi_{6,3,7} + \phi_{9,4,11} - \phi_{9,4,10} + \phi_{12,5,14} - \phi_{12,5,13}$
29	$2\phi_{6,3,8} - 2\phi_{6,3,7} - \phi_{9,4,11} + \phi_{9,4,10} - \phi_{12,5,14} + \phi_{12,5,13}$
30	$\phi_{9,4,11} - \phi_{9,4,10} - \phi_{12,5,14} + \phi_{12,5,13}$
31	$\tau_{6,3,2,4} + \tau_{6,3,2,5} + \tau_{7,3,2,4} + \tau_{7,3,2,5} + \tau_{8,3,2,4} + \tau_{8,3,2,5} + \tau_{9,4,2,5} + \tau_{9,4,2,3} + \tau_{10,4,2,5} + \tau_{10,4,2,3}$ $+\tau_{11,4,2,5} + \tau_{11,4,2,3} + \tau_{12,5,2,3} + \tau_{12,5,2,4} + \tau_{13,5,2,3} + \tau_{13,5,2,4} + \tau_{14,5,2,3} + \tau_{14,5,2,4}$
32	$2\tau_{6,3,2,4} + 2\tau_{6,3,2,5} + 2\tau_{7,3,2,4} + 2\tau_{7,3,2,5} + 2\tau_{8,3,2,4} + 2\tau_{8,3,2,5} - \tau_{9,4,2,5} - \tau_{9,4,2,3} - \tau_{10,4,2,5} - \tau_{10,4,2,3}$ $-\tau_{11,4,2,5} - \tau_{11,4,2,3} - \tau_{12,5,2,3} - \tau_{12,5,2,4} - \tau_{13,5,2,3} - \tau_{13,5,2,4} - \tau_{14,5,2,3} - \tau_{14,5,2,4}$
33	$\tau_{9,4,2,5} + \tau_{9,4,2,3} + \tau_{10,4,2,5} + \tau_{10,4,2,3} + \tau_{11,4,2,5} + \tau_{11,4,2,3} - \tau_{12,5,2,3} - \tau_{12,5,2,4} - \tau_{13,5,2,3} - \tau_{13,5,2,4}$ $-\tau_{14,5,2,3} - \tau_{14,5,2,4}$

Table S228: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	240.77	247.42	240.78	240.78	1
2	279.99	283.97	280.06	280.06	0
3	279.99	283.97	280.06	280.06	0
4	373.11	367.48	373.12	373.12	0
5	417.26	414.44	417.23	417.23	0
6	417.26	414.46	417.24	417.24	0
7	847.53	843.27	847.58	847.58	0
8	1063.58	1062.41	1063.60	1063.60	1
9	1065.00	1064.36	1065.07	1065.07	0
10	1065.00	1064.38	1065.07	1065.07	0
11	1120.56	1119.47	1120.57	1120.57	0
12	1120.56	1119.48	1120.57	1120.57	0
13	1215.49	1209.15	1215.49	1215.49	0
14	1309.86	1301.46	1309.96	1309.96	0
15	1309.86	1301.47	1309.96	1309.96	0
16	1436.74	1430.47	1436.63	1436.63	0
17	1436.74	1430.50	1436.63	1436.63	0
18	1478.58	1472.09	1478.61	1478.61	0
19	1488.68	1491.19	1488.67	1488.67	0
20	1488.69	1491.20	1488.67	1488.67	0
21	1496.49	1498.35	1496.49	1496.49	0
22	1508.19	1511.17	1508.14	1508.14	0
23	1517.12	1519.89	1517.11	1517.11	0
24	1517.12	1519.90	1517.11	1517.11	0
25	2925.30	2943.11	2925.61	2925.61	0
26	2925.30	2943.19	2925.61	2925.61	0
27	2934.80	2949.46	2935.12	2935.12	0
28	3068.49	3088.65	3068.19	3068.19	0
29	3068.49	3088.66	3068.19	3068.19	0
30	3071.93	3089.56	3071.61	3071.61	0
31	3112.25	3137.91	3112.25	3112.25	0
32	3116.44	3140.69	3116.43	3116.43	0
33	3116.44	3140.74	3116.43	3116.43	0

S1.77 Isobutane

Geometries

Table S229: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	H	−2.77578707	0.00000000	0.00000000
2	C	−0.70454753	0.00000000	0.00000000
3	C	0.20096794	−1.37289317	−2.37792072
4	C	0.20096794	2.74578634	−0.00000000
5	C	0.20096794	−1.37289317	2.37792072
6	H	2.26618320	−1.40919603	−2.44079912
7	H	−0.46875139	−0.42944159	−4.09015926
8	H	−0.46875139	−3.32746103	−2.41698695
9	H	2.26618320	2.81839206	0.00000000
10	H	−0.46875139	3.75690262	1.67317231
11	H	−0.46875139	3.75690262	−1.67317231
12	H	2.26618320	−1.40919603	2.44079912
13	H	−0.46875139	−3.32746103	2.41698695
14	H	−0.46875139	−0.42944159	4.09015926

Natural Internal Coordinates

Frequencies

Table S230: Symmetrized, unnormalized natural internal coordinates for Isobutane.

1	$r_{1,2}$
2	$r_{2,3} + r_{2,4} + r_{2,5}$
3	$2r_{2,3} - r_{2,4} - r_{2,5}$
4	$r_{2,4} - r_{2,5}$
5	$r_{3,6} + r_{3,7} + r_{3,8} + r_{4,9} + r_{4,10} + r_{4,11} + r_{5,12} + r_{5,13} + r_{5,14}$
6	$2r_{3,6} + 2r_{3,7} + 2r_{3,8} - r_{4,9} - r_{4,10} - r_{4,11} - r_{5,12} - r_{5,13} - r_{5,14}$
7	$r_{4,9} + r_{4,10} + r_{4,11} - r_{5,12} - r_{5,13} - r_{5,14}$
8	$2r_{3,6} - r_{3,7} - r_{3,8} + 2r_{4,9} - r_{4,10} - r_{4,11} + 2r_{5,12} - r_{5,13} - r_{5,14}$
9	$4r_{3,6} - 2r_{3,7} - 2r_{3,8} - 2r_{4,9} + r_{4,10} + r_{4,11} - 2r_{5,12} + r_{5,13} + r_{5,14}$
10	$2r_{4,9} - r_{4,10} - r_{4,11} - 2r_{5,12} + r_{5,13} + r_{5,14}$
11	$r_{3,7} - r_{3,8} + r_{4,10} - r_{4,11} + r_{5,13} - r_{5,14}$
12	$2r_{3,7} - 2r_{3,8} - r_{4,10} + r_{4,11} - r_{5,13} + r_{5,14}$
13	$r_{4,10} - r_{4,11} - r_{5,13} + r_{5,14}$
14	$\phi_{4,2,5} + \phi_{3,2,4} + \phi_{3,2,5} - \phi_{1,2,3} - \phi_{1,2,4} - \phi_{1,2,5}$
15	$2\phi_{4,2,5} - \phi_{3,2,4} - \phi_{3,2,5}$
16	$\phi_{3,2,4} - \phi_{3,2,5}$
17	$2\phi_{1,2,3} - \phi_{1,2,4} - \phi_{1,2,5}$
18	$\phi_{1,2,4} - \phi_{1,2,5}$
19	$\phi_{7,3,8} + \phi_{6,3,7} + \phi_{6,3,8} - \phi_{6,3,2} - \phi_{7,3,2} - \phi_{8,3,2} + \phi_{10,4,11} + \phi_{9,4,10} + \phi_{9,4,11} - \phi_{9,4,2}$ $-\phi_{10,4,2} - \phi_{11,4,2} + \phi_{13,5,14} + \phi_{12,5,13} + \phi_{12,5,14} - \phi_{12,5,2} - \phi_{13,5,2} - \phi_{14,5,2}$
20	$2\phi_{7,3,8} + 2\phi_{6,3,7} + 2\phi_{6,3,8} - 2\phi_{6,3,2} - 2\phi_{7,3,2} - 2\phi_{8,3,2} - \phi_{10,4,11} - \phi_{9,4,10} - \phi_{9,4,11} + \phi_{9,4,2}$ $+\phi_{10,4,2} + \phi_{11,4,2} - \phi_{13,5,14} - \phi_{12,5,13} - \phi_{12,5,14} + \phi_{12,5,2} + \phi_{13,5,2} + \phi_{14,5,2}$
21	$\phi_{10,4,11} + \phi_{9,4,10} + \phi_{9,4,11} - \phi_{9,4,2} - \phi_{10,4,2} - \phi_{11,4,2} - \phi_{13,5,14} - \phi_{12,5,13} - \phi_{12,5,14} + \phi_{12,5,2}$ $+\phi_{13,5,2} + \phi_{14,5,2}$
22	$2\phi_{7,3,8} - \phi_{6,3,7} - \phi_{6,3,8} + 2\phi_{10,4,11} - \phi_{9,4,10} - \phi_{9,4,11} + 2\phi_{13,5,14} - \phi_{12,5,13} - \phi_{12,5,14}$
23	$4\phi_{7,3,8} - 2\phi_{6,3,7} - 2\phi_{6,3,8} - 2\phi_{10,4,11} + \phi_{9,4,10} + \phi_{9,4,11} - 2\phi_{13,5,14} + \phi_{12,5,13} + \phi_{12,5,14}$
24	$2\phi_{10,4,11} - \phi_{9,4,10} - \phi_{9,4,11} - 2\phi_{13,5,14} + \phi_{12,5,13} + \phi_{12,5,14}$
25	$\phi_{6,3,7} - \phi_{6,3,8} + \phi_{9,4,10} - \phi_{9,4,11} + \phi_{12,5,13} - \phi_{12,5,14}$
26	$2\phi_{6,3,7} - 2\phi_{6,3,8} - \phi_{9,4,10} + \phi_{9,4,11} - \phi_{12,5,13} + \phi_{12,5,14}$
27	$\phi_{9,4,10} - \phi_{9,4,11} - \phi_{12,5,13} + \phi_{12,5,14}$
28	$2\phi_{6,3,2} - \phi_{7,3,2} - \phi_{8,3,2} + 2\phi_{9,4,2} - \phi_{10,4,2} - \phi_{11,4,2} + 2\phi_{12,5,2} - \phi_{13,5,2} - \phi_{14,5,2}$
29	$4\phi_{6,3,2} - 2\phi_{7,3,2} - 2\phi_{8,3,2} - 2\phi_{9,4,2} + \phi_{10,4,2} + \phi_{11,4,2} - 2\phi_{12,5,2} + \phi_{13,5,2} + \phi_{14,5,2}$
30	$2\phi_{9,4,2} - \phi_{10,4,2} - \phi_{11,4,2} - 2\phi_{12,5,2} + \phi_{13,5,2} + \phi_{14,5,2}$
31	$\phi_{7,3,2} - \phi_{8,3,2} + \phi_{10,4,2} - \phi_{11,4,2} + \phi_{13,5,2} - \phi_{14,5,2}$
32	$2\phi_{7,3,2} - 2\phi_{8,3,2} - \phi_{10,4,2} + \phi_{11,4,2} - \phi_{13,5,2} + \phi_{14,5,2}$
33	$\phi_{10,4,2} - \phi_{11,4,2} - \phi_{13,5,2} + \phi_{14,5,2}$
34	$\tau_{6,3,2,4} + \tau_{7,3,2,4} + \tau_{8,3,2,4} + \tau_{9,4,2,5} + \tau_{10,4,2,5} + \tau_{11,4,2,5} + \tau_{12,5,2,3} + \tau_{13,5,2,3} + \tau_{14,5,2,3}$
35	$2\tau_{6,3,2,4} + 2\tau_{7,3,2,4} + 2\tau_{8,3,2,4} - \tau_{9,4,2,5} - \tau_{10,4,2,5} - \tau_{11,4,2,5} - \tau_{12,5,2,3} - \tau_{13,5,2,3} - \tau_{14,5,2,3}$
36	$\tau_{9,4,2,5} + \tau_{10,4,2,5} + \tau_{11,4,2,5} - \tau_{12,5,2,3} - \tau_{13,5,2,3} - \tau_{14,5,2,3}$

Table S231: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	200.11	205.13	200.19	200.19	0
2	258.96	263.39	259.02	259.02	0
3	258.96	263.39	259.02	259.02	0
4	359.15	356.07	359.16	359.16	0
5	359.15	356.09	359.16	359.16	0
6	423.35	422.48	423.39	423.39	0
7	808.93	807.93	808.93	808.93	0
8	921.64	920.60	921.69	921.69	0
9	921.64	920.60	921.69	921.69	0
10	952.74	950.37	952.75	952.75	0
11	984.82	983.60	984.84	984.84	0
12	984.82	983.61	984.84	984.84	0
13	1199.43	1196.81	1199.50	1199.50	0
14	1199.43	1196.82	1199.50	1199.50	0
15	1214.06	1208.65	1214.11	1214.11	0
16	1361.63	1353.22	1361.73	1361.73	0
17	1361.63	1353.24	1361.73	1361.73	0
18	1401.34	1391.26	1401.20	1401.20	0
19	1401.34	1391.28	1401.22	1401.22	0
20	1425.68	1417.35	1425.71	1425.71	0
21	1487.52	1489.53	1487.51	1487.51	0
22	1493.96	1494.69	1493.94	1493.94	0
23	1493.96	1494.70	1493.94	1493.94	0
24	1511.91	1514.46	1511.87	1511.87	0
25	1511.92	1514.46	1511.87	1511.87	0
26	1519.45	1521.04	1519.40	1519.40	0
27	3019.98	3032.54	3019.14	3019.14	0
28	3019.98	3032.58	3019.97	3019.97	0
29	3020.64	3035.24	3021.43	3021.43	0
30	3024.99	3042.96	3024.98	3024.98	0
31	3092.85	3118.66	3092.79	3092.79	0
32	3092.85	3118.71	3092.84	3092.84	0
33	3092.89	3119.00	3093.02	3093.02	0
34	3096.86	3121.60	3096.85	3096.85	0
35	3096.86	3121.66	3096.86	3096.86	0
36	3102.02	3125.72	3102.03	3102.03	0

S1.78 n-Butane

Geometries

Table S232: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−3.68479476	0.24819108	−0.00000000
2	C	−1.06753027	−0.97316796	−0.00000000
3	C	1.06753027	0.97316796	−0.00000000
4	C	3.68479476	−0.24819108	0.00000000
5	H	−5.18541024	−1.16829556	−0.00000000
6	H	−3.93796232	1.44128610	−1.66759012
7	H	−3.93796232	1.44128610	1.66759012
8	H	−0.86739103	−2.19780833	1.65727692
9	H	−0.86739103	−2.19780833	−1.65727692
10	H	0.86739103	2.19780833	1.65727692
11	H	0.86739103	2.19780833	−1.65727692
12	H	5.18541024	1.16829556	0.00000000
13	H	3.93796232	−1.44128610	−1.66759012
14	H	3.93796232	−1.44128610	1.66759012

Natural Internal Coordinates

Frequencies

Table S233: Symmetrized, unnormalized natural internal coordinates for n-Butane.

