

Table S1. CCFDF contributions to the fundamental IR intensities of the hydrocarbons calculated with the 6-311++G(3d,3p) and cc-pVTZ basis sets at the MP2 and QCISD levels.

Molecule	Q_i		C^2	CF^2	DF^2	CXCF	CXDF	CFXDF	Total
CH₄									
MP2/cc-pVTZ									
F ₂	CH str	Q ₃	0.3	980.5	1512.5	35.4	-44.0	-2434.8	49.9
F ₂	CH bend	Q ₄	0.5	78.0	195.5	-13.1	20.7	-247.0	34.6
MP2/6-311++G(3d,3p)									
F ₂	CH str	Q ₃	2.6	1141.2	1561.9	-109.6	128.2	-2670.2	54.1
F ₂	CH bend	Q ₄	4.5	45.9	209.0	28.8	-61.5	-195.8	30.9
QCISD/cc-pVTZ									
F ₂	CH str	Q ₃	0.1	902.3	1452.3	-15.0	19.1	-2289.5	69.3
F ₂	CH bend	Q ₄	0.1	81.5	220.1	5.9	-9.8	-267.8	30.0
QCISD/6-311++G(3d,3p)									
F ₂	CH str	Q ₃	5.2	1010.3	1446.8	-145.0	173.5	-2417.9	72.9
F ₂	CH bend	Q ₄	9.0	48.6	236.7	41.9	-92.5	-214.4	29.3
C₂H₂									
QCISD/6-311++G(3d,3p)									
Σ_u	CH str	Q ₃	25.2	1785.0	1429.8	424.1	-379.4	-3194.0	90.7
Π_u	CH bend	Q ₅	50.4	0.00	29.8	0.00	77.5	0.00	157.7
MP2/6-311++G(3d,3p)									
Σ_u	CH str	Q ₃	30.4	1810.2	1437.1	468.8	-417.7	-3225.9	103.0
Π_u	CH bend	Q ₅	60.7	0.0	9.5	0.0	48.1	0.0	118.3
C₂H₄									
MP2/cc-pVTZ									
B _{1u}	CH ₂ wag	Q ₇	4.8	0.0	59.6	0.0	33.8	0.0	98.2
B _{2u}	CH ₂ str	Q ₉	3.6	797.9	1145.9	107.3	-128.6	-1912.4	13.7
	CH ₂ rock	Q ₁₀	1.2	13.1	8.4	-7.8	6.3	-20.9	0.3
B _{2u}	CH ₂ str	Q ₁₁	1.4	21.6	78.5	10.8	-20.6	-82.4	9.3
	CH ₂ scis	Q ₁₂	3.4	511.9	573.0	-83.9	88.7	-1083.1	10.0
MP2/6-311++G(3d,3p)									
B _{1u}	CH ₂ wag	Q ₇	0.1	0.0	103.2	0.0	-6.1	0.0	97.2
B _{2u}	CH ₂ str	Q ₉	0.1	1005.9	1263.6	-16.6	18.6	-2254.9	16.8
	CH ₂ rock	Q ₁₀	0.0	8.5	3.9	0.9	-0.6	-11.5	1.2
B _{2u}	CH ₂ str	Q ₁₁	0.0	218.6	326.3	-4.8	5.8	-534.1	11.8
	CH ₂ scis	Q ₁₂	0.1	191.3	284.0	7.1	-8.6	-466.2	7.7
QCISD/cc-pVTZ									
B _{1u}	CH ₂ wag	Q ₇	2.0	0.0	64.4	0.0	22.7	0.00	89.1
B _{2u}	CH ₂ str	Q ₉	1.5	774.0	1135.4	68.3	-82.7	-1874.9	21.6
	CH ₂ rock	Q ₁₀	0.5	14.1	6.8	-5.3	3.7	-19.5	0.3
B _{2u}	CH ₂ str	Q ₁₁	0.6	8.5	50.9	4.4	-10.8	-41.6	12.0
	CH ₂ scis	Q ₁₂	1.4	573.0	660.5	-57.3	61.6	-1230.5	8.7
QCISD/6-311++G(3d,3p)									
B _{1u}	CH ₂ wag	Q ₇	1.0	0.0	113.3	0.0	-21.0	0.0	93.3
B _{2u}	CH ₂ str	Q ₉	0.7	926.9	1181.3	-51.9	58.6	-2092.8	22.8
	CH ₂ rock	Q ₁₀	0.2	9.2	4.3	3.0	-2.0	-12.5	2.1
B _{2u}	CH ₂ str	Q ₁₁	0.3	188.4	291.8	-14.5	18.0	-468.9	15.1
	CH ₂ wag	Q ₁₂	0.7	197.7	299.6	23.4	-28.8	-486.7	5.8