1	$r_{1,2} + r_{3,4}$
2	$r_{1,2} - r_{3,4}$
3	$r_{2,3}$
4	$r_{2,8} + r_{2,9} + r_{3,10} + r_{3,11}$
5	$r_{2,8} + r_{2,9} - r_{3,10} - r_{3,11}$
6	$r_{2,8} - r_{2,9} + r_{3,10} - r_{3,11}$
7	$r_{2,8} - r_{2,9} - r_{3,10} + r_{3,11}$
8	$r_{1,5} + r_{1,6} + r_{1,7} + r_{4,12} + r_{4,13} + r_{4,14}$
9	$r_{1,5} + r_{1,6} + r_{1,7} - r_{4,12} - r_{4,13} - r_{4,14}$
10	$2r_{1,5} - r_{1,6} - r_{1,7} + 2r_{4,12} - r_{4,13} - r_{4,14}$
11	$2r_{1,5} - r_{1,6} - r_{1,7} - 2r_{4,12} + r_{4,13} + r_{4,14}$
12	$r_{1,6} - r_{1,7} + r_{4,13} - r_{4,14}$
13	$r_{1,6} - r_{1,7} - r_{4,13} + r_{4,14}$
14	$\phi_{1,2,3} + \phi_{2,3,4}$
15	$\phi_{1,2,3} - \phi_{2,3,4}$
16	$4\phi_{8,2,9} - \phi_{8,2,1} - \phi_{8,2,3} - \phi_{9,2,1} - \phi_{9,2,3} + 4\phi_{10,3,11} - \phi_{10,3,2} - \phi_{10,3,4} - \phi_{11,3,2} - \phi_{11,3,4}$
17	$4\phi_{8,2,9} - \phi_{8,2,1} - \phi_{8,2,3} - \phi_{9,2,1} - \phi_{9,2,3} - 4\phi_{10,3,11} + \phi_{10,3,2} + \phi_{10,3,4} + \phi_{11,3,2} + \phi_{11,3,4}$
18	$\phi_{8,2,1} + \phi_{8,2,3} - \phi_{9,2,1} - \phi_{9,2,3} + \phi_{10,3,2} + \phi_{10,3,4} - \phi_{11,3,2} - \phi_{11,3,4}$
19	$\phi_{8,2,1} + \phi_{8,2,3} - \phi_{9,2,1} - \phi_{9,2,3} - \phi_{10,3,2} - \phi_{10,3,4} + \phi_{11,3,2} + \phi_{11,3,4}$
20	$\phi_{8,2,1} - \phi_{8,2,3} + \phi_{9,2,1} - \phi_{9,2,3} + \phi_{10,3,2} - \phi_{10,3,4} + \phi_{11,3,2} - \phi_{11,3,4}$
21	$\phi_{8,2,1} - \phi_{8,2,3} + \phi_{9,2,1} - \phi_{9,2,3} - \phi_{10,3,2} + \phi_{10,3,4} - \phi_{11,3,2} + \phi_{11,3,4}$
22	$\phi_{8,2,1} - \phi_{8,2,3} - \phi_{9,2,1} + \phi_{9,2,3} + \phi_{10,3,2} - \phi_{10,3,4} - \phi_{11,3,2} + \phi_{11,3,4}$
23	$\phi_{8,2,1} - \phi_{8,2,3} - \phi_{9,2,1} + \phi_{9,2,3} - \phi_{10,3,2} + \phi_{10,3,4} + \phi_{11,3,2} - \phi_{11,3,4}$
24	$\phi_{5,1,2} + \phi_{6,1,2} + \phi_{7,1,2} - \phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7} + \phi_{12,4,3} + \phi_{13,4,3} + \phi_{14,4,3} - \phi_{13,4,14} - \phi_{12,4,13} - \phi_{12,4,14}$
25	$\phi_{5,1,2} + \phi_{6,1,2} + \phi_{7,1,2} - \phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7} - \phi_{12,4,3} - \phi_{13,4,3} - \phi_{14,4,3} + \phi_{13,4,14} + \phi_{12,4,13} + \phi_{12,4,14}$
26	$2\phi_{5,1,2} - \phi_{6,1,2} - \phi_{7,1,2} + 2\phi_{12,4,3} - \phi_{13,4,3} - \phi_{14,4,3}$
27	$2\phi_{5,1,2} - \phi_{6,1,2} - \phi_{7,1,2} - 2\phi_{12,4,3} + \phi_{13,4,3} + \phi_{14,4,3}$
28	$\phi_{6,1,2} - \phi_{7,1,2} + \phi_{13,4,3} - \phi_{14,4,3}$
29	$\phi_{6,1,2} - \phi_{7,1,2} - \phi_{13,4,3} + \phi_{14,4,3}$
30	$2\phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7} + 2\phi_{13,4,14} - \phi_{12,4,13} - \phi_{12,4,14}$
31	$2\phi_{6,1,7} - \phi_{5,1,6} - \phi_{5,1,7} - 2\phi_{13,4,14} + \phi_{12,4,13} + \phi_{12,4,14}$
32	$\phi_{5,1,6} - \phi_{5,1,7} + \phi_{12,4,13} - \phi_{12,4,14}$
33	$\phi_{5,1,6} - \phi_{5,1,7} - \phi_{12,4,13} + \phi_{12,4,14}$
34	$\tau_{1,2,3,4}$
35	$\tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{7,1,2,3} + \tau_{12,4,3,2} + \tau_{13,4,3,2} + \tau_{14,4,3,2}$
36	$\tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{7,1,2,3} - \tau_{12,4,3,2} - \tau_{13,4,3,2} - \tau_{14,4,3,2}$

Table S234: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	115.69	117.41	115.69	115.69	0
2	221.77	224.72	221.78	221.78	0
3	253.43	251.97	253.43	253.43	0
4	257.32	261.42	257.33	257.33	0
5	422.71	421.23	422.72	422.72	0
6	733.72	734.90	733.73	733.73	0
7	807.44	807.24	807.46	807.46	0
8	848.71	848.58	848.73	848.73	0
9	957.85	957.29	957.87	957.87	0
10	977.87	976.61	977.88	977.88	0
11	1032.28	1031.42	1032.31	1032.31	0
12	1082.98	1082.83	1083.02	1083.02	0
13	1175.12	1172.34	1175.16	1175.16	0
14	1213.01	1207.91	1213.03	1213.03	0
15	1290.42	1288.70	1290.43	1290.43	0
16	1318.77	1311.28	1318.78	1318.78	0
17	1332.59	1332.31	1332.59	1332.59	0
18	1398.23	1385.10	1398.90	1398.90	0
19	1412.55	1403.95	1411.89	1411.89	0
20	1414.03	1406.14	1413.99	1413.99	0
21	1490.65	1489.39	1490.72	1490.72	0
22	1496.91	1497.33	1497.12	1497.12	0
23	1505.13	1507.69	1505.12	1505.12	0
24	1506.70	1509.56	1506.69	1506.69	0
25	1511.27	1513.15	1511.15	1511.15	0
26	1515.99	1516.15	1515.77	1515.77	0
27	3016.77	3032.41	3016.90	3016.90	0
28	3023.91	3039.18	3025.69	3025.69	0
29	3028.05	3041.16	3026.24	3026.24	0
30	3028.91	3042.96	3028.75	3028.75	0
31	3042.42	3069.35	3042.36	3042.36	0
32	3064.03	3090.75	3064.01	3064.01	0
33	3097.42	3123.33	3097.46	3097.46	0
34	3101.23	3126.12	3101.28	3101.28	0
35	3105.51	3130.84	3105.53	3105.53	0
36	3106.19	3131.40	3106.24	3106.24	0

S1.79 Furan

Geometries

Table S235: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	X	0.00000000	0.00000000	−0.25784671
2	O	0.00000000	0.00000000	−2.14757323
3	C	−0.00000000	2.06569237	−0.60265967
4	C	−0.00000000	−2.06569237	−0.60265967
5	C	−0.00000000	−1.36012563	1.87072136
6	C	0.00000000	1.36012563	1.87072136
7	H	0.00000000	3.87067042	−1.53834798
8	H	−0.00000000	−3.87067042	−1.53834798
9	H	0.00000000	−2.60420194	3.48152751
10	H	0.00000000	2.60420194	3.48152751

Natural Internal Coordinates

Table S236: Symmetrized, unnormalized natural internal coordinates for Furan.

1	$r_{5,6} + r_{3,6} + r_{4,5} + r_{2,3} + r_{2,4}$
2	$3r_{5,6} + r_{3,6} + r_{4,5} - 3r_{2,3} - 3r_{2,4}$
3	$2r_{3,6} - 2r_{4,5} + r_{2,3} - r_{2,4}$
4	$3r_{5,6} - 3r_{3,6} - 3r_{4,5} + r_{2,3} + r_{2,4}$
5	$r_{3,6} - r_{4,5} - 2r_{2,3} + 2r_{2,4}$
6	$r_{3,7} + r_{4,8}$
7	$r_{3,7} - r_{4,8}$
8	$r_{6,10} + r_{5,9}$
9	$r_{6,10} - r_{5,9}$
10	$3\phi_{4,5,6} - 3\phi_{5,6,3} + \phi_{6,3,2} + \phi_{3,2,4} - 3\phi_{2,4,5}$
11	$-\phi_{5,6,3} + 2\phi_{6,3,2} - 2\phi_{3,2,4} + \phi_{2,4,5}$
12	$\phi_{7,3,2} - \phi_{7,3,6} + \phi_{8,4,5} - \phi_{8,4,2}$
13	$\phi_{7,3,2} - \phi_{7,3,6} - \phi_{8,4,5} + \phi_{8,4,2}$
14	$\phi_{10,6,3} - \phi_{10,6,5} + \phi_{9,5,6} - \phi_{9,5,4}$
15	$\phi_{10,6,3} - \phi_{10,6,5} - \phi_{9,5,6} + \phi_{9,5,4}$
16	$\tau_{5,6,3,2} - 3\tau_{6,3,2,4} + 3\tau_{3,2,4,5} - 3\tau_{2,4,5,6} + \tau_{3,6,5,4}$
17	$-2\tau_{5,6,3,2} + \tau_{6,3,2,4} - \tau_{2,4,5,6} + 2\tau_{3,6,5,4}$
18	$\gamma_{7,3,2,6} + \gamma_{8,4,5,2}$
19	$\gamma_{7,3,2,6} - \gamma_{8,4,5,2}$
20	$\gamma_{10,6,3,5} + \gamma_{9,5,6,4}$
21	$\gamma_{10,6,3,5} - \gamma_{9,5,6,4}$

Frequencies

Table S237: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	603.17	607.85	603.36	603.27	1
2	612.43	624.20	612.52	612.52	0
3	731.42	727.34	731.57	731.33	1
4	759.65	759.46	759.66	759.66	0
5	844.41	838.39	844.34	844.34	0
6	860.43	860.49	860.16	860.43	2
7	877.52	872.05	877.55	877.55	0
8	882.50	876.45	882.52	882.52	0
9	1012.31	1009.76	1012.43	1012.43	0
10	1061.14	1060.69	1061.35	1061.17	1
11	1090.49	1093.31	1090.46	1090.46	0
12	1160.71	1156.62	1160.70	1160.70	0
13	1217.77	1226.87	1217.73	1217.77	2
14	1289.60	1285.69	1289.59	1289.59	0
15	1416.47	1398.90	1416.52	1416.52	0
16	1524.35	1512.97	1524.25	1524.25	0
17	1591.82	1583.30	1591.71	1591.80	1
18	3257.60	3274.65	3257.62	3257.62	0
19	3268.39	3284.34	3268.39	3268.39	0
20	3287.59	3303.22	3287.58	3287.58	0
21	3295.05	3310.29	3295.04	3295.04	0

S1.80 1,3−Butadiene

Geometries

Table S238: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.14744698	−2.89273316	0.96440626
2	C	−0.23148527	−1.37327643	−1.03135868
3	C	0.23148527	1.37327643	−1.03135868
4	C	−0.14744698	2.89273316	0.96440626
5	H	0.89800063	−2.16342975	2.72536418
6	H	−0.26186351	−4.89440210	0.86513287
7	H	−0.89144700	−2.19256181	−2.79330602
8	H	0.89144700	2.19256181	−2.79330602
9	H	−0.89800063	2.16342975	2.72536418
10	H	0.26186351	4.89440210	0.86513287

Natural Internal Coordinates

Table S239: Symmetrized, unnormalized natural internal coordinates for 1,3−Butadiene.

1	$r_{1,2} + r_{3,4}$
2	$r_{1,2} - r_{3,4}$
3	$r_{2,3}$
4	$r_{1,5} + r_{1,6} + r_{4,9} + r_{4,10}$
5	$r_{1,5} + r_{1,6} - r_{4,9} - r_{4,10}$
6	$r_{1,5} - r_{1,6} + r_{4,9} - r_{4,10}$
7	$r_{1,5} - r_{1,6} - r_{4,9} + r_{4,10}$
8	$r_{2,7} + r_{3,8}$
9	$r_{2,7} - r_{3,8}$
10	$\phi_{1,2,3} + \phi_{2,3,4}$
11	$\phi_{1,2,3} - \phi_{2,3,4}$
12	$2\phi_{5,1,6} - \phi_{5,1,2} - \phi_{6,1,2} + 2\phi_{9,4,10} - \phi_{9,4,3} - \phi_{10,4,3}$
13	$2\phi_{5,1,6} - \phi_{5,1,2} - \phi_{6,1,2} - 2\phi_{9,4,10} + \phi_{9,4,3} + \phi_{10,4,3}$
14	$\phi_{5,1,2} - \phi_{6,1,2} + \phi_{9,4,3} - \phi_{10,4,3}$
15	$\phi_{5,1,2} - \phi_{6,1,2} - \phi_{9,4,3} + \phi_{10,4,3}$
16	$\phi_{7,2,1} - \phi_{7,2,3} + \phi_{8,3,2} - \phi_{8,3,4}$
17	$\phi_{7,2,1} - \phi_{7,2,3} - \phi_{8,3,2} + \phi_{8,3,4}$
18	$\tau_{1,2,3,4}$
19	$\tau_{5,1,2,3} + \tau_{6,1,2,3} + \tau_{9,4,3,2} + \tau_{10,4,3,2}$
20	$\tau_{5,1,2,3} + \tau_{6,1,2,3} - \tau_{9,4,3,2} - \tau_{10,4,3,2}$
21	$\gamma_{2,1,5,6} + \gamma_{3,4,9,10}$
22	$\gamma_{2,1,5,6} - \gamma_{3,4,9,10}$
23	$\gamma_{7,2,1,3} + \gamma_{8,3,2,4}$
24	$\gamma_{7,2,1,3} - \gamma_{8,3,2,4}$

Frequencies

Table S240: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	164.78	173.70	164.89	164.89	0
2	271.87	267.75	271.84	271.84	0
3	466.84	468.32	467.02	467.02	0
4	610.05	611.18	609.97	609.97	0
5	742.41	753.06	742.58	742.58	0
6	886.41	884.96	886.50	886.50	0
7	927.69	933.10	927.66	927.66	0
8	929.55	934.50	929.55	929.55	0
9	998.56	1010.88	998.70	998.70	0
10	1017.20	1032.35	1017.18	1017.18	0
11	1058.55	1056.31	1058.29	1058.29	0
12	1098.92	1095.22	1098.97	1098.97	0
13	1301.44	1299.57	1301.44	1301.44	0
14	1333.34	1330.93	1333.51	1333.51	0
15	1437.31	1435.30	1437.28	1437.28	0
16	1468.45	1465.89	1468.37	1468.37	0
17	1666.75	1656.11	1666.67	1666.67	0
18	1674.83	1666.91	1674.81	1674.81	0
19	3143.07	3159.11	3143.35	3143.35	0
20	3145.60	3161.35	3145.62	3145.62	0
21	3152.06	3169.91	3151.79	3151.79	0
22	3164.73	3181.75	3164.69	3164.69	0
23	3237.22	3258.54	3237.23	3237.23	0
24	3238.88	3260.07	3238.87	3238.87	0

S1.81 2-Butyne

Geometries

Table S241: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.00000000	1.14516096	0.00000000
2	C	−0.00000000	−1.14516096	0.00000000
3	C	−0.00000000	3.91831322	0.00000000
4	C	0.00000000	−3.91831322	−0.00000000
5	H	1.67000248	4.64975827	−0.96417659
6	H	−1.67000265	4.64975827	−0.96417629
7	H	0.00000018	4.64975827	1.92835287
8	H	−0.00000018	−4.64975827	1.92835287
9	H	1.67000266	−4.64975827	−0.96417628
10	H	−1.67000248	−4.64975827	−0.96417659

Natural Internal Coordinates

Table S242: Symmetrized, unnormalized natural internal coordinates for 2-Butyne.

1	$r_{1,2}$
2	$r_{1,3} + r_{2,4}$
3	$r_{1,3} - r_{2,4}$
4	$r_{3,6} + r_{3,5} + r_{3,7} + r_{4,10} + r_{4,8} + r_{4,9}$
5	$r_{3,6} + r_{3,5} + r_{3,7} - r_{4,10} - r_{4,8} - r_{4,9}$
6	$2r_{3,6} - r_{3,5} - r_{3,7} + 2r_{4,10} - r_{4,8} - r_{4,9}$
7	$2r_{3,6} - r_{3,5} - r_{3,7} - 2r_{4,10} + r_{4,8} + r_{4,9}$
8	$r_{3,5} - r_{3,7} + r_{4,8} - r_{4,9}$
9	$r_{3,5} - r_{3,7} - r_{4,8} + r_{4,9}$
10	$\phi_{6,3,1} + \phi_{5,3,1} + \phi_{7,3,1} - \phi_{5,3,7} - \phi_{6,3,5} - \phi_{6,3,7} + \phi_{10,4,2} + \phi_{8,4,2} + \phi_{9,4,2} - \phi_{8,4,9} - \phi_{10,4,8} - \phi_{10,4,9}$
11	$\phi_{6,3,1} + \phi_{5,3,1} + \phi_{7,3,1} - \phi_{5,3,7} - \phi_{6,3,5} - \phi_{6,3,7} - \phi_{10,4,2} - \phi_{8,4,2} - \phi_{9,4,2} + \phi_{8,4,9} + \phi_{10,4,8} + \phi_{10,4,9}$
12	$2\phi_{6,3,1} - \phi_{5,3,1} - \phi_{7,3,1} + 2\phi_{10,4,2} - \phi_{8,4,2} - \phi_{9,4,2}$
13	$2\phi_{6,3,1} - \phi_{5,3,1} - \phi_{7,3,1} - 2\phi_{10,4,2} + \phi_{8,4,2} + \phi_{9,4,2}$
14	$\phi_{5,3,1} - \phi_{7,3,1} + \phi_{8,4,2} - \phi_{9,4,2}$
15	$\phi_{5,3,1} - \phi_{7,3,1} - \phi_{8,4,2} + \phi_{9,4,2}$
16	$2\phi_{5,3,7} - \phi_{6,3,5} - \phi_{6,3,7} + 2\phi_{8,4,9} - \phi_{10,4,8} - \phi_{10,4,9}$
17	$2\phi_{5,3,7} - \phi_{6,3,5} - \phi_{6,3,7} - 2\phi_{8,4,9} + \phi_{10,4,8} + \phi_{10,4,9}$
18	$\phi_{6,3,5} - \phi_{6,3,7} + \phi_{10,4,8} - \phi_{10,4,9}$
19	$\phi_{6,3,5} - \phi_{6,3,7} - \phi_{10,4,8} + \phi_{10,4,9}$
20	$\tau_{5,3,4,9} + \tau_{6,3,4,10} + \tau_{7,3,4,8}$
21	$2\alpha^x_{6,3,1,2} - \alpha^x_{5,3,1,2} - \alpha^x_{7,3,1,2} + 2\alpha^x_{10,4,2,1} - \alpha^x_{8,4,2,1} - \alpha^x_{9,4,2,1}$
22	$2\alpha^x_{6,3,1,2} - \alpha^x_{5,3,1,2} - \alpha^x_{7,3,1,2} - 2\alpha^x_{10,4,2,1} + \alpha^x_{8,4,2,1} + \alpha^x_{9,4,2,1}$
23	$\alpha^x_{5,3,1,2} - \alpha^x_{7,3,1,2} + \alpha^x_{8,4,2,1} - \alpha^x_{9,4,2,1}$
24	$\alpha^x_{5,3,1,2} - \alpha^x_{7,3,1,2} - \alpha^x_{8,4,2,1} + \alpha^x_{9,4,2,1}$

Frequencies

Table S243: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	17.80	19.92	17.80	17.80	0
2	197.33	197.41	197.33	197.33	0
3	197.35	197.41	197.35	197.35	0
4	348.81	354.25	348.83	348.82	1
5	348.82	354.29	348.83	348.82	1
6	716.45	714.98	716.46	716.46	0
7	1046.03	1046.54	1046.04	1046.05	1
8	1046.03	1046.55	1046.04	1046.05	1
9	1067.92	1065.64	1067.94	1067.94	0
10	1067.92	1065.65	1067.94	1067.94	0
11	1167.27	1165.94	1167.28	1167.28	0
12	1415.87	1408.81	1415.86	1415.86	0
13	1420.58	1413.47	1420.60	1420.60	0
14	1492.10	1494.21	1492.09	1492.09	0
15	1492.12	1494.22	1492.11	1492.11	0
16	1493.14	1495.33	1493.14	1493.14	0
17	1493.16	1495.35	1493.15	1493.15	0
18	2324.07	2302.31	2324.07	2324.07	0
19	3042.19	3054.20	3042.11	3042.11	0
20	3042.56	3055.26	3042.49	3042.49	0
21	3113.29	3136.90	3113.29	3113.29	0
22	3113.29	3136.94	3113.35	3113.35	0
23	3113.85	3137.62	3113.84	3113.84	0
24	3113.85	3137.69	3113.93	3113.93	0

S1.82 Bicylcobutane

Geometries

Table S244: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.14477327	−0.00000001	0.59607608
2	X	−0.00000000	0.00000000	−0.59997220
3	C	2.14477327	0.00000001	0.59607608
4	C	0.00000000	−1.41792102	−0.59997220
5	C	−0.00000000	1.41792102	−0.59997220
6	H	0.00000005	−2.68099401	−2.19312163
7	H	−0.00000005	2.68099401	−2.19312163
8	H	−2.30669887	−0.00000001	2.64760291
9	H	−3.93191124	−0.00000001	−0.40809085
10	H	2.30669887	0.00000001	2.64760291
11	H	3.93191124	0.00000001	−0.40809085

Natural Internal Coordinates

Table S245: Symmetrized, unnormalized natural internal coordinates for Bicylcobutane.

1	$r_{4,5}$
2	$r_{4,1} + r_{4,3} + r_{5,1} + r_{5,3}$
3	$r_{4,1} + r_{4,3} - r_{5,1} - r_{5,3}$
4	$r_{4,1} - r_{4,3} + r_{5,1} - r_{5,3}$
5	$r_{4,1} - r_{4,3} - r_{5,1} + r_{5,3}$
6	$r_{4,6} + r_{5,7}$
7	$r_{4,6} - r_{5,7}$
8	$r_{1,8} + r_{1,9} + r_{3,10} + r_{3,11}$
9	$r_{1,8} + r_{1,9} - r_{3,10} - r_{3,11}$
10	$r_{1,8} - r_{1,9} + r_{3,10} - r_{3,11}$
11	$r_{1,8} - r_{1,9} - r_{3,10} + r_{3,11}$
12	$\phi_{6,4,1} - \phi_{6,4,3} + \phi_{7,5,1} - \phi_{7,5,3}$
13	$\phi_{6,4,1} - \phi_{6,4,3} - \phi_{7,5,1} + \phi_{7,5,3}$
14	$4\phi_{8,1,9} - \phi_{8,1,4} - \phi_{8,1,5} - \phi_{9,1,4} - \phi_{9,1,5} + 4\phi_{10,3,11} - \phi_{10,3,4} - \phi_{10,3,5} - \phi_{11,3,4} - \phi_{11,3,5}$
15	$4\phi_{8,1,9} - \phi_{8,1,4} - \phi_{8,1,5} - \phi_{9,1,4} - \phi_{9,1,5} - 4\phi_{10,3,11} + \phi_{10,3,4} + \phi_{10,3,5} + \phi_{11,3,4} + \phi_{11,3,5}$
16	$\phi_{8,1,4} + \phi_{8,1,5} - \phi_{9,1,4} - \phi_{9,1,5} + \phi_{10,3,4} + \phi_{10,3,5} - \phi_{11,3,4} - \phi_{11,3,5}$
17	$\phi_{8,1,4} + \phi_{8,1,5} - \phi_{9,1,4} - \phi_{9,1,5} - \phi_{10,3,4} - \phi_{10,3,5} + \phi_{11,3,4} + \phi_{11,3,5}$
18	$\phi_{8,1,4} - \phi_{8,1,5} + \phi_{9,1,4} - \phi_{9,1,5} + \phi_{10,3,4} - \phi_{10,3,5} + \phi_{11,3,4} - \phi_{11,3,5}$
19	$\phi_{8,1,4} - \phi_{8,1,5} + \phi_{9,1,4} - \phi_{9,1,5} - \phi_{10,3,4} + \phi_{10,3,5} - \phi_{11,3,4} + \phi_{11,3,5}$
20	$\phi_{8,1,4} - \phi_{8,1,5} - \phi_{9,1,4} + \phi_{9,1,5} + \phi_{10,3,4} - \phi_{10,3,5} - \phi_{11,3,4} + \phi_{11,3,5}$
21	$\phi_{8,1,4} - \phi_{8,1,5} - \phi_{9,1,4} + \phi_{9,1,5} - \phi_{10,3,4} + \phi_{10,3,5} + \phi_{11,3,4} - \phi_{11,3,5}$
22	$\tau_{3,4,5,1}$
23	$\gamma_{6,4,1,3} + \gamma_{7,5,3,1}$
24	$\gamma_{6,4,1,3} - \gamma_{7,5,3,1}$

Frequencies

Table S246: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	413.18	409.77	413.31	413.31	0
2	664.94	655.84	665.01	665.01	0
3	751.54	749.52	751.66	751.66	0
4	865.50	859.13	866.00	865.93	1
5	867.00	870.33	866.95	866.95	0
6	925.74	927.99	925.71	925.77	1
7	948.54	949.43	948.56	948.56	0
8	1003.90	997.61	1004.02	1004.02	0
9	1091.12	1082.06	1090.90	1090.90	0
10	1106.79	1106.54	1106.86	1106.86	0
11	1109.26	1107.92	1109.31	1109.31	0
12	1145.12	1137.90	1146.41	1146.41	0
13	1172.20	1163.71	1170.76	1170.76	0
14	1185.40	1177.59	1185.26	1185.26	0
15	1290.37	1287.31	1290.31	1290.31	0
16	1320.75	1312.78	1320.80	1320.80	0
17	1498.45	1496.02	1498.36	1498.36	0
18	1533.54	1531.42	1533.52	1533.52	0
19	3076.39	3091.77	3076.43	3076.43	0
20	3082.35	3099.87	3082.41	3082.41	0
21	3182.39	3203.94	3182.35	3182.35	0
22	3184.18	3206.66	3184.11	3184.11	0
23	3259.49	3276.75	3259.49	3259.49	0
24	3272.01	3288.97	3272.00	3272.00	0

S1.83 Cyclobutane

Geometries

Table S247: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	X	0.00000000	0.00000000	−1.56928405
2	C	−1.27271501	0.00000000	1.49443431
3	C	1.27271501	0.00000000	1.49443431
4	C	−1.48500902	−0.00000000	−1.37404402
5	C	1.48500902	0.00000000	−1.37404402
6	H	−2.68110230	−0.00000000	2.97904070
7	H	2.68110230	0.00000000	2.97904070
8	H	−2.34440091	1.68113477	−2.20625364
9	H	−2.34440091	−1.68113477	−2.20625364
10	H	2.34440091	−1.68113477	−2.20625364
11	H	2.34440091	1.68113477	−2.20625364

Natural Internal Coordinates

Table S248: Symmetrized, unnormalized natural internal coordinates for Cyclobutane.

1	$r_{2,3} + r_{4,5} + r_{2,4} + r_{3,5}$
2	$r_{2,3} + r_{4,5} - r_{2,4} - r_{3,5}$
3	$r_{2,3} - r_{4,5}$
4	$r_{2,4} - r_{3,5}$
5	$r_{2,6} + r_{3,7}$
6	$r_{2,6} - r_{3,7}$
7	$r_{4,8} + r_{4,9} + r_{5,10} + r_{5,11}$
8	$r_{4,8} + r_{4,9} - r_{5,10} - r_{5,11}$
9	$r_{4,8} - r_{4,9} + r_{5,10} - r_{5,11}$
10	$r_{4,8} - r_{4,9} - r_{5,10} + r_{5,11}$
11	$\phi_{2,3,5} - \phi_{3,5,4} + \phi_{5,4,2} - \phi_{4,2,3}$
12	$\phi_{6,2,3} - \phi_{6,2,4} + \phi_{7,3,2} - \phi_{7,3,5}$
13	$\phi_{6,2,3} - \phi_{6,2,4} - \phi_{7,3,2} + \phi_{7,3,5}$
14	$4\phi_{8,4,9} - \phi_{8,4,2} - \phi_{8,4,5} - \phi_{9,4,2} - \phi_{9,4,5} + 4\phi_{10,5,11} - \phi_{10,5,3} - \phi_{10,5,4} - \phi_{11,5,3} - \phi_{11,5,4}$
15	$4\phi_{8,4,9} - \phi_{8,4,2} - \phi_{8,4,5} - \phi_{9,4,2} - \phi_{9,4,5} - 4\phi_{10,5,11} + \phi_{10,5,3} + \phi_{10,5,4} + \phi_{11,5,3} + \phi_{11,5,4}$
16	$\phi_{8,4,2} + \phi_{8,4,5} - \phi_{9,4,2} - \phi_{9,4,5} + \phi_{10,5,3} + \phi_{10,5,4} - \phi_{11,5,3} - \phi_{11,5,4}$
17	$\phi_{8,4,2} + \phi_{8,4,5} - \phi_{9,4,2} - \phi_{9,4,5} - \phi_{10,5,3} - \phi_{10,5,4} + \phi_{11,5,3} + \phi_{11,5,4}$
18	$\phi_{8,4,2} - \phi_{8,4,5} + \phi_{9,4,2} - \phi_{9,4,5} + \phi_{10,5,3} - \phi_{10,5,4} + \phi_{11,5,3} - \phi_{11,5,4}$
19	$\phi_{8,4,2} - \phi_{8,4,5} + \phi_{9,4,2} - \phi_{9,4,5} - \phi_{10,5,3} + \phi_{10,5,4} - \phi_{11,5,3} + \phi_{11,5,4}$
20	$\phi_{8,4,2} - \phi_{8,4,5} - \phi_{9,4,2} + \phi_{9,4,5} + \phi_{10,5,3} - \phi_{10,5,4} - \phi_{11,5,3} + \phi_{11,5,4}$
21	$\phi_{8,4,2} - \phi_{8,4,5} - \phi_{9,4,2} + \phi_{9,4,5} - \phi_{10,5,3} + \phi_{10,5,4} + \phi_{11,5,3} - \phi_{11,5,4}$
22	$\tau_{2,3,5,4} - \tau_{3,5,4,2} + \tau_{5,4,2,3} - \tau_{4,2,3,5}$
23	$\gamma_{6,2,3,4} + \gamma_{7,3,5,2}$
24	$\gamma_{6,2,3,4} - \gamma_{7,3,5,2}$

Frequencies

Table S249: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	302.28	295.95	302.36	302.36	0
2	644.45	643.28	644.54	644.54	0
3	856.43	843.87	856.50	856.50	0
4	864.96	868.94	864.92	864.92	0
5	895.58	896.44	895.65	895.65	0
6	901.87	902.24	901.88	901.88	0
7	916.36	927.16	916.68	916.68	0
8	1002.35	1002.52	1002.36	1002.36	0
9	1029.84	1024.24	1029.74	1029.74	0
10	1099.90	1100.17	1099.88	1099.88	0
11	1134.81	1131.89	1135.05	1135.05	0
12	1176.53	1173.10	1176.36	1176.36	0
13	1219.17	1205.37	1218.92	1218.92	0
14	1232.80	1226.09	1233.04	1233.04	0
15	1323.48	1315.33	1323.27	1323.27	0
16	1470.95	1467.98	1470.90	1470.90	0
17	1493.88	1490.12	1493.91	1493.91	0
18	1604.92	1595.32	1604.88	1604.88	0
19	3052.18	3070.00	3052.17	3052.17	0
20	3058.21	3073.98	3058.21	3058.21	0
21	3097.01	3123.92	3097.00	3097.00	0
22	3111.42	3136.64	3111.42	3111.42	0
23	3181.94	3198.25	3181.94	3181.94	0
24	3213.66	3230.26	3213.66	3213.66	0

S1.84 Methylenecyclopropane

Geometries

Table S250: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.00000000	−0.00000000	−3.08775292
2	C	−0.00000000	−0.00000000	−0.58010955
3	C	1.45965770	−0.00000000	1.78621232
4	C	−1.45965770	0.00000000	1.78621232
5	H	1.75483322	−0.00000000	−4.14277197
6	H	−1.75483322	0.00000000	−4.14277197
7	H	2.39963805	1.72748285	2.35547647
8	H	2.39963805	−1.72748285	2.35547647
9	H	−2.39963805	−1.72748285	2.35547647
10	H	−2.39963805	1.72748285	2.35547647

Natural Internal Coordinates

Table S251: Symmetrized, unnormalized natural internal coordinates for Methylenecyclopropane.

1	$r_{1,2}$
2	$r_{3,4} + r_{2,3} + r_{2,4}$
3	$2r_{3,4} - r_{2,3} - r_{2,4}$
4	$r_{2,3} - r_{2,4}$
5	$r_{1,5} + r_{1,6}$
6	$r_{1,5} - r_{1,6}$
7	$r_{3,7} + r_{3,8} + r_{4,9} + r_{4,10}$
8	$r_{3,7} + r_{3,8} - r_{4,9} - r_{4,10}$
9	$r_{3,7} - r_{3,8} + r_{4,9} - r_{4,10}$
10	$r_{3,7} - r_{3,8} - r_{4,9} + r_{4,10}$
11	$\phi_{1,2,3} - \phi_{1,2,4}$
12	$2\phi_{5,1,6} - \phi_{5,1,2} - \phi_{6,1,2}$
13	$\phi_{5,1,2} - \phi_{6,1,2}$
14	$4\phi_{7,3,8} - \phi_{7,3,2} - \phi_{7,3,4} - \phi_{8,3,2} - \phi_{8,3,4} + 4\phi_{9,4,10} - \phi_{9,4,2} - \phi_{9,4,3} - \phi_{10,4,2} - \phi_{10,4,3}$
15	$4\phi_{7,3,8} - \phi_{7,3,2} - \phi_{7,3,4} - \phi_{8,3,2} - \phi_{8,3,4} - 4\phi_{9,4,10} + \phi_{9,4,2} + \phi_{9,4,3} + \phi_{10,4,2} + \phi_{10,4,3}$
16	$\phi_{7,3,2} + \phi_{7,3,4} - \phi_{8,3,2} - \phi_{8,3,4} + \phi_{9,4,2} + \phi_{9,4,3} - \phi_{10,4,2} - \phi_{10,4,3}$
17	$\phi_{7,3,2} + \phi_{7,3,4} - \phi_{8,3,2} - \phi_{8,3,4} - \phi_{9,4,2} - \phi_{9,4,3} + \phi_{10,4,2} + \phi_{10,4,3}$
18	$\phi_{7,3,2} - \phi_{7,3,4} + \phi_{8,3,2} - \phi_{8,3,4} + \phi_{9,4,2} - \phi_{9,4,3} + \phi_{10,4,2} - \phi_{10,4,3}$
19	$\phi_{7,3,2} - \phi_{7,3,4} + \phi_{8,3,2} - \phi_{8,3,4} - \phi_{9,4,2} + \phi_{9,4,3} - \phi_{10,4,2} + \phi_{10,4,3}$
20	$\phi_{7,3,2} - \phi_{7,3,4} - \phi_{8,3,2} + \phi_{8,3,4} + \phi_{9,4,2} - \phi_{9,4,3} - \phi_{10,4,2} + \phi_{10,4,3}$
21	$\phi_{7,3,2} - \phi_{7,3,4} - \phi_{8,3,2} + \phi_{8,3,4} - \phi_{9,4,2} + \phi_{9,4,3} + \phi_{10,4,2} - \phi_{10,4,3}$
22	$\tau_{5,1,2,3} + \tau_{5,1,2,4} + \tau_{6,1,2,3} + \tau_{6,1,2,4}$
23	$\gamma_{1,2,3,4}$
24	$\gamma_{2,1,5,6}$

Frequencies

Table S252: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	277.65	274.80	277.71	277.71	0
2	349.27	348.13	349.32	349.32	0
3	615.74	618.36	616.06	616.06	0
4	737.67	740.32	737.77	737.77	0
5	753.14	752.42	753.12	753.12	0
6	907.70	905.44	907.70	907.70	0
7	908.26	914.21	908.30	908.30	0
8	953.99	961.00	953.80	953.80	0
9	1041.01	1026.72	1041.24	1041.24	0
10	1055.32	1057.26	1055.09	1055.09	0
11	1072.85	1060.07	1072.96	1072.96	0
12	1097.51	1095.05	1097.51	1097.51	0
13	1147.39	1137.20	1147.30	1147.30	0
14	1171.65	1170.63	1171.64	1171.64	0
15	1450.53	1449.23	1450.58	1450.58	0
16	1455.65	1453.46	1455.61	1455.61	0
17	1493.03	1489.04	1493.01	1493.01	0
18	1819.35	1813.46	1819.30	1819.30	0
19	3126.92	3142.67	3126.92	3126.92	0
20	3130.33	3144.86	3130.32	3130.32	0
21	3139.91	3155.36	3139.89	3139.89	0
22	3207.30	3229.97	3207.33	3207.33	0
23	3219.40	3241.35	3219.40	3219.40	0
24	3225.95	3247.72	3225.95	3225.95	0

S1.85 Cyclobutane

Geometries

Table S253: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	1.44092954	1.44092961	0.27437752
2	C	−1.44092954	−1.44092961	0.27437752
3	C	−1.44092961	1.44092954	−0.27437752
4	C	1.44092961	−1.44092954	−0.27437752
5	H	2.65209587	2.65209594	−0.87006940
6	H	1.80908702	1.80908712	2.27117006
7	H	−2.65209587	−2.65209594	−0.87006940
8	H	−1.80908702	−1.80908712	2.27117006
9	H	−2.65209600	2.65209581	0.87006940
10	H	−1.80908711	1.80908703	−2.27117006
11	H	2.65209600	−2.65209581	0.87006940
12	H	1.80908711	−1.80908703	−2.27117006

Natural Internal Coordinates

Frequencies

Table S254: Symmetrized, unnormalized natural internal coordinates for Cyclobutane.