C ₂ H ₆			MP2/cc-pVTZ						
A _{2u}	CH ₂ str	Q ₅	0.0	79.0	249.3	-3.3	5.9	-280.6	50.3
	CH ₂ def	Q ₆	0.2	213.4	261.3	13.7	-15.1	-472.2	1.2
E _u	CH ₂ str	Q ₇	0.2	1116.2	1878.2	-32.5	42.2	-2895.9	108.5
	CH ₂ rock	Q ₈	0.1	7.0	53.8	1.9	-5.3	-38.8	18.7
	CH ₂ def	Q ₉	0.1	40.7	94.1	4.7	-7.2	-123.7	8.8
			MP2/6-311++G(3d.3p)						
A _{2u}	CH ₂ str	Q ₅	1.1	85.2	236.6	-19.6	32.7	-283.9	52.1
	CH ₂ def	Q ₆	7.3	171.5	271.3	70.7	-88.9	-431.4	0.5
E _u	CH ₂ str	Q ₇	15.7	1312.3	1921.3	-203.1	245.8	-3175.7	116.2
	CH ₂ rock	Q ₈	4.4	2.8	47.4	6.9	-28.6	-22.7	10.1
	CH ₂ def	Q ₉	4.6	26.6	114.3	22.2	-45.9	-110.4	11.4
			QCISD/cc-pVTZ						
A _{2u}	CH ₂ str	Q ₅	0.3	69.4	232.7	-9.3	17.0	-254.1	56.0
	CH ₂ def	Q ₆	1.9	225.4	310.2	41.9	-49.1	-528.8	1.5
E _u	CH ₂ str	Q ₇	2.1	1036.8	1750.7	-93.3	121.3	-2694.5	123.0
	CH ₂ rock	Q ₈	1.2	7.9	51.0	6.1	-15.4	-40.1	10.6
	CH ₂ def	Q ₉	1.2	42.6	108.0	14.6	-23.2	-135.6	7.6
			QCISD/6-311++G(3d.3p)						
A _{2u}	CH ₂ str	Q ₅	1.9	70.8	212.1	-23.1	40.0	-245.0	56.7
	CH ₂ def	Q ₆	12.2	177.7	309.3	93.1	-122.7	-468.7	0.8
E _u	CH ₂ str	Q ₇	13.1	1175.8	1755.9	-248.2	303.3	-2873.8	126.2
	CH ₂ rock	Q ₈	7.3	3.2	63.8	9.7	-43.0	-28.7	12.2
	CH ₂ def	Q ₉	7.8	27.8	139.2	29.3	-65.8	-124.0	14.3
C ₃ H ₄			QCISD/6-311++G(3d.3p)						
(prop.)	<i>sp</i> CH str	Q ₁	9.5	1047.8	784.7	199.2	-172.4	-1813.5	55.3
	<i>sp</i> ³ CH str	Q ₂	0.1	38.5	99.9	-2.8	4.5	-124.1	16.1
	C str	Q ₃	2.9	9.7	0	-10.7	-0.5	0.9	2.3
	CH ₃ bend	Q ₄	0.3	155.8	142.9	14.5	-13.9	-298.2	1.4
	C-C str	Q ₅	2.8	1.1	2.5	3.5	-5.3	-3.3	1.3
	<i>sp</i> ³ CH str	Q ₆	0.4	629.6	788.2	-28.6	32.0	-1409.0	12.6
	CH ₃ bend	Q ₇	0.0	7.6	34.0	0.6	-1.4	-32.0	8.8
	CH ₃ rock	Q ₈	3.4	8.8	37.2	10.8	-22.4	-36.0	1.8
	CH bend	Q ₉	19.0	0.0	13.2	-0.8	31.6	-0.6	62.4
	C-C bend	Q ₁₀	7.2	0.2	2.6	2.4	8.8	1.4	22.6
			MP2/6-311++G(3d.3p)						
	<i>sp</i> CH str	Q ₁	12.3	1014.0	744.2	223.7	-191.6	-1737.4	65.2
	<i>sp</i> ³ CH str	Q ₂	0.0	47.5	117.6	0.6	-1.0	-149.4	15.3
	C str	Q ₃	2.6	6.8	0.3	-8.4	-1.7	2.7	2.3
	CH ₃ bend	Q ₄	0.0	148.3	120.5	-1.6	1.5	-267.1	1.5
	C-C str	Q ₅	2.8	0.0	1.1	0.5	-3.5	-0.3	0.6
	<i>sp</i> ³ CH str	Q ₆	0.0	689.2	868.4	5.5	-6.2	-1547.0	9.8
	CH ₃ bend	Q ₇	0.1	6.9	37.4	-1.9	4.5	-31.9	15.1
	CH ₃ rock	Q ₈	1.8	7.8	32.7	7.4	-15.1	-31.8	2.8
	CH bend	Q ₉	24.9	0.0	8.5	-0.5	29.1	-0.3	61.7
	C-C bend	Q ₁₀	7.4	0.2	1.9	2.5	7.4	1.3	20.6
C ₃ H ₄			MP2/6-311++G(3d.3p)						
(allene)	CH str	Q ₅	0.5	307.5	354.4	25.6	-27.5	-660.3	0.3
	C=C str	Q ₆	5.6	189.8	17.3	-64.9	19.6	-114.4	52.8
	CH ₂ bend	Q ₇	3.4	227.9	239.8	-55.9	57.4	-467.5	5.0
	CH str	Q ₈	1.9	985.6	1104.9	87.1	-92.2	-2087.0	0.2
	CH ₂ rock	Q ₉	1.3	23.4	9.4	11.1	-7.1	-29.7	8.6