1	$r_{1,3} + r_{3,2} + r_{2,4} + r_{4,5}$
2	$r_{1,3} + r_{3,2} - r_{2,4} - r_{4,5}$
3	$r_{1,3} - r_{3,2} + r_{2,4} - r_{4,5}$
4	$r_{1,3} - r_{3,2} - r_{2,4} + r_{4,5}$
5	$r_{1,5} + r_{1,6} + r_{3,9} + r_{3,10} + r_{2,7} + r_{2,8} + r_{4,11} + r_{4,12}$
6	$r_{1,5} + r_{1,6} + r_{3,9} + r_{3,10} - r_{2,7} - r_{2,8} - r_{4,11} - r_{4,12}$
7	$r_{1,5} + r_{1,6} - r_{3,9} - r_{3,10} + r_{2,7} + r_{2,8} - r_{4,11} - r_{4,12}$
8	$r_{1,5} + r_{1,6} - r_{3,9} - r_{3,10} - r_{2,7} - r_{2,8} + r_{4,11} + r_{4,12}$
9	$r_{1,5} - r_{1,6} + r_{3,9} - r_{3,10} + r_{2,7} - r_{2,8} + r_{4,11} - r_{4,12}$
10	$r_{1,5} - r_{1,6} + r_{3,9} - r_{3,10} - r_{2,7} + r_{2,8} - r_{4,11} + r_{4,12}$
11	$r_{1,5} - r_{1,6} - r_{3,9} + r_{3,10} + r_{2,7} - r_{2,8} - r_{4,11} + r_{4,12}$
12	$r_{1,5} - r_{1,6} - r_{3,9} + r_{3,10} - r_{2,7} + r_{2,8} + r_{4,11} - r_{4,12}$
13	$\phi_{4,1,3} - \phi_{1,3,2} + \phi_{2,3,4} - \phi_{2,4,1}$
14	$4\phi_{5,1,6} - \phi_{5,1,3} - \phi_{5,1,4} - \phi_{6,1,3} - \phi_{6,1,4} + 4\phi_{9,3,10} - \phi_{9,3,1} - \phi_{9,3,2} - \phi_{10,3,1} - \phi_{10,3,2}$ $+4\phi_{7,2,8} - \phi_{7,2,3} - \phi_{7,2,4} - \phi_{8,2,3} - \phi_{8,2,4} + 4\phi_{11,4,12} - \phi_{11,4,2} - \phi_{11,4,1} - \phi_{12,4,2} - \phi_{12,4,1}$
15	$4\phi_{5,1,6} - \phi_{5,1,3} - \phi_{5,1,4} - \phi_{6,1,3} - \phi_{6,1,4} + 4\phi_{9,3,10} - \phi_{9,3,1} - \phi_{9,3,2} - \phi_{10,3,1} - \phi_{10,3,2}$ $-4\phi_{7,2,8} + \phi_{7,2,3} + \phi_{7,2,4} + \phi_{8,2,3} + \phi_{8,2,4} - 4\phi_{11,4,12} + \phi_{11,4,2} + \phi_{11,4,1} + \phi_{12,4,2} + \phi_{12,4,1}$
16	$4\phi_{5,1,6} - \phi_{5,1,3} - \phi_{5,1,4} - \phi_{6,1,3} - \phi_{6,1,4} - 4\phi_{9,3,10} + \phi_{9,3,1} + \phi_{9,3,2} + \phi_{10,3,1} + \phi_{10,3,2}$ $+4\phi_{7,2,8} - \phi_{7,2,3} - \phi_{7,2,4} - \phi_{8,2,3} - \phi_{8,2,4} - 4\phi_{11,4,12} + \phi_{11,4,2} + \phi_{11,4,1} + \phi_{12,4,2} + \phi_{12,4,1}$
17	$4\phi_{5,1,6} - \phi_{5,1,3} - \phi_{5,1,4} - \phi_{6,1,3} - \phi_{6,1,4} - 4\phi_{9,3,10} + \phi_{9,3,1} + \phi_{9,3,2} + \phi_{10,3,1} + \phi_{10,3,2}$ $-4\phi_{7,2,8} + \phi_{7,2,3} + \phi_{7,2,4} + \phi_{8,2,3} + \phi_{8,2,4} + 4\phi_{11,4,12} - \phi_{11,4,2} - \phi_{11,4,1} - \phi_{12,4,2} - \phi_{12,4,1}$
18	$\phi_{5,1,3} + \phi_{5,1,4} - \phi_{6,1,3} - \phi_{6,1,4} + \phi_{9,3,1} + \phi_{9,3,2} - \phi_{10,3,1} - \phi_{10,3,2} + \phi_{7,2,3} + \phi_{7,2,4}$ $-\phi_{8,2,3} - \phi_{8,2,4} + \phi_{11,4,2} + \phi_{11,4,1} - \phi_{12,4,2} - \phi_{12,4,1}$
19	$\phi_{5,1,3} + \phi_{5,1,4} - \phi_{6,1,3} - \phi_{6,1,4} + \phi_{9,3,1} + \phi_{9,3,2} - \phi_{10,3,1} - \phi_{10,3,2} - \phi_{7,2,3} - \phi_{7,2,4}$ $+\phi_{8,2,3} + \phi_{8,2,4} - \phi_{11,4,2} - \phi_{11,4,1} + \phi_{12,4,2} + \phi_{12,4,1}$
20	$\phi_{5,1,3} + \phi_{5,1,4} - \phi_{6,1,3} - \phi_{6,1,4} - \phi_{9,3,1} - \phi_{9,3,2} + \phi_{10,3,1} + \phi_{10,3,2} + \phi_{7,2,3} + \phi_{7,2,4}$ $-\phi_{8,2,3} - \phi_{8,2,4} - \phi_{11,4,2} - \phi_{11,4,1} + \phi_{12,4,2} + \phi_{12,4,1}$
21	$\phi_{5,1,3} + \phi_{5,1,4} - \phi_{6,1,3} - \phi_{6,1,4} - \phi_{9,3,1} - \phi_{9,3,2} + \phi_{10,3,1} + \phi_{10,3,2} - \phi_{7,2,3} - \phi_{7,2,4}$ $+\phi_{8,2,3} + \phi_{8,2,4} + \phi_{11,4,2} + \phi_{11,4,1} - \phi_{12,4,2} - \phi_{12,4,1}$
22	$\phi_{5,1,3} - \phi_{5,1,4} + \phi_{6,1,3} - \phi_{6,1,4} + \phi_{9,3,1} - \phi_{9,3,2} + \phi_{10,3,1} - \phi_{10,3,2} + \phi_{7,2,3} - \phi_{7,2,4}$ $+\phi_{8,2,3} - \phi_{8,2,4} + \phi_{11,4,2} - \phi_{11,4,1} + \phi_{12,4,2} - \phi_{12,4,1}$
23	$\phi_{5,1,3} - \phi_{5,1,4} + \phi_{6,1,3} - \phi_{6,1,4} + \phi_{9,3,1} - \phi_{9,3,2} + \phi_{10,3,1} - \phi_{10,3,2} - \phi_{7,2,3} + \phi_{7,2,4}$ $-\phi_{8,2,3} + \phi_{8,2,4} - \phi_{11,4,2} + \phi_{11,4,1} - \phi_{12,4,2} + \phi_{12,4,1}$
24	$\phi_{5,1,3} - \phi_{5,1,4} + \phi_{6,1,3} - \phi_{6,1,4} - \phi_{9,3,1} + \phi_{9,3,2} - \phi_{10,3,1} + \phi_{10,3,2} + \phi_{7,2,3} - \phi_{7,2,4}$ $+\phi_{8,2,3} - \phi_{8,2,4} - \phi_{11,4,2} + \phi_{11,4,1} - \phi_{12,4,2} + \phi_{12,4,1}$
25	$\phi_{5,1,3} - \phi_{5,1,4} + \phi_{6,1,3} - \phi_{6,1,4} - \phi_{9,3,1} + \phi_{9,3,2} - \phi_{10,3,1} + \phi_{10,3,2} - \phi_{7,2,3} + \phi_{7,2,4}$ $-\phi_{8,2,3} + \phi_{8,2,4} + \phi_{11,4,2} - \phi_{11,4,1} + \phi_{12,4,2} - \phi_{12,4,1}$
26	$\phi_{5,1,3} - \phi_{5,1,4} - \phi_{6,1,3} + \phi_{6,1,4} + \phi_{9,3,1} - \phi_{9,3,2} - \phi_{10,3,1} + \phi_{10,3,2} + \phi_{7,2,3} - \phi_{7,2,4}$ $-\phi_{8,2,3} + \phi_{8,2,4} + \phi_{11,4,2} - \phi_{11,4,1} - \phi_{12,4,2} + \phi_{12,4,1}$
27	$\phi_{5,1,3} - \phi_{5,1,4} - \phi_{6,1,3} + \phi_{6,1,4} + \phi_{9,3,1} - \phi_{9,3,2} - \phi_{10,3,1} + \phi_{10,3,2} - \phi_{7,2,3} + \phi_{7,2,4}$ $+\phi_{8,2,3} - \phi_{8,2,4} - \phi_{11,4,2} + \phi_{11,4,1} + \phi_{12,4,2} - \phi_{12,4,1}$
28	$\phi_{5,1,3} - \phi_{5,1,4} - \phi_{6,1,3} + \phi_{6,1,4} - \phi_{9,3,1} + \phi_{9,3,2} + \phi_{10,3,1} - \phi_{10,3,2} + \phi_{7,2,3} - \phi_{7,2,4}$ $-\phi_{8,2,3} + \phi_{8,2,4} - \phi_{11,4,2} + \phi_{11,4,1} + \phi_{12,4,2} - \phi_{12,4,1}$
29	$\phi_{5,1,3} - \phi_{5,1,4} - \phi_{6,1,3} + \phi_{6,1,4} - \phi_{9,3,1} + \phi_{9,3,2} + \phi_{10,3,1} - \phi_{10,3,2} - \phi_{7,2,3} + \phi_{7,2,4}$ $+\phi_{8,2,3} - \phi_{8,2,4} + \phi_{11,4,2} - \phi_{11,4,1} - \phi_{12,4,2} + \phi_{12,4,1}$
30	$\tau_{1,3,2,4} - \tau_{3,2,4,1} + \tau_{2,4,1,3} - \tau_{4,1,3,2}$

Table S255: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	230.64	224.33	230.65	230.65	0
2	620.26	615.47	620.48	620.48	0
3	755.06	753.12	755.09	755.09	0
4	755.06	755.55	755.15	755.15	0
5	909.40	904.46	909.35	909.35	0
6	916.90	919.07	916.93	916.93	0
7	916.90	919.24	916.94	916.94	0
8	942.94	946.24	943.02	943.02	0
9	958.26	960.15	958.27	958.27	0
10	1025.35	1025.14	1025.36	1025.36	0
11	1167.70	1166.92	1168.70	1168.70	0
12	1180.55	1173.25	1180.20	1180.20	0
13	1253.51	1250.66	1254.01	1254.01	0
14	1253.51	1252.80	1254.90	1254.90	0
15	1254.84	1255.04	1255.42	1255.42	0
16	1259.25	1257.25	1257.39	1257.39	0
17	1288.37	1278.43	1287.68	1287.68	0
18	1288.37	1282.44	1287.86	1287.86	0
19	1486.52	1484.22	1486.47	1486.47	0
20	1486.52	1485.56	1486.66	1486.66	0
21	1493.48	1492.94	1493.33	1493.33	0
22	1526.19	1524.61	1526.11	1526.11	0
23	3058.08	3075.29	3058.23	3058.23	0
24	3058.79	3075.72	3058.69	3058.69	0
25	3058.79	3075.89	3058.90	3058.90	0
26	3063.38	3078.66	3063.85	3063.85	0
27	3104.84	3128.89	3104.28	3104.28	0
28	3115.63	3141.23	3115.46	3115.46	0
29	3115.63	3141.39	3115.62	3115.62	0
30	3131.28	3155.62	3131.38	3131.38	0

S1.86 Isobutene

Geometries

Table S256: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.00000000	0.00000000	2.71646372
2	C	−0.00000000	0.00000000	0.18428612
3	C	0.00000001	2.41084481	−1.32906270
4	C	−0.00000001	−2.41084481	−1.32906270
5	H	0.00000000	1.75056828	3.77931442
6	H	−0.00000000	−1.75056828	3.77931442
7	H	0.00000001	4.07103635	−0.10803955
8	H	1.66120238	2.49911784	−2.55785943
9	H	−1.66120264	2.49911759	−2.55785931
10	H	−0.00000001	−4.07103635	−0.10803955
11	H	−1.66120238	−2.49911784	−2.55785943
12	H	1.66120264	−2.49911759	−2.55785931

Natural Internal Coordinates

Frequencies

Table S257: Symmetrized, unnormalized natural internal coordinates for Isobutene.

1	$r_{1,2}$
2	$r_{2,3} + r_{2,4}$
3	$r_{2,3} - r_{2,4}$
4	$r_{1,5} + r_{1,6}$
5	$r_{1,5} - r_{1,6}$
6	$r_{3,7} + r_{3,9} + r_{3,8} + r_{4,10} + r_{4,11} + r_{4,12}$
7	$r_{3,7} + r_{3,9} + r_{3,8} - r_{4,10} - r_{4,11} - r_{4,12}$
8	$2r_{3,7} - r_{3,9} - r_{3,8} + 2r_{4,10} - r_{4,11} - r_{4,12}$
9	$2r_{3,7} - r_{3,9} - r_{3,8} - 2r_{4,10} + r_{4,11} + r_{4,12}$
10	$r_{3,9} - r_{3,8} + r_{4,11} - r_{4,12}$
11	$r_{3,9} - r_{3,8} - r_{4,11} + r_{4,12}$
12	$2\phi_{3,2,4} - \phi_{3,2,1} - \phi_{4,2,1}$
13	$\phi_{3,2,1} - \phi_{4,2,1}$
14	$2\phi_{5,1,6} - \phi_{5,1,2} - \phi_{6,1,2}$
15	$\phi_{5,1,2} - \phi_{6,1,2}$
16	$\phi_{7,3,2} + \phi_{9,3,2} + \phi_{8,3,2} - \phi_{8,3,9} - \phi_{7,3,9} - \phi_{7,3,8} + \phi_{10,4,2} + \phi_{11,4,2} + \phi_{12,4,2} - \phi_{11,4,12} - \phi_{10,4,11} - \phi_{10,4,12}$
17	$\phi_{7,3,2} + \phi_{9,3,2} + \phi_{8,3,2} - \phi_{8,3,9} - \phi_{7,3,9} - \phi_{7,3,8} - \phi_{10,4,2} - \phi_{11,4,2} - \phi_{12,4,2} + \phi_{11,4,12} + \phi_{10,4,11} + \phi_{10,4,12}$
18	$2\phi_{7,3,2} - \phi_{9,3,2} - \phi_{8,3,2} + 2\phi_{10,4,2} - \phi_{11,4,2} - \phi_{12,4,2}$
19	$2\phi_{7,3,2} - \phi_{9,3,2} - \phi_{8,3,2} - 2\phi_{10,4,2} + \phi_{11,4,2} + \phi_{12,4,2}$
20	$\phi_{9,3,2} - \phi_{8,3,2} + \phi_{11,4,2} - \phi_{12,4,2}$
21	$\phi_{9,3,2} - \phi_{8,3,2} - \phi_{11,4,2} + \phi_{12,4,2}$
22	$2\phi_{8,3,9} - \phi_{7,3,9} - \phi_{7,3,8} + 2\phi_{11,4,12} - \phi_{10,4,11} - \phi_{10,4,12}$
23	$2\phi_{8,3,9} - \phi_{7,3,9} - \phi_{7,3,8} - 2\phi_{11,4,12} + \phi_{10,4,11} + \phi_{10,4,12}$
24	$\phi_{7,3,9} - \phi_{7,3,8} + \phi_{10,4,11} - \phi_{10,4,12}$
25	$\phi_{7,3,9} - \phi_{7,3,8} - \phi_{10,4,11} + \phi_{10,4,12}$
26	$\gamma_{1,2,3,4}$
27	$\gamma_{2,1,5,6}$
28	$\tau_{6,1,2,4} + \tau_{5,1,2,3}$
29	$\tau_{7,3,2,1} + \tau_{9,3,2,1} + \tau_{8,3,2,1} + \tau_{7,3,2,4} + \tau_{9,3,2,4} + \tau_{8,3,2,4} + \tau_{10,4,2,1} + \tau_{11,4,2,1} + \tau_{12,4,2,1} + \tau_{10,4,2,3} + \tau_{11,4,2,3} + \tau_{12,4,2,3}$
30	$\tau_{7,3,2,1} + \tau_{9,3,2,1} + \tau_{8,3,2,1} + \tau_{7,3,2,4} + \tau_{9,3,2,4} + \tau_{8,3,2,4} - \tau_{10,4,2,1} - \tau_{11,4,2,1} - \tau_{12,4,2,1} - \tau_{10,4,2,3} - \tau_{11,4,2,3} - \tau_{12,4,2,3}$

Table S258: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	161.02	164.97	161.05	161.05	0
2	206.05	210.54	206.05	206.05	0
3	368.49	367.10	368.49	368.49	0
4	424.36	424.74	424.33	424.33	0
5	426.37	425.38	426.42	426.42	0
6	702.97	710.00	703.22	703.22	0
7	818.69	817.06	818.71	818.71	0
8	905.25	910.55	905.26	905.26	0
9	963.57	959.99	963.59	963.59	0
10	988.25	985.44	988.26	988.26	0
11	1019.76	1021.15	1019.60	1019.60	0
12	1081.39	1078.02	1081.42	1081.42	0
13	1103.26	1099.42	1103.27	1103.27	0
14	1305.99	1297.70	1306.08	1306.08	0
15	1410.43	1402.46	1410.68	1410.68	0
16	1414.34	1402.74	1414.23	1414.23	0
17	1447.53	1445.17	1447.34	1447.34	0
18	1478.41	1478.95	1478.40	1478.40	0
19	1491.26	1491.93	1491.25	1491.25	0
20	1495.10	1496.74	1495.09	1495.09	0
21	1506.87	1507.53	1506.89	1506.89	0
22	1710.58	1703.28	1710.53	1710.53	0
23	3020.52	3033.41	3020.58	3020.58	0
24	3024.21	3036.24	3024.28	3024.28	0
25	3077.66	3103.20	3077.67	3077.67	0
26	3079.75	3104.29	3079.60	3079.60	0
27	3119.46	3143.27	3119.46	3119.46	0
28	3121.46	3144.54	3121.48	3121.48	0
29	3140.78	3155.98	3140.77	3140.77	0
30	3226.12	3248.14	3226.11	3226.11	0

S1.87 Pyrrole

Geometries

Table S259: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	N	0.00000000	0.00000000	−2.12001408
2	C	−0.00000000	2.12543160	−0.62715050
3	C	−0.00000000	−2.12543160	−0.62715050
4	C	−0.00000000	−1.34928425	1.86128652
5	C	0.00000000	1.34928425	1.86128652
6	H	0.00000000	3.98802740	−1.44697684
7	H	−0.00000000	−3.98802740	−1.44697684
8	H	0.00000000	−2.57429947	3.48805942
9	H	0.00000000	2.57429947	3.48805942
10	H	0.00000000	0.00000000	−4.01523914

Natural Internal Coordinates

Table S260: Symmetrized, unnormalized natural internal coordinates for Pyrrole.

1	$r_{1,10}$
2	$r_{4,5} + r_{2,5} + r_{3,4} + r_{1,2} + r_{1,3}$
3	$3r_{4,5} + r_{2,5} + r_{3,4} - 3r_{1,2} - 3r_{1,3}$
4	$2r_{2,5} - 2r_{3,4} + r_{1,2} - r_{1,3}$
5	$3r_{4,5} - 3r_{2,5} - 3r_{3,4} + r_{1,2} + r_{1,3}$
6	$r_{2,5} - r_{3,4} - 2r_{1,2} + 2r_{1,3}$
7	$r_{2,6} + r_{3,7}$
8	$r_{2,6} - r_{3,7}$
9	$r_{4,8} + r_{5,9}$
10	$r_{4,8} - r_{5,9}$
11	$\phi_{10,1,2} - \phi_{10,1,3}$
12	$3\phi_{2,1,3} - 3\phi_{1,2,5} - 3\phi_{1,3,4} + \phi_{2,5,4} + \phi_{3,4,5}$
13	$-\phi_{1,2,5} + \phi_{1,3,4} + 2\phi_{2,5,4} - 2\phi_{3,4,5}$
14	$\phi_{6,2,1} - \phi_{6,2,5} + \phi_{7,3,1} - \phi_{7,3,4}$
15	$\phi_{6,2,1} - \phi_{6,2,5} - \phi_{7,3,1} + \phi_{7,3,4}$
16	$\phi_{8,4,3} - \phi_{8,4,5} + \phi_{9,5,2} - \phi_{9,5,4}$
17	$\phi_{8,4,3} - \phi_{8,4,5} - \phi_{9,5,2} + \phi_{9,5,4}$
18	$3\tau_{2,5,4,3} + \tau_{4,3,1,2} + \tau_{3,1,2,5} - 3\tau_{5,4,3,1} - 3\tau_{1,2,5,4}$
19	$2\tau_{4,3,1,2} - 2\tau_{3,1,2,5} - \tau_{5,4,3,1} + \tau_{1,2,5,4}$
20	$\gamma_{10,1,3,2}$
21	$\gamma_{6,2,1,5} + \gamma_{7,3,4,1}$
22	$\gamma_{6,2,1,5} - \gamma_{7,3,4,1}$
23	$\gamma_{8,4,5,3} + \gamma_{9,5,2,4}$
24	$\gamma_{8,4,5,3} - \gamma_{9,5,2,4}$

Frequencies

Table S261: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	441.88	475.16	442.38	442.35	1
2	615.62	619.22	615.74	615.64	1
3	634.23	643.44	634.28	634.15	1
4	689.51	679.30	689.71	689.71	0
5	732.17	729.73	732.24	732.26	1
6	825.18	817.74	824.81	824.91	1
7	854.80	853.99	854.55	854.62	1
8	868.69	862.38	868.76	868.76	0
9	889.60	884.03	889.61	889.61	0
10	1032.96	1031.24	1033.01	1033.01	0
11	1065.99	1063.65	1066.05	1066.05	0
12	1094.84	1100.08	1095.54	1095.02	2
13	1159.51	1160.93	1160.11	1159.45	1
14	1167.23	1164.53	1167.19	1167.19	0
15	1310.43	1305.07	1310.64	1310.64	0
16	1423.16	1415.40	1423.60	1423.12	2
17	1465.60	1468.23	1465.76	1465.33	2
18	1508.88	1506.22	1508.04	1508.86	2
19	1572.76	1562.95	1571.83	1572.74	1
20	3246.88	3264.03	3246.85	3246.85	0
21	3257.75	3273.66	3257.77	3257.77	0
22	3272.13	3287.47	3272.10	3272.10	0
23	3279.10	3294.26	3279.12	3279.12	0
24	3700.44	3711.27	3700.44	3700.44	0

S1.88 Pyradine

Geometries

Table S262: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.00000000	0.00000000	−2.67675277
2	C	−0.00000000	2.26370499	−1.32678046
3	C	0.00000000	−2.26370499	−1.32678046
4	C	0.00000000	2.15769726	1.31051941
5	C	−0.00000000	−2.15769726	1.31051941
6	N	−0.00000000	−0.00000000	2.64318946
7	H	−0.00000000	0.00000000	−4.72321779
8	H	0.00000000	4.07198424	−2.28221500
9	H	−0.00000000	−4.07198424	−2.28221500
10	H	0.00000000	3.88716851	2.41055970
11	H	−0.00000000	−3.88716851	2.41055970

Natural Internal Coordinates

Table S263: Symmetrized, unnormalized natural internal coordinates for Pyradine.

1	$r_{5,3} + r_{3,1} + r_{1,2} + r_{2,4} + r_{4,6} + r_{6,5}$
2	$r_{5,3} - r_{3,1} + r_{1,2} - r_{2,4} + r_{4,6} - r_{6,5}$
3	$2r_{5,3} - r_{3,1} - r_{1,2} + 2r_{2,4} - r_{4,6} - r_{6,5}$
4	$2r_{5,3} + r_{3,1} - r_{1,2} - 2r_{2,4} - r_{4,6} + r_{6,5}$
5	$r_{3,1} + r_{1,2} - r_{4,6} - r_{6,5}$
6	$r_{3,1} - r_{1,2} + r_{4,6} - r_{6,5}$
7	$r_{5,11} + r_{4,10}$
8	$r_{5,11} - r_{4,10}$
9	$r_{3,9} + r_{2,8}$
10	$r_{3,9} - r_{2,8}$
11	$r_{1,7}$
12	$\phi_{5,3,1} - \phi_{3,1,2} + \phi_{1,2,4} - \phi_{2,4,6} + \phi_{4,6,5} - \phi_{6,5,3}$
13	$2\phi_{5,3,1} - \phi_{3,1,2} - \phi_{1,2,4} + 2\phi_{2,4,6} - \phi_{4,6,5} - \phi_{6,5,3}$
14	$\phi_{3,1,2} - \phi_{1,2,4} + \phi_{4,6,5} - \phi_{6,5,3}$
15	$\phi_{11,5,6} - \phi_{11,5,3} + \phi_{10,4,6} - \phi_{10,4,2}$
16	$\phi_{11,5,6} - \phi_{11,5,3} - \phi_{10,4,6} + \phi_{10,4,2}$
17	$\phi_{9,3,5} - \phi_{9,3,1} + \phi_{8,2,1} - \phi_{8,2,4}$
18	$\phi_{9,3,5} - \phi_{9,3,1} - \phi_{8,2,1} + \phi_{8,2,4}$
19	$\phi_{7,1,2} - \phi_{7,1,3}$
20	$\tau_{5,3,1,2} - \tau_{3,1,2,4} + \tau_{1,2,4,6} - \tau_{2,4,6,5} + \tau_{4,6,5,3} - \tau_{6,5,3,1}$
21	$\tau_{5,3,1,2} - \tau_{1,2,4,6} + \tau_{2,4,6,5} - \tau_{6,5,3,1}$
22	$-\tau_{5,3,1,2} + 2\tau_{3,1,2,4} - \tau_{1,2,4,6} - \tau_{2,4,6,5} + 2\tau_{4,6,5,3} - \tau_{6,5,3,1}$
23	$\gamma_{11,5,3,6} + \gamma_{10,4,6,2}$
24	$\gamma_{11,5,3,6} - \gamma_{10,4,6,2}$
25	$\gamma_{9,3,1,5} + \gamma_{8,2,4,1}$
26	$\gamma_{9,3,1,5} - \gamma_{8,2,4,1}$
27	$\gamma_{7,1,2,3}$

Frequencies

Table S264: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	378.44	380.58	378.45	378.45	0
2	409.22	410.92	409.23	409.23	0
3	603.31	598.28	603.33	603.33	0
4	656.98	653.89	656.99	656.99	0
5	711.89	721.89	712.25	712.25	0
6	753.17	755.51	753.19	752.87	1
7	890.79	900.98	891.35	891.35	0
8	953.64	949.47	953.76	953.76	0
9	995.11	993.06	994.60	994.60	0
10	996.87	1001.37	996.46	996.71	1
11	1001.24	1001.53	1001.41	1001.41	0
12	1043.14	1040.70	1043.14	1043.14	0
13	1071.35	1070.09	1071.42	1071.42	0
14	1087.86	1085.89	1087.79	1087.79	0
15	1158.82	1164.77	1163.69	1160.84	1
16	1236.72	1236.85	1236.80	1236.80	0
17	1266.95	1373.79	1294.55	1267.51	1
18	1379.21	1387.70	1356.60	1376.98	3
19	1464.66	1462.98	1458.21	1465.11	1
20	1510.12	1499.80	1510.22	1510.22	0
21	1618.43	1607.59	1617.95	1617.95	0
22	1630.29	1615.76	1630.11	1630.11	0
23	3168.42	3184.23	3168.42	3168.42	0
24	3169.83	3185.67	3169.86	3169.86	0
25	3187.57	3203.93	3187.62	3187.62	0
26	3204.49	3221.97	3204.47	3204.47	0
27	3212.85	3228.80	3212.79	3212.79	0

S1.89 Sulfur Dioxide

Geometries

Table S265: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	S	0.00000000	0.00000000	0.68492417
2	O	0.00000000	−2.35105565	−0.68454394
3	O	0.00000000	2.35105565	−0.68454394

Natural Internal Coordinates

Table S266: Symmetrized, unnormalized natural internal coordinates for Sulfur Dioxide.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$\phi_{2,1,3}$

Frequencies

Table S267: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	519.25	515.52	519.27	519.27	0
2	1169.10	1164.04	1169.09	1169.09	0
3	1388.91	1395.57	1388.91	1388.91	0

S1.90 Hydrogen Sulfide

Geometries

Table S268: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	S	0.00000000	0.00000000	0.10390451
2	H	0.00000000	−1.82244988	−1.64812453
3	H	0.00000000	1.82244988	−1.64812453

Natural Internal Coordinates

Table S269: Symmetrized, unnormalized natural internal coordinates for Hydrogen Sulfide.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$\phi_{2,1,3}$

Frequencies

Table S270: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1209.65	1208.58	1209.65	1209.65	0
2	2722.07	2745.91	2722.08	2722.08	0
3	2736.76	2764.62	2736.76	2736.76	0

S1.91 Carbonyl Sulfide

Geometries

Table S271: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	S	−0.00000000	−0.00000000	1.97114916
2	C	0.00000000	−0.00000000	−0.99620667
3	X	1.88972652	−0.00000000	−0.99620667
4	O	0.00000000	0.00000000	−3.19271727
5	X	0.00000000	1.88972652	−0.99620667

Natural Internal Coordinates

Table S272: Symmetrized, unnormalized natural internal coordinates for Carbonyl Sulfide.

1	$r_{1,2}$
2	$r_{2,4}$
3	$\theta_{1,2,4,3}$
4	$\theta_{1,2,4,5}$

Frequencies

Table S273: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	523.09	525.27	523.09	523.09	0
2	523.09	525.29	523.09	523.09	0
3	869.09	879.34	869.41	869.09	1
4	2091.68	2124.84	2091.55	2091.68	1

S1.92 Thiirane

Geometries

Table S274: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	S	−0.00000000	0.00000000	−1.50417512
2	C	−1.40520404	0.00000000	1.64054308
3	C	1.40520404	0.00000000	1.64054308
4	H	−2.36308175	1.72968642	2.16271655
5	H	−2.36308175	−1.72968642	2.16271655
6	H	2.36308175	−1.72968642	2.16271655
7	H	2.36308175	1.72968642	2.16271655

Natural Internal Coordinates

Table S275: Symmetrized, unnormalized natural internal coordinates for Thiirane.