CCC bend	Q ₁₀	1.3	0.0	81.9	-0.4	20.2	-3.5	99.4
CCC bend	Q ₁₁	14.5	0.1	0.9	2.7	-7.4	-0.7	10.2

QCISD/cc-pVTZ

CH str	Q ₅	0.5	660.4	723.3	35	-36.8	-1379	3.4
C=C str	Q ₆	49.5	8519.5	6036.4	-1298.5	1093	-14342.2	57.7
CH ₂ bend	Q ₇	10.3	447.5	434.2	-135.9	133.6	-880.0	9.7
CH str	Q ₈	3.0	697.0	907.6	91.6	-104.4	-1590.4	4.4
CH ₂ rock	Q ₉	17.4	39.4	62.6	52.4	-66.0	-99.2	6.6
CCC bend	Q ₁₀	0.4	1.6	86.4	-0.2	10.8	-4.6	94.4
CCC bend	Q ₁₁	99.8	0.0	53.8	1.8	-146.6	-1.4	7.4

QCISD/6-311++G(3d.3p)

CH str	Q ₅	0.0	225.7	321.1	5.4	-6.4	-536.0	9.8
C=C str	Q ₆	7.1	282.2	21.8	-89.2	20.0	-126.6	115.2
CH ₂ bend	Q ₇	1.2	246.2	279.6	-33.9	36.1	-523.9	5.3
CH str	Q ₈	0.3	911.1	1047.1	30.8	-33.0	-1953.3	2.9
CH ₂ rock	Q ₉	2.6	29.4	10.6	16.3	-9.2	-30.9	18.9
CCC bend	Q ₁₀	0.0	0.1	108.0	0.0	1.7	-4.2	105.5
CCC bend	Q ₁₁	13.7	0.1	0.9	2.1	-6.7	-0.5	9.5

C₃H₆

MP2/6-311++G(3d.3p)

CH str	Q ₆	0.3	1464.9	1768.2	-39.9	43.9	-3218.8	18.5
CH ₂ rock	Q ₇	0.1	20.6	41.5	2.8	-4.0	-58.5	2.5
CH str	Q ₈	0.1	357.6	585.8	-12.6	16.1	-915.4	31.7
CH ₂ def	Q ₉	0.3	205.3	253.5	15.3	-17.0	-455.9	1.4
CH ₂ bend	Q ₁₀	0.3	93.2	227.5	11.2	-17.5	-290.9	23.8
ring	Q ₁₁	0.0	6.1	72.4	0.4	-1.4	-40.9	36.6

QCISD/cc-pVTZ

CH str	Q ₆	1.1	1138.2	1618.6	68.4	-81.6	-2714.6	30.1
CH ₂ rock	Q ₇	0.4	32.4	27.3	-6.9	6.4	-59.4	0.0
CH str	Q ₈	0.4	227.9	494.4	19.7	-29.0	-671.3	42.1
CH ₂ def	Q ₉	1.1	239.3	244.2	-32.0	32.3	-483.4	1.4
CH ₂ bend	Q ₁₀	1.2	115.2	178.2	-23.9	29.7	-286.5	14.0
ring	Q ₁₁	0.1	6.0	64.8	-1.0	3.7	-37.9	35.6

QCISD/6-311++G(3d.3p)

CH str	Q ₆	2.1	1347.8	1688.4	-105.5	118.1	-3017.1	33.8
CH ₂ rock	Q ₇	0.7	20.8	53.7	7.8	-12.6	-66.8	3.7
CH str	Q ₈	0.8	309.1	537.0	-32.3	42.6	-814.8	42.4
CH ₂ def	Q ₉	2.2	229.9	256.7	44.4	-46.9	-485.5	0.7
CH ₂ bend	Q ₁₀	2.5	102.2	257.6	32.1	-51.1	-324.1	19.3
ring	Q ₁₁	0.1	6.6	82.2	1.4	-5.1	-44.8	40.3