1	$r_{1,2} + r_{1,3} + r_{2,3}$
2	$r_{1,2} - r_{1,3}$
3	$-r_{1,2} - r_{1,3} + 2r_{2,3}$
4	$r_{2,4} + r_{2,5} + r_{3,6} + r_{3,7}$
5	$r_{2,4} + r_{2,5} - r_{3,6} - r_{3,7}$
6	$r_{2,4} - r_{2,5} + r_{3,6} - r_{3,7}$
7	$r_{2,4} - r_{2,5} - r_{3,6} + r_{3,7}$
8	$4\phi_{4,2,5} + 4\phi_{6,3,7} - \phi_{1,2,4} - \phi_{3,2,4} - \phi_{1,2,5} - \phi_{3,2,5} - \phi_{1,3,6} - \phi_{2,3,6} - \phi_{1,3,7} - \phi_{2,3,7}$
9	$4\phi_{4,2,5} - 4\phi_{6,3,7} - \phi_{1,2,4} - \phi_{3,2,4} - \phi_{1,2,5} - \phi_{3,2,5} + \phi_{1,3,6} + \phi_{2,3,6} + \phi_{1,3,7} + \phi_{2,3,7}$
10	$\phi_{1,2,4} + \phi_{3,2,4} - \phi_{1,2,5} - \phi_{3,2,5} + \phi_{1,3,6} + \phi_{2,3,6} - \phi_{1,3,7} - \phi_{2,3,7}$
11	$\phi_{1,2,4} + \phi_{3,2,4} - \phi_{1,2,5} - \phi_{3,2,5} - \phi_{1,3,6} - \phi_{2,3,6} + \phi_{1,3,7} + \phi_{2,3,7}$
12	$\phi_{1,2,4} - \phi_{3,2,4} + \phi_{1,2,5} - \phi_{3,2,5} + \phi_{1,3,6} - \phi_{2,3,6} + \phi_{1,3,7} - \phi_{2,3,7}$
13	$\phi_{1,2,4} - \phi_{3,2,4} + \phi_{1,2,5} - \phi_{3,2,5} - \phi_{1,3,6} + \phi_{2,3,6} - \phi_{1,3,7} + \phi_{2,3,7}$
14	$\phi_{1,2,4} - \phi_{3,2,4} - \phi_{1,2,5} + \phi_{3,2,5} + \phi_{1,3,6} - \phi_{2,3,6} - \phi_{1,3,7} + \phi_{2,3,7}$
15	$\phi_{1,2,4} - \phi_{3,2,4} - \phi_{1,2,5} + \phi_{3,2,5} - \phi_{1,3,6} + \phi_{2,3,6} + \phi_{1,3,7} - \phi_{2,3,7}$

Frequencies

Table S276: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	640.95	643.30	640.97	640.97	0
2	679.82	687.93	679.84	679.84	0
3	833.27	834.17	833.28	833.28	0
4	904.36	909.91	904.39	904.39	0
5	962.71	962.53	962.70	962.70	0
6	1048.53	1045.38	1048.62	1048.62	0
7	1073.84	1065.63	1073.84	1073.84	0
8	1139.93	1139.42	1139.91	1139.91	0
9	1198.60	1195.98	1198.58	1198.58	0
10	1477.31	1477.33	1477.31	1477.31	0
11	1502.57	1499.43	1502.52	1502.52	0
12	3139.04	3154.95	3139.05	3139.05	0
13	3142.69	3157.09	3142.68	3142.68	0
14	3224.34	3246.37	3224.34	3224.34	0
15	3238.02	3259.14	3238.01	3238.01	0

S1.93 Dimethyl Sulfide

Geometries

Table S277: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	S	−0.00000000	−0.00000000	1.12636820
2	C	−0.00000000	−2.58599764	−1.11200562
3	C	−0.00000000	2.58599764	−1.11200562
4	H	0.00000000	−4.33900174	−0.03161213
5	H	1.68595712	−2.53090490	−2.29714225
6	H	−1.68595712	−2.53090490	−2.29714225
7	H	−0.00000000	4.33900174	−0.03161213
8	H	−1.68595712	2.53090490	−2.29714225
9	H	1.68595712	2.53090490	−2.29714225

Natural Internal Coordinates

Table S278: Symmetrized, unnormalized natural internal coordinates for Dimethyl Sulfide.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$r_{2,4} + r_{2,5} + r_{2,6} + r_{3,7} + r_{3,8} + r_{3,9}$
4	$r_{2,4} + r_{2,5} + r_{2,6} - r_{3,7} - r_{3,8} - r_{3,9}$
5	$2r_{2,4} - r_{2,5} - r_{2,6} + 2r_{3,7} - r_{3,8} - r_{3,9}$
6	$2r_{2,4} - r_{2,5} - r_{2,6} - 2r_{3,7} + r_{3,8} + r_{3,9}$
7	$r_{2,5} - r_{2,6} + r_{3,8} - r_{3,9}$
8	$r_{2,5} - r_{2,6} - r_{3,8} + r_{3,9}$
9	$\phi_{2,1,3}$
10	$\phi_{4,2,1} + \phi_{5,2,1} + \phi_{6,2,1} - \phi_{5,2,6} - \phi_{4,2,5} - \phi_{4,2,6} + \phi_{7,3,1} + \phi_{8,3,1} + \phi_{9,3,1} - \phi_{8,3,9} - \phi_{7,3,8} - \phi_{7,3,9}$
11	$\phi_{4,2,1} + \phi_{5,2,1} + \phi_{6,2,1} - \phi_{5,2,6} - \phi_{4,2,5} - \phi_{4,2,6} - \phi_{7,3,1} - \phi_{8,3,1} - \phi_{9,3,1} + \phi_{8,3,9} + \phi_{7,3,8} + \phi_{7,3,9}$
12	$2\phi_{4,2,1} - \phi_{5,2,1} - \phi_{6,2,1} + 2\phi_{7,3,1} - \phi_{8,3,1} - \phi_{9,3,1}$
13	$2\phi_{4,2,1} - \phi_{5,2,1} - \phi_{6,2,1} - 2\phi_{7,3,1} + \phi_{8,3,1} + \phi_{9,3,1}$
14	$\phi_{5,2,1} - \phi_{6,2,1} + \phi_{8,3,1} - \phi_{9,3,1}$
15	$\phi_{5,2,1} - \phi_{6,2,1} - \phi_{8,3,1} + \phi_{9,3,1}$
16	$2\phi_{5,2,6} - \phi_{4,2,5} - \phi_{4,2,6} + 2\phi_{8,3,9} - \phi_{7,3,8} - \phi_{7,3,9}$
17	$2\phi_{5,2,6} - \phi_{4,2,5} - \phi_{4,2,6} - 2\phi_{8,3,9} + \phi_{7,3,8} + \phi_{7,3,9}$
18	$\phi_{4,2,5} - \phi_{4,2,6} + \phi_{7,3,8} - \phi_{7,3,9}$
19	$\phi_{4,2,5} - \phi_{4,2,6} - \phi_{7,3,8} + \phi_{7,3,9}$
20	$\tau_{4,2,1,3} + \tau_{5,2,1,3} + \tau_{6,2,1,3} + \tau_{7,3,2,1} + \tau_{8,3,2,1} + \tau_{9,3,2,1}$
21	$\tau_{4,2,1,3} + \tau_{5,2,1,3} + \tau_{6,2,1,3} - \tau_{7,3,2,1} - \tau_{8,3,2,1} - \tau_{9,3,2,1}$

Frequencies

Table S279: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	174.71	179.11	174.72	174.72	1
2	186.14	189.92	186.15	186.14	1
3	262.33	259.82	262.34	262.34	0
4	708.45	709.73	708.46	708.46	0
5	762.13	763.02	762.16	762.16	0
6	911.61	913.67	911.62	911.62	0
7	953.94	956.03	953.96	953.96	1
8	990.25	991.78	990.27	990.27	1
9	1050.49	1049.35	1050.52	1050.52	0
10	1343.74	1338.40	1343.73	1343.73	0
11	1368.12	1362.90	1368.12	1368.12	0
12	1469.60	1472.07	1469.59	1469.59	0
13	1478.62	1481.45	1478.61	1478.61	0
14	1486.48	1488.71	1486.47	1486.47	0
15	1494.03	1496.77	1494.01	1494.01	0
16	3034.90	3046.89	3034.90	3034.90	0
17	3038.72	3052.17	3038.73	3038.73	0
18	3113.45	3136.84	3113.45	3113.45	0
19	3120.93	3145.50	3120.93	3120.93	0
20	3138.71	3161.79	3138.70	3138.70	0
21	3139.38	3163.12	3139.36	3139.36	0

S1.94 Thioethanol

Geometries

Table S280: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	S	−1.94413062	0.32139246	0.00000000
2	C	1.11416252	−1.29182836	0.00000000
3	C	3.20028202	0.69835977	0.00000000
4	H	−3.38597804	−1.75712103	−0.00000000
5	H	1.25064962	−2.48270008	1.67469531
6	H	1.25064962	−2.48270008	−1.67469531
7	H	5.05305419	−0.20846079	0.00000000
8	H	3.06777149	1.90075538	1.67101309
9	H	3.06777149	1.90075538	−1.67101309

Natural Internal Coordinates

Table S281: Symmetrized, unnormalized natural internal coordinates for Thioethanol.

1	$r_{3,2}$
2	$r_{3,1}$
3	$r_{1,4}$
4	$r_{3,7} + r_{3,8} + r_{3,9}$
5	$2r_{3,7} - r_{3,8} - r_{3,9}$
6	$r_{3,8} - r_{3,9}$
7	$r_{2,5} + r_{2,6}$
8	$r_{2,5} - r_{2,6}$
9	$\phi_{3,2,1}$
10	$\phi_{2,1,4}$
11	$\phi_{7,3,2} + \phi_{8,3,2} + \phi_{9,3,2} - \phi_{8,3,9} - \phi_{7,3,8} - \phi_{7,3,9}$
12	$2\phi_{7,3,2} - \phi_{8,3,2} - \phi_{9,3,2}$
13	$\phi_{8,3,2} - \phi_{9,3,2}$
14	$2\phi_{8,3,9} - \phi_{7,3,8} - \phi_{7,3,9}$
15	$\phi_{7,3,8} - \phi_{7,3,9}$
16	$2\phi_{5,2,6} - \phi_{5,2,3} - \phi_{5,2,1} - \phi_{6,2,3} - \phi_{6,2,1}$
17	$\phi_{5,2,3} + \phi_{5,2,1} - \phi_{6,2,3} - \phi_{6,2,1}$
18	$\phi_{5,2,3} - \phi_{5,2,1} + \phi_{6,2,3} - \phi_{6,2,1}$
19	$\phi_{5,2,3} - \phi_{5,2,1} - \phi_{6,2,3} + \phi_{6,2,1}$
20	$\tau_{7,3,2,1} + \tau_{8,3,2,1} + \tau_{9,3,2,1}$
21	$\tau_{3,2,1,4}$

Frequencies

Table S282: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	177.40	180.91	177.41	177.41	0
2	252.94	257.21	252.94	252.94	0
3	301.94	302.94	302.01	302.01	0
4	687.08	690.71	687.12	687.12	0
5	789.89	790.16	789.89	789.89	0
6	863.95	860.49	863.94	863.94	0
7	1001.77	1000.80	1001.81	1001.81	0
8	1046.64	1047.51	1046.70	1046.70	0
9	1116.09	1114.46	1116.11	1116.11	0
10	1271.87	1271.30	1271.84	1271.84	0
11	1302.20	1295.28	1302.20	1302.20	0
12	1413.61	1405.61	1413.60	1413.60	0
13	1496.40	1496.44	1496.43	1496.43	0
14	1500.20	1502.56	1500.19	1500.19	0
15	1510.01	1512.18	1509.94	1509.94	0
16	2709.33	2735.18	2709.33	2709.33	0
17	3040.58	3052.88	3040.63	3040.63	0
18	3068.16	3084.44	3068.12	3068.12	0
19	3107.06	3132.13	3107.08	3107.08	0
20	3118.15	3142.84	3118.13	3118.13	0
21	3129.76	3153.76	3129.77	3129.77	0

S1.95 Dimethyl Sulfoxide

Geometries

Table S283: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	S	−0.79551986	−0.28979430	−0.00000000
2	O	0.70249582	−2.66735948	−0.00000000
3	C	0.42748211	1.65658768	2.53093481
4	C	0.42748211	1.65658768	−2.53093481
5	H	−0.13039689	0.76873497	4.30213494
6	H	−0.39926512	3.54058228	2.39620963
7	H	2.48361526	1.72913497	2.39620963
8	H	−0.13039689	0.76873497	−4.30213494
9	H	2.48361526	1.72913497	−2.39620963
10	H	−0.39926512	3.54058228	−2.39620963

Natural Internal Coordinates

Table S284: Symmetrized, unnormalized natural internal coordinates for Dimethyl Sulfoxide.

1	$r_{1,2}$
2	$r_{1,3} + r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$r_{3,5} + r_{3,6} + r_{3,7} + r_{4,8} + r_{4,9} + r_{4,10}$
5	$r_{3,5} + r_{3,6} + r_{3,7} - r_{4,8} - r_{4,9} - r_{4,10}$
6	$2r_{3,5} - r_{3,6} - r_{3,7} + 2r_{4,8} - r_{4,9} - r_{4,10}$
7	$2r_{3,5} - r_{3,6} - r_{3,7} - 2r_{4,8} + r_{4,9} + r_{4,10}$
8	$r_{3,6} - r_{3,7} + r_{4,9} - r_{4,10}$
9	$r_{3,6} - r_{3,7} - r_{4,9} + r_{4,10}$
10	$2\phi_{3,1,4} - \phi_{2,1,3} - \phi_{2,1,4}$
11	$\phi_{2,1,3} - \phi_{2,1,4}$
12	$\phi_{5,3,1} + \phi_{6,3,1} + \phi_{7,3,1} - \phi_{6,3,7} - \phi_{5,3,6} - \phi_{5,3,7} + \phi_{8,4,1} + \phi_{9,4,1} + \phi_{10,4,1} - \phi_{9,4,10} - \phi_{8,4,9} - \phi_{8,4,10}$
13	$\phi_{5,3,1} + \phi_{6,3,1} + \phi_{7,3,1} - \phi_{6,3,7} - \phi_{5,3,6} - \phi_{5,3,7} - \phi_{8,4,1} - \phi_{9,4,1} - \phi_{10,4,1} + \phi_{9,4,10} + \phi_{8,4,9} + \phi_{8,4,10}$
14	$2\phi_{5,3,1} - \phi_{6,3,1} - \phi_{7,3,1} + 2\phi_{8,4,1} - \phi_{9,4,1} - \phi_{10,4,1}$
15	$2\phi_{5,3,1} - \phi_{6,3,1} - \phi_{7,3,1} - 2\phi_{8,4,1} + \phi_{9,4,1} + \phi_{10,4,1}$
16	$\phi_{6,3,1} - \phi_{7,3,1} + \phi_{9,4,1} - \phi_{10,4,1}$
17	$\phi_{6,3,1} - \phi_{7,3,1} - \phi_{9,4,1} + \phi_{10,4,1}$
18	$2\phi_{6,3,7} - \phi_{5,3,6} - \phi_{5,3,7} + 2\phi_{9,4,10} - \phi_{8,4,9} - \phi_{8,4,10}$
19	$2\phi_{6,3,7} - \phi_{5,3,6} - \phi_{5,3,7} - 2\phi_{9,4,10} + \phi_{8,4,9} + \phi_{8,4,10}$
20	$\phi_{5,3,6} - \phi_{5,3,7} + \phi_{8,4,9} - \phi_{8,4,10}$
21	$\phi_{5,3,6} - \phi_{5,3,7} - \phi_{8,4,9} + \phi_{8,4,10}$
22	$\tau_{5,3,1,4} + \tau_{6,3,1,4} + \tau_{7,3,1,4} + \tau_{8,4,1,3} + \tau_{9,4,1,3} + \tau_{10,4,1,3}$
23	$\tau_{5,3,1,4} + \tau_{6,3,1,4} + \tau_{7,3,1,4} - \tau_{8,4,1,3} - \tau_{9,4,1,3} - \tau_{10,4,1,3}$
24	$\gamma_{2,1,3,4}$

Frequencies

Table S285: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	179.27	181.45	179.49	179.33	1
2	238.88	242.22	239.20	239.20	0
3	290.44	290.22	290.26	290.26	0
4	314.56	314.81	314.55	314.55	0
5	368.56	368.28	368.57	368.56	1
6	669.27	670.43	669.35	669.35	0
7	693.75	691.80	693.77	693.77	0
8	886.07	883.37	886.08	886.11	1
9	924.12	922.91	924.13	924.13	0
10	955.70	954.59	955.88	955.74	2
11	1024.64	1020.25	1024.65	1024.65	0
12	1134.06	1153.60	1133.92	1134.04	1
13	1315.06	1307.53	1315.07	1315.07	0
14	1337.37	1329.52	1337.37	1337.37	0
15	1446.99	1447.15	1446.96	1446.96	0
16	1460.90	1462.20	1460.89	1460.89	0
17	1463.94	1466.37	1463.91	1463.91	0
18	1482.86	1485.95	1482.85	1482.85	0
19	3039.48	3051.27	3039.49	3039.49	0
20	3041.26	3052.17	3041.22	3041.22	0
21	3141.10	3163.13	3141.05	3141.05	0
22	3145.65	3167.13	3145.67	3145.67	0
23	3152.29	3174.30	3152.29	3152.29	0
24	3153.52	3175.30	3153.59	3153.59	0

S1.96 Thiopene

Geometries

Table S286: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	X	0.00000000	0.00000000	−0.28192818
2	S	0.00000000	0.00000000	−2.17165471
3	C	0.00000000	2.33762887	0.09177468
4	C	−0.00000000	−2.33762887	0.09177468
5	C	−0.00000000	−1.35030259	2.48887766
6	C	0.00000000	1.35030259	2.48887766
7	H	0.00000000	4.29941975	−0.45873605
8	H	−0.00000000	−4.29941975	−0.45873605
9	H	−0.00000000	−2.49824704	4.17795384
10	H	0.00000000	2.49824704	4.17795384

Natural Internal Coordinates

Table S287: Symmetrized, unnormalized natural internal coordinates for Thiopene.

1	$r_{5,6} + r_{3,6} + r_{4,5} + r_{2,3} + r_{2,4}$
2	$3r_{5,6} + r_{3,6} + r_{4,5} - 3r_{2,3} - 3r_{2,4}$
3	$2r_{3,6} - 2r_{4,5} + r_{2,3} - r_{2,4}$
4	$3r_{5,6} - 3r_{3,6} - 3r_{4,5} + r_{2,3} + r_{2,4}$
5	$r_{3,6} - r_{4,5} - 2r_{2,3} + 2r_{2,4}$
6	$r_{3,7} + r_{4,8}$
7	$r_{3,7} - r_{4,8}$
8	$r_{6,10} + r_{5,9}$
9	$r_{6,10} - r_{5,9}$
10	$3\phi_{3,2,4} - 3\phi_{2,3,6} - 3\phi_{2,4,5} + \phi_{3,6,5} + \phi_{4,5,6}$
11	$-\phi_{2,3,6} + \phi_{2,4,5} + 2\phi_{3,6,5} - 2\phi_{4,5,6}$
12	$\phi_{7,3,2} - \phi_{7,3,6} + \phi_{8,4,5} - \phi_{8,4,2}$
13	$\phi_{7,3,2} - \phi_{7,3,6} - \phi_{8,4,5} + \phi_{8,4,2}$
14	$\phi_{10,6,3} - \phi_{10,6,5} + \phi_{9,5,6} - \phi_{9,5,4}$
15	$\phi_{10,6,3} - \phi_{10,6,5} - \phi_{9,5,6} + \phi_{9,5,4}$
16	$3\tau_{3,6,5,4} + \tau_{6,3,2,4} + \tau_{3,2,4,5} - 3\tau_{5,6,3,2} - 3\tau_{2,4,5,6}$
17	$2\tau_{6,3,2,4} - 2\tau_{3,2,4,5} - \tau_{5,6,3,2} + \tau_{2,4,5,6}$
18	$\gamma_{7,3,2,6} + \gamma_{8,4,5,2}$
19	$\gamma_{7,3,2,6} - \gamma_{8,4,5,2}$
20	$\gamma_{10,6,3,5} + \gamma_{9,5,6,4}$
21	$\gamma_{10,6,3,5} - \gamma_{9,5,6,4}$

Frequencies

Table S288: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	453.25	459.14	453.37	453.34	1
2	565.53	571.96	565.75	565.53	1
3	609.94	606.71	610.00	609.95	1
4	688.05	680.28	688.19	688.19	0
5	725.76	728.43	725.74	725.74	0
6	758.88	753.31	758.94	758.94	0
7	845.49	847.36	845.64	845.56	2
8	875.51	867.37	875.47	875.48	1
9	878.28	875.65	878.29	878.29	0
10	902.59	900.27	902.35	902.49	1
11	1051.60	1050.01	1051.60	1051.60	0
12	1098.26	1093.06	1098.27	1098.23	1
13	1100.85	1098.46	1100.87	1100.87	0
14	1278.90	1269.49	1278.87	1278.87	0
15	1396.08	1386.94	1396.85	1396.07	1
16	1442.59	1431.23	1441.73	1442.59	3
17	1545.40	1531.83	1545.37	1545.37	0
18	3213.82	3230.60	3213.83	3213.83	0
19	3227.81	3243.42	3227.80	3227.80	0
20	3256.05	3271.37	3256.06	3256.06	0
21	3259.29	3274.25	3259.28	3259.28	0

S1.97 Methanol

Geometries

Table S289: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−1.37507311	−0.02427686	0.00000035
2	O	1.30601636	0.12070128	0.00000030
3	H	−2.07787395	1.90961292	−0.00007991
4	H	−2.10898758	−0.97927269	1.68197389
5	H	−2.10898055	−0.97940393	−1.68190173
6	H	1.94117467	−1.57749284	−0.00000131

Natural Internal Coordinates

Table S290: Symmetrized, unnormalized natural internal coordinates for Methanol.

1	$r_{1,2}$
2	$r_{2,6}$
3	$r_{1,3} + r_{1,4} + r_{1,5}$
4	$r_{1,4} - r_{1,5}$
5	$2r_{1,3} - r_{1,4} - r_{1,5}$
6	$\phi_{1,2,6}$
7	$2\phi_{3,1,2} - \phi_{4,1,2} - \phi_{5,1,2}$
8	$\phi_{3,1,2} + \phi_{4,1,2} + \phi_{5,1,2}$
9	$\phi_{4,1,2} - \phi_{5,1,2}$
10	$-\phi_{3,1,4} - \phi_{3,1,5} + 2\phi_{4,1,5}$
11	$\phi_{3,1,4} - \phi_{3,1,5}$
12	$\tau_{3,1,2,6}$

Frequencies

Table S291: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	304.11	306.45	304.13	304.13	0
2	1065.02	1062.30	1065.28	1065.28	0
3	1095.54	1097.63	1095.56	1095.56	0
4	1179.62	1182.53	1179.63	1179.63	0
5	1393.88	1383.49	1393.72	1393.72	0
6	1487.64	1489.03	1487.62	1487.62	0
7	1507.67	1514.46	1507.70	1507.70	0
8	1523.24	1529.06	1523.20	1523.20	0
9	3009.29	3023.79	3009.34	3009.34	0
10	3064.49	3090.54	3064.51	3064.51	0
11	3128.11	3153.00	3128.03	3128.03	0
12	3864.98	3883.16	3864.97	3864.97	0

S1.98 Propene

Geometries

Table S292: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−2.37687297	0.33833882	0.00000007
2	C	0.19870321	−0.85510046	−0.00000006
3	C	2.37314150	0.43515597	0.00000003
4	H	0.26291668	−2.90753182	−0.00000011
5	H	4.18218979	−0.52060166	−0.00000005
6	H	2.38999877	2.48486451	0.00000016
7	H	−2.23672093	2.39600543	−0.00000030
8	H	−3.45993967	−0.24053555	−1.66145087
9	H	−3.45993980	−0.24053625	1.66145068

Natural Internal Coordinates

Table S293: Symmetrized, unnormalized natural internal coordinates for Propene.

1	$r_{1,2}$
2	$r_{2,3}$
3	$r_{1,7} + r_{1,8} + r_{1,9}$
4	$2r_{1,7} - r_{1,8} - r_{1,9}$
5	$r_{1,8} - r_{1,9}$
6	$r_{2,4}$
7	$r_{3,5} + r_{3,6}$
8	$r_{3,5} - r_{3,6}$
9	$2\phi_{1,2,3} - \phi_{4,2,1} - \phi_{4,2,3}$
10	$\phi_{4,2,1} - \phi_{4,2,3}$
11	$\phi_{7,1,2} + \phi_{8,1,2} + \phi_{9,1,2} - \phi_{8,1,9} - \phi_{7,1,8} - \phi_{7,1,9}$
12	$2\phi_{7,1,2} - \phi_{8,1,2} - \phi_{9,1,2}$
13	$\phi_{8,1,2} - \phi_{9,1,2}$
14	$2\phi_{8,1,9} - \phi_{7,1,8} - \phi_{7,1,9}$
15	$\phi_{7,1,8} - \phi_{7,1,9}$
16	$2\phi_{5,3,6} - \phi_{5,3,2} - \phi_{6,3,2}$
17	$\phi_{5,3,2} - \phi_{6,3,2}$
18	$\tau_{7,1,2,3} + \tau_{8,1,2,3} + \tau_{9,1,2,3}$
19	$\tau_{5,3,2,1} + \tau_{6,3,2,1}$
20	$\gamma_{4,2,1,3}$
21	$\gamma_{2,3,5,6}$

Frequencies

Table S294: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	199.43	203.87	199.44	199.44	0
2	418.07	417.01	418.08	418.08	0
3	582.65	587.09	582.77	582.77	0
4	925.24	929.74	925.24	925.24	0
5	930.94	931.88	930.97	930.97	0
6	942.38	939.58	942.39	942.39	0
7	1014.26	1029.36	1014.22	1014.22	0
8	1067.99	1066.45	1067.98	1067.98	0
9	1191.64	1187.57	1191.68	1191.68	0
10	1320.29	1319.32	1320.34	1320.34	0
11	1408.10	1401.19	1408.25	1408.25	0
12	1455.83	1453.33	1455.66	1455.66	0
13	1488.14	1489.93	1488.13	1488.13	0
14	1501.66	1503.15	1501.66	1501.66	0
15	1696.39	1688.42	1696.34	1696.34	0
16	3029.48	3042.19	3029.51	3029.51	0
17	3089.80	3115.11	3089.77	3089.77	0
18	3113.17	3137.28	3113.21	3113.21	0
19	3138.19	3154.55	3138.27	3138.27	0
20	3151.66	3170.07	3151.54	3151.54	0
21	3230.27	3252.34	3230.27	3230.27	0

S1.99 Oxirane

Geometries

Table S295: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	O	0.00000000	−0.00000000	1.51705162
2	C	0.00000000	−1.38721508	−0.80610774
3	C	−0.00000000	1.38721508	−0.80610774
4	H	−1.73830814	−2.39048176	−1.22008415
5	H	1.73830814	−2.39048176	−1.22008415
6	H	−1.73830814	2.39048176	−1.22008415
7	H	1.73830814	2.39048176	−1.22008415

Natural Internal Coordinates

Table S296: Symmetrized, unnormalized natural internal coordinates for Oxirane.

1	$r_{1,2} + r_{1,3} + r_{2,3}$
2	$r_{1,2} - r_{1,3}$
3	$-r_{1,2} - r_{1,3} + 2r_{2,3}$
4	$r_{2,4} + r_{2,5} + r_{3,6} + r_{3,7}$
5	$r_{2,4} + r_{2,5} - r_{3,6} - r_{3,7}$
6	$r_{2,4} - r_{2,5} + r_{3,6} - r_{3,7}$
7	$r_{2,4} - r_{2,5} - r_{3,6} + r_{3,7}$
8	$4\phi_{4,2,5} + 4\phi_{6,3,7} - \phi_{1,2,4} - \phi_{3,2,4} - \phi_{1,2,5} - \phi_{3,2,5} - \phi_{1,3,6} - \phi_{2,3,6} - \phi_{1,3,7} - \phi_{2,3,7}$
9	$4\phi_{4,2,5} - 4\phi_{6,3,7} - \phi_{1,2,4} - \phi_{3,2,4} - \phi_{1,2,5} - \phi_{3,2,5} + \phi_{1,3,6} + \phi_{2,3,6} + \phi_{1,3,7} + \phi_{2,3,7}$
10	$\phi_{1,2,4} + \phi_{3,2,4} - \phi_{1,2,5} - \phi_{3,2,5} + \phi_{1,3,6} + \phi_{2,3,6} - \phi_{1,3,7} - \phi_{2,3,7}$
11	$\phi_{1,2,4} + \phi_{3,2,4} - \phi_{1,2,5} - \phi_{3,2,5} - \phi_{1,3,6} - \phi_{2,3,6} + \phi_{1,3,7} + \phi_{2,3,7}$
12	$\phi_{1,2,4} - \phi_{3,2,4} + \phi_{1,2,5} - \phi_{3,2,5} + \phi_{1,3,6} - \phi_{2,3,6} + \phi_{1,3,7} - \phi_{2,3,7}$
13	$\phi_{1,2,4} - \phi_{3,2,4} + \phi_{1,2,5} - \phi_{3,2,5} - \phi_{1,3,6} + \phi_{2,3,6} - \phi_{1,3,7} + \phi_{2,3,7}$
14	$\phi_{1,2,4} - \phi_{3,2,4} - \phi_{1,2,5} + \phi_{3,2,5} + \phi_{1,3,6} - \phi_{2,3,6} - \phi_{1,3,7} + \phi_{2,3,7}$
15	$\phi_{1,2,4} - \phi_{3,2,4} - \phi_{1,2,5} + \phi_{3,2,5} - \phi_{1,3,6} + \phi_{2,3,6} + \phi_{1,3,7} - \phi_{2,3,7}$

Frequencies

Table S297: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	816.26	819.77	816.27	816.27	0
2	849.93	856.01	850.01	850.01	0
3	899.68	900.96	899.78	899.78	0
4	1052.00	1054.88	1052.00	1052.00	0
5	1156.67	1150.36	1156.61	1156.61	0
6	1157.92	1151.72	1157.90	1157.90	0
7	1175.07	1175.40	1175.07	1175.07	0
8	1176.57	1175.52	1176.58	1176.58	0
9	1300.14	1301.10	1300.15	1300.15	0
10	1513.26	1516.14	1513.26	1513.26	0
11	1549.96	1548.52	1549.91	1549.91	0
12	3109.14	3125.28	3109.14	3109.14	0
13	3117.42	3132.89	3117.39	3117.39	0
14	3196.11	3219.80	3196.14	3196.14	0
15	3210.77	3233.79	3210.76	3210.76	0

S1.100 Hydrogen Cycanide

Geometries

Table S298: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	X	−0.00000000	−1.00000000	−1.06129487
2	C	−0.00000000	0.00000000	−1.06129487
3	X	−1.00000000	0.00000000	−1.06129487
4	H	−0.00000000	−0.00000000	−3.07732615
5	N	0.00000000	−0.00000000	1.13096201

Natural Internal Coordinates

Table S299: Symmetrized, unnormalized natural internal coordinates for Hydrogen Cycanide.

1	$r_{2,4}$
2	$r_{2,5}$
3	$\theta_{4,2,5,1}$
4	$\theta_{4,2,5,3}$

Frequencies

Table S300: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	716.01	723.18	716.01	716.01	0
2	716.01	723.19	716.01	716.01	0
3	2111.38	2072.67	2111.51	2111.51	0
4	3443.43	3455.99	3443.35	3443.35	0

S1.101 Triplet Carbene

Geometries

Table S301: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	0.00000000	0.00000000	0.11580983
2	H	0.00000000	−1.87219122	−0.68946391
3	H	0.00000000	1.87219122	−0.68946391

Natural Internal Coordinates

Table S302: Symmetrized, unnormalized natural internal coordinates for Triplet Carbene.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$\phi_{2,1,3}$

Frequencies

Table S303: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1105.77	1122.31	1105.77	1105.77	0
2	3139.22	3154.90	3139.22	3139.22	0
3	3365.40	3391.01	3365.40	3365.40	0

S1.102 Formyl Radical

Geometries

Table S304: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−1.17736294	0.18900598	0.00000000
2	H	−2.55461370	−1.42021423	0.00000000
3	O	1.04426684	−0.05231315	0.00000000

Natural Internal Coordinates

Table S305: Symmetrized, unnormalized natural internal coordinates for Formyl Radical.

1	$r_{1,2}$
2	$r_{1,3}$
3	$\phi_{2,1,3}$

Frequencies

Table S306: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1122.70	1077.12	1123.00	1123.00	0
2	1888.38	1898.35	1888.27	1888.27	0
3	2691.42	2706.97	2691.37	2691.37	0

S1.103 Vinyl Radical

Geometries

Table S307: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	1.17395959	−0.03986833	0.00000000
2	H	2.10304999	−1.87918602	0.00000000
3	H	2.39183520	1.60942624	0.00000000
4	C	−1.30772223	0.15626308	0.00000000
5	H	−2.90219632	−1.11613248	0.00000000

Natural Internal Coordinates

Table S308: Symmetrized, unnormalized natural internal coordinates for Vinyl Radical.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$r_{1,4}$
4	$r_{4,5}$
5	$\phi_{1,4,5}$
6	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{3,1,4}$
7	$\phi_{2,1,4} - \phi_{3,1,4}$
8	$\tau_{2,1,4,5} + \tau_{3,1,4,5}$
9	$\tau_{2,1,4,5} - \tau_{3,1,4,5}$

Frequencies

Table S309: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	726.00	722.51	726.16	726.16	0
2	806.12	818.34	806.24	806.24	0
3	914.78	924.31	914.68	914.68	0
4	1070.93	1067.67	1070.84	1070.84	0
5	1395.98	1398.34	1395.98	1395.98	0
6	1614.03	1615.88	1614.06	1614.06	0
7	3074.49	3099.49	3074.69	3074.69	0
8	3178.90	3204.67	3178.70	3178.70	0
9	3246.53	3263.15	3246.51	3246.51	0

S1.104 Acetyl Radical

Geometries

Table S310: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.25873690	0.80450304	0.00000000
2	O	−2.19121944	−0.33285589	0.00000000
3	C	2.40971826	−0.24563821	0.00000000
4	H	2.38285691	−2.30895956	0.00000000
5	H	3.39100957	0.46865813	−1.66422836
6	H	3.39100957	0.46865813	1.66422836

Natural Internal Coordinates

Table S311: Symmetrized, unnormalized natural internal coordinates for Acetyl Radical.

1	$r_{3,1}$
2	$r_{1,2}$
3	$r_{3,4} + r_{3,5} + r_{3,6}$
4	$2r_{3,4} - r_{3,5} - r_{3,6}$
5	$r_{3,5} - r_{3,6}$
6	$\phi_{3,1,2}$
7	$\phi_{4,3,1} + \phi_{5,3,1} + \phi_{6,3,1} - \phi_{5,3,6} - \phi_{4,3,5} - \phi_{4,3,6}$
8	$2\phi_{4,3,1} - \phi_{5,3,1} - \phi_{6,3,1}$
9	$\phi_{5,3,1} - \phi_{6,3,1}$
10	$2\phi_{5,3,6} - \phi_{4,3,5} - \phi_{4,3,6}$
11	$\phi_{4,3,5} - \phi_{4,3,6}$
12	$\tau_{4,3,1,2}$

Frequencies

Table S312: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	98.52	90.81	98.61	98.60	1
2	466.47	462.95	466.86	466.50	1
3	861.02	859.24	861.13	861.13	0
4	954.71	953.10	954.72	954.72	0
5	1050.41	1040.22	1050.28	1050.45	1
6	1355.85	1349.67	1355.84	1355.84	0
7	1467.61	1470.72	1467.61	1467.61	1
8	1468.66	1471.61	1468.61	1468.61	0
9	1899.32	1911.57	1899.29	1899.29	0
10	3039.37	3052.44	3039.38	3039.38	0
11	3137.39	3159.37	3137.38	3137.38	0
12	3143.08	3166.75	3143.08	3143.08	0

S1.105 Hydroxymethyl Radical

Geometries

Table S313: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−1.37903910	0.02323044	0.05754946
2	O	1.20513902	−0.11712615	−0.00535801
3	H	1.86898304	1.56393483	0.15950651
4	H	−2.27904852	1.78239326	−0.47148778
5	H	−2.29638299	−1.76405192	−0.28821473

Natural Internal Coordinates

Table S314: Symmetrized, unnormalized natural internal coordinates for Hydroxymethyl Radical.

1	$r_{1,4} + r_{1,5}$
2	$r_{1,4} - r_{1,5}$
3	$r_{1,2}$
4	$r_{2,3}$
5	$\phi_{1,2,3}$
6	$2\phi_{4,1,5} - \phi_{4,1,2} - \phi_{5,1,2}$
7	$\phi_{4,1,2} - \phi_{5,1,2}$
8	$\tau_{4,1,2,3} + \tau_{5,1,2,3}$
9	$\tau_{4,1,2,3} - \tau_{5,1,2,3}$

Frequencies

Table S315: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	432.11	433.91	432.33	432.13	1
2	620.09	613.31	620.00	620.15	1
3	1064.75	1066.45	1064.99	1064.99	0
4	1209.21	1204.96	1209.27	1209.27	0
5	1383.73	1375.21	1383.55	1383.55	0
6	1498.77	1505.91	1498.71	1498.71	0
7	3139.51	3156.77	3139.52	3139.52	0
8	3280.03	3305.27	3280.01	3280.01	0
9	3861.95	3878.86	3861.95	3861.95	0

S1.106 Triplet Silylene

Geometries

Table S316: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	Si	0.00000000	0.00000000	0.09643776
2	H	0.00000000	−2.40430265	−1.33854198
3	H	0.00000000	2.40430265	−1.33854198

Natural Internal Coordinates

Table S317: Symmetrized, unnormalized natural internal coordinates for Triplet Silylene.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$\phi_{2,1,3}$

Frequencies

Table S318: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	890.15	908.61	890.17	890.17	0
2	2189.75	2216.29	2189.74	2189.74	0
3	2249.86	2272.92	2249.86	2249.86	0

S1.107 Silyl Radical

Geometries

Table S319: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	X	−1.97286216	−0.00000000	0.00000000
2	SI	−0.08313564	−0.00000000	0.00000000
3	H	0.76927368	−1.33284055	−2.30854755
4	H	0.76927368	2.66568110	0.00000000
5	H	0.76927368	−1.33284055	2.30854755

Natural Internal Coordinates

Table S320: Symmetrized, unnormalized natural internal coordinates for Silyl Radical.

1	$r_{2,3} + r_{2,4} + r_{2,5}$
2	$2r_{2,3} - r_{2,4} - r_{2,5}$
3	$r_{2,4} - r_{2,5}$
4	$2\phi_{3,2,4} - \phi_{3,2,5} - \phi_{4,2,5}$
5	$\phi_{3,2,5} - \phi_{4,2,5}$
6	$\gamma_{3,2,4,5} + \gamma_{4,2,3,5} + \gamma_{5,2,3,4}$

Frequencies

Table S321: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	778.72	789.22	778.85	778.85	0
2	943.18	953.24	943.08	943.08	0
3	943.18	962.71	943.18	943.18	0
4	2217.25	2237.61	2217.24	2217.24	0
5	2250.40	2270.42	2250.40	2250.40	0
6	2250.40	2270.49	2250.40	2250.40	0

S1.108 Phosphino Radical

Geometries

Table S322: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	P	0.00000000	0.00000000	0.11404634
2	H	0.00000000	−1.92750368	−1.75250871
3	H	0.00000000	1.92750368	−1.75250871

Natural Internal Coordinates

Table S323: Symmetrized, unnormalized natural internal coordinates for Phosphino Radical.

1	$r_{1,2} + r_{1,3}$
2	$r_{1,2} - r_{1,3}$
3	$\phi_{2,1,3}$

Frequencies

Table S324: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1128.13	1137.28	1128.13	1128.13	0
2	2389.74	2417.26	2389.74	2389.74	0
3	2397.35	2426.90	2397.35	2397.35	0

S1.109 Nitrogen Dioxide

Geometries

Table S325: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	O	0.00000000	−2.08779511	0.26863662
2	N	0.00000000	0.00000000	−0.61369664
3	O	0.00000000	2.08779511	0.26863662

Natural Internal Coordinates

Table S326: Symmetrized, unnormalized natural internal coordinates for Nitrogen Dioxide.

1	$r_{1,2} + r_{2,3}$
2	$r_{1,2} - r_{2,3}$
3	$\phi_{1,2,3}$

Frequencies

Table S327: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	758.21	766.81	758.94	758.21	1
2	1350.21	1349.16	1349.80	1350.21	1
3	1679.70	1888.26	1679.70	1679.70	0

S1.110 Amino Radical

Geometries

Table S328: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	H	0.00000000	−1.51058428	1.06481029
2	N	0.00000000	0.00000000	−0.15327241
3	H	0.00000000	1.51058428	1.06481029

Natural Internal Coordinates

Table S329: Symmetrized, unnormalized natural internal coordinates for Amino Radical.

1	$r_{1,2} + r_{2,3}$
2	$r_{1,2} - r_{2,3}$
3	$\phi_{1,2,3}$

Frequencies

Table S330: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	1557.74	1551.54	1557.75	1557.75	0
2	3364.81	3388.84	3364.81	3364.81	0
3	3457.67	3491.44	3457.67	3457.67	0

S1.111 Ethyl Radical

Geometries

Table S331: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.00547866	−1.35440696	0.00000000
2	C	−0.01937298	1.46550160	0.00000000
3	H	1.92815108	−2.11168584	0.00000000
4	H	−0.94432912	−2.11610453	1.67223598
5	H	−0.94432912	−2.11610453	−1.67223598
6	H	0.12820569	2.51055499	−1.74949553
7	H	0.12820569	2.51055499	1.74949553

Natural Internal Coordinates

Table S332: Symmetrized, unnormalized natural internal coordinates for Ethyl Radical.

1	$r_{1,2}$
2	$r_{2,6} + r_{2,7}$
3	$r_{2,6} - r_{2,7}$
4	$r_{1,4} + r_{1,5} + r_{1,3}$
5	$-r_{1,4} - r_{1,5} + 2r_{1,3}$
6	$r_{1,4} - r_{1,5}$
7	$2\phi_{6,2,7} - \phi_{6,2,1} - \phi_{7,2,1}$
8	$\phi_{6,2,1} - \phi_{7,2,1}$
9	$\phi_{2,1,3} + \phi_{2,1,4} + \phi_{2,1,5} - \phi_{4,1,5} - \phi_{4,1,3} - \phi_{5,1,3}$
10	$2\phi_{2,1,3} - \phi_{2,1,4} - \phi_{2,1,5}$
11	$\phi_{2,1,4} - \phi_{2,1,5}$
12	$2\phi_{4,1,5} - \phi_{4,1,3} - \phi_{5,1,3}$
13	$\phi_{4,1,3} - \phi_{5,1,3}$
14	$\tau_{6,2,1,3} + \tau_{6,2,1,4} + \tau_{6,2,1,5} + \tau_{7,2,1,3} + \tau_{7,2,1,4} + \tau_{7,2,1,5}$
15	$\gamma_{1,2,6,7}$

Frequencies

Table S333: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	128.41	128.72	128.45	128.43	1
2	469.48	486.59	469.53	469.49	2
3	809.09	812.51	809.11	809.11	0
4	987.41	985.90	987.43	987.45	1
5	1069.91	1072.27	1069.94	1069.94	0
6	1200.87	1202.11	1200.89	1200.89	0
7	1403.42	1401.45	1403.49	1403.49	0
8	1479.97	1485.11	1479.99	1479.99	1
9	1492.29	1497.05	1492.28	1492.28	1
10	1493.37	1497.86	1493.27	1493.27	0
11	2983.43	3005.26	2984.13	2984.13	0
12	3064.92	3088.67	3064.22	3064.22	0
13	3108.80	3135.14	3108.81	3108.81	0
14	3157.24	3175.87	3157.22	3157.22	0
15	3260.35	3286.01	3260.35	3260.35	0

S1.112 tert − Butyl Radical

Geometries

Table S334: CCSD(T)/cc-pVTZ Cartesian Coordinates (Bohr)

1	C	−0.32334039	−0.00000205	0.00000000
2	C	0.06114007	−1.40087768	−2.42638089
3	C	0.06102027	2.80175965	0.00000000
4	C	0.06114007	−1.40087768	2.42638089
5	H	2.08693792	−1.64409780	−2.84744106
6	H	−0.76540572	−0.38822110	−4.02548203
7	H	−0.76556895	−3.29200016	−2.34898777
8	H	2.08679900	3.28810311	0.00000000
9	H	−0.76564669	3.68025423	1.67650059
10	H	−0.76564669	3.68025423	−1.67650059
11	H	2.08693792	−1.64409780	2.84744106
12	H	−0.76556895	−3.29200016	2.34898777
13	H	−0.76540572	−0.38822110	4.02548203

Natural Internal Coordinates

Frequencies

Table S335: Symmetrized, unnormalized natural internal coordinates for tert–Butyl Radical.

1	$r_{1,2} + r_{1,3} + r_{1,4}$
2	$2r_{1,2} - r_{1,3} - r_{1,4}$
3	$r_{1,3} - r_{1,4}$
4	$r_{2,5} + r_{2,6} + r_{2,7} + r_{3,8} + r_{3,9} + r_{3,10} + r_{4,11} + r_{4,12} + r_{4,13}$
5	$2r_{2,5} + 2r_{2,6} + 2r_{2,7} - r_{3,8} - r_{3,9} - r_{3,10} - r_{4,11} - r_{4,12} - r_{4,13}$
6	$r_{3,8} + r_{3,9} + r_{3,10} - r_{4,11} - r_{4,12} - r_{4,13}$
7	$2r_{2,5} - r_{2,6} - r_{2,7} + 2r_{3,8} - r_{3,9} - r_{3,10} + 2r_{4,11} - r_{4,12} - r_{4,13}$
8	$4r_{2,5} - 2r_{2,6} - 2r_{2,7} - 2r_{3,8} + r_{3,9} + r_{3,10} - 2r_{4,11} + r_{4,12} + r_{4,13}$
9	$2r_{3,8} - r_{3,9} - r_{3,10} - 2r_{4,11} + r_{4,12} + r_{4,13}$
10	$r_{2,6} - r_{2,7} + r_{3,9} - r_{3,10} + r_{4,12} - r_{4,13}$
11	$2r_{2,6} - 2r_{2,7} - r_{3,9} + r_{3,10} - r_{4,12} + r_{4,13}$
12	$r_{3,9} - r_{3,10} - r_{4,12} + r_{4,13}$
13	$2\phi_{3,1,4} - \phi_{2,1,3} - \phi_{2,1,4}$
14	$\phi_{2,1,3} - \phi_{2,1,4}$
15	$\phi_{1,2,5} + \phi_{1,2,6} + \phi_{1,2,7} - \phi_{6,2,7} - \phi_{5,2,6} - \phi_{5,2,7} + \phi_{1,3,8} + \phi_{1,3,9} + \phi_{1,3,10} - \phi_{9,3,10}$ $-\phi_{8,3,9} - \phi_{8,3,10} + \phi_{1,4,11} + \phi_{1,4,12} + \phi_{1,4,13} - \phi_{12,4,13} - \phi_{11,4,12} - \phi_{11,4,13}$
16	$2\phi_{1,2,5} + 2\phi_{1,2,6} + 2\phi_{1,2,7} - 2\phi_{6,2,7} - 2\phi_{5,2,6} - 2\phi_{5,2,7} - \phi_{1,3,8} - \phi_{1,3,9} - \phi_{1,3,10} + \phi_{9,3,10}$ $+\phi_{8,3,9} + \phi_{8,3,10} - \phi_{1,4,11} - \phi_{1,4,12} - \phi_{1,4,13} + \phi_{12,4,13} + \phi_{11,4,12} + \phi_{11,4,13}$
17	$\phi_{1,3,8} + \phi_{1,3,9} + \phi_{1,3,10} - \phi_{9,3,10} - \phi_{8,3,9} - \phi_{8,3,10} - \phi_{1,4,11} - \phi_{1,4,12} - \phi_{1,4,13} + \phi_{12,4,13}$ $+\phi_{11,4,12} + \phi_{11,4,13}$
18	$2\phi_{1,2,5} - \phi_{1,2,6} - \phi_{1,2,7} + 2\phi_{1,3,8} - \phi_{1,3,9} - \phi_{1,3,10} + 2\phi_{1,4,11} - \phi_{1,4,12} - \phi_{1,4,13}$
19	$4\phi_{1,2,5} - 2\phi_{1,2,6} - 2\phi_{1,2,7} - 2\phi_{1,3,8} + \phi_{1,3,9} + \phi_{1,3,10} - 2\phi_{1,4,11} + \phi_{1,4,12} + \phi_{1,4,13}$
20	$2\phi_{1,3,8} - \phi_{1,3,9} - \phi_{1,3,10} - 2\phi_{1,4,11} + \phi_{1,4,12} + \phi_{1,4,13}$
21	$\phi_{1,2,6} - \phi_{1,2,7} + \phi_{1,3,9} - \phi_{1,3,10} + \phi_{1,4,12} - \phi_{1,4,13}$
22	$2\phi_{1,2,6} - 2\phi_{1,2,7} - \phi_{1,3,9} + \phi_{1,3,10} - \phi_{1,4,12} + \phi_{1,4,13}$
23	$\phi_{1,3,9} - \phi_{1,3,10} - \phi_{1,4,12} + \phi_{1,4,13}$
24	$2\phi_{6,2,7} - \phi_{5,2,6} - \phi_{5,2,7} + 2\phi_{9,3,10} - \phi_{8,3,9} - \phi_{8,3,10} + 2\phi_{12,4,13} - \phi_{11,4,12} - \phi_{11,4,13}$
25	$4\phi_{6,2,7} - 2\phi_{5,2,6} - 2\phi_{5,2,7} - 2\phi_{9,3,10} + \phi_{8,3,9} + \phi_{8,3,10} - 2\phi_{12,4,13} + \phi_{11,4,12} + \phi_{11,4,13}$
26	$2\phi_{9,3,10} - \phi_{8,3,9} - \phi_{8,3,10} - 2\phi_{12,4,13} + \phi_{11,4,12} + \phi_{11,4,13}$
27	$\phi_{5,2,6} - \phi_{5,2,7} + \phi_{8,3,9} - \phi_{8,3,10} - \phi_{11,4,12} + \phi_{11,4,13}$
28	$2\phi_{5,2,6} - 2\phi_{5,2,7} - \phi_{8,3,9} + \phi_{8,3,10} + \phi_{11,4,12} - \phi_{11,4,13}$
29	$\phi_{8,3,9} - \phi_{8,3,10} + \phi_{11,4,12} - \phi_{11,4,13}$
30	$\tau_{5,2,1,3} + \tau_{5,2,1,4} + \tau_{6,2,1,3} + \tau_{6,2,1,4} + \tau_{7,2,1,3} + \tau_{7,2,1,4} + \tau_{8,3,1,2} + \tau_{8,3,1,4} + \tau_{9,3,1,2} + \tau_{9,3,1,4}$ $+\tau_{10,3,1,2} + \tau_{10,3,1,4} + \tau_{11,4,1,2} + \tau_{11,4,1,3} + \tau_{12,4,1,2} + \tau_{12,4,1,3} + \tau_{13,4,1,2} + \tau_{13,4,1,3}$
31	$2\tau_{5,2,1,3} + 2\tau_{5,2,1,4} + 2\tau_{6,2,1,3} + 2\tau_{6,2,1,4} + 2\tau_{7,2,1,3} + 2\tau_{7,2,1,4} - \tau_{8,3,1,2} - \tau_{8,3,1,4} - \tau_{9,3,1,2} - \tau_{9,3,1,4}$ $-\tau_{10,3,1,2} - \tau_{10,3,1,4} - \tau_{11,4,1,2} - \tau_{11,4,1,3} - \tau_{12,4,1,2} - \tau_{12,4,1,3} - \tau_{13,4,1,2} - \tau_{13,4,1,3}$
32	$\tau_{8,3,1,2} + \tau_{8,3,1,4} + \tau_{9,3,1,2} + \tau_{9,3,1,4} + \tau_{10,3,1,2} + \tau_{10,3,1,4} - \tau_{11,4,1,2} - \tau_{11,4,1,3} - \tau_{12,4,1,2} - \tau_{12,4,1,3}$ $-\tau_{13,4,1,2} - \tau_{13,4,1,3}$
33	$\gamma_{2,1,3,4} + \gamma_{3,1,4,2} + \gamma_{4,1,2,3}$

Table S336: Harmonic frequencies for reference and CMA data.

	Reference		CMA-0A	CMA-2A(0.05)	n
	CCSD(T) /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	MP2 /cc-pVTZ	
1	132.72	133.81	132.73	132.73	1
2	147.62	149.41	147.65	147.65	2
3	147.75	149.44	147.79	147.78	2
4	261.22	256.88	261.24	261.24	0
5	367.05	366.68	367.04	367.04	0
6	367.07	366.69	367.06	367.06	0
7	767.88	765.54	767.91	767.91	0
8	933.80	929.75	933.83	933.83	0
9	933.83	929.76	933.84	933.84	0
10	964.11	963.08	964.13	964.13	0
11	1013.92	1013.43	1013.95	1013.95	0
12	1013.95	1013.43	1013.98	1013.98	0
13	1105.28	1098.54	1105.28	1105.28	0
14	1303.87	1299.34	1303.90	1303.90	0
15	1303.90	1299.35	1303.91	1303.91	0
16	1397.75	1390.31	1397.76	1397.76	0
17	1397.76	1390.34	1397.79	1397.79	0
18	1419.84	1412.99	1419.88	1419.88	0
19	1474.27	1475.99	1474.25	1474.25	1
20	1477.68	1479.52	1477.66	1477.66	0
21	1477.70	1479.53	1477.66	1477.66	0
22	1496.35	1498.88	1496.29	1496.29	0
23	1497.72	1500.47	1497.71	1497.71	2
24	1497.74	1500.48	1497.76	1497.76	2
25	2947.90	2970.74	2948.56	2948.56	0
26	2947.91	2970.81	2948.57	2948.57	0
27	2954.07	2973.89	2954.77	2954.77	0
28	3052.83	3074.49	3052.20	3052.20	0
29	3052.84	3074.85	3052.20	3052.20	0
30	3054.29	3074.87	3053.59	3053.59	0
31	3098.03	3124.14	3098.03	3098.03	0
32	3102.33	3127.25	3102.32	3102.32	0
33	3102.34	3127.31	3102.34	3102.34	0