Supplementary Information

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TABLE I. CH_2F_2. Convergence of the CCSD(T) harmonic intensities (km/mol) with respect to the dimension of the basis set.

modes	symm.	CCSD(T)/ cc-pVTZ	CCSD(T)/ aug-cc-pVTZ	CCSD(T)/ cc-pVQZ	CCSD(T)/ aug-cc-pVQZ	CCSD(T)/ aug-cc-pVQZ+CV	assignments[a]
ν_6	B_1	41.56 (14.88)	27.40 (0.72)	32.74 (6.06)	27.39 (0.71)	26.68	CH_2 A stretch.
ν_1	A_1	44.28 (6.30)	38.29 (0.31)	40.68 (2.70)	38.31 (0.33)	37.98	CH_2 S stretch.
ν_2	A_1	1.37 (1.14)	0.43 (0.20)	0.68 (0.45)	0.36 (0.13)	0.23	CH_2 scissor
ν_8	B_2	21.59 (8.05)	14.51 (0.97)	15.76 (2.22)	13.99 (0.45)	13.54	CH_2 wag
ν_5	A_2	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00	CH_2 twist
ν_7	B_1	20.19 (3.42)	16.87 (0.10)	18.56 (1.79)	16.99 (0.22)	16.77	CH_2 rock
ν_3	A_1	97.53 (0.26)	96.24 (-1.03)	97.21 (-0.06)	97.34 (0.07)	97.27	CF_2 S stretch.
ν_9	B_2	224.41 (-20.78)	243.73 (-1.46)	234.13 (-11.06)	245.35 (0.16)	245.19	CF_2 A stretch.
ν_4	A_1	5.07 (-0.13)	5.18 (-0.02)	5.03 (-0.17)	5.18 (-0.02)	5.20	CF_2 bend
MAE[b]		6.11	0.53	2.72	0.23	0.00	

[a] A and S refer to Asymmetric and Symmetric modes, respectively.
[b] The Mean Absolute Error (MAE) for each basis set has been calculated by summing the absolute errors on each mode.

TABLE II. CH_2CHF. Convergence of the CCSD(T) harmonic intensities (km/mol) with respect to the dimension of the basis set.

modes	symm.	CCSD(T)/ cc-pVTZ	CCSD(T)/ aug-cc-pVTZ	CCSD(T)/ cc-pVQZ	CCSD(T)/ aug-cc-pVQZ	CCSD(T)/ aug-cc-pVQZ+CV	assignments[a]
ν_1	A’	1.83 (0.73)	1.48 (0.38)	1.32 (0.22)	1.24 (0.14)	1.10	CH_2 A stretch
ν_2	A’	6.65 (1.92)	4.81 (0.08)	5.70 (0.97)	4.83 (0.10)	4.73	CH stretch
ν_3	A’	0.64 (0.12)	0.78 (0.02)	0.71 (-0.05)	0.73 (-0.03)	0.76	CH_2 S stretch
ν_4	A’	88.00 (-8.15)	94.63 (-1.52)	93.45 (-2.70)	95.69 (-0.46)	96.15	C=C stretch
ν_5	A’	5.46 (-0.42)	6.43 (0.55)	5.71 (-0.17)	5.99 (0.11)	5.88	CH_2 bend
ν_6	A’	1.97 (-0.03)	1.76 (-0.24)	2.17 (0.17)	1.99 (-0.01)	2.00	CHF bend
ν_7	A’	85.39 (-6.49)	90.12 (-1.76)	89.75 (-2.13)	91.45 (-0.43)	91.88	CF stretch
ν_{10}	A“	35.76 (1.82)	40.80 (6.86)	34.50 (0.56)	34.78 (0.84)	33.94	(oop) torsion
ν_8	A’	36.19 (-3.17)	39.61 (0.25)	36.33 (-3.03)	39.51 (0.15)	39.36	CH_2 rock
ν_{11}	A“	40.92 (-0.67)	34.95 (-6.64)	41.22 (-0.37)	40.40 (-1.19)	41.59	(oop) CH_2 S bend
ν_{12}	A“	1.87 (-1.85)	3.42 (-0.30)	2.69 (-1.03)	3.63 (-0.09)	3.72	(oop) CH_2 A bend
ν_9	A’	4.24 (0.14)	4.08 (-0.02)	4.13 (0.03)	4.11 (0.01)	4.10	C=CF bend
MAE[b]		2.13	1.55	0.95	0.30	0.00	

[a] A and S refer to Asymmetric and Symmetric modes, respectively, oop refers to out of plane bending modes.
[b] The Mean Absolute Error (MAE) for each basis set has been calculated by summing the absolute errors on each mode.

TABLE III. Valence angles (degrees) and Mean Absolute Errors (MAEs) with respect to CCSD(T)/REF.

	B3LYP/ SNSD	B2PLYP/ cc-pVTZ(-PP)	CCSD(T)/ REF
	CH_2F_2		
H-C-H	113.79	113.16	113.36
F-C-F	108.51	108.63	108.33
F-C-H	108.61	108.74	108.76
	$CHBrF_2$		
H-C-Br	108.58	108.28	108.80
H-C-F	110.20	110.36	110.22
F-C-Br	109.73	109.66	109.70
F-C-F	108.40	108.53	108.18
	CF_3Br		
F-C-Br	110.25	110.16	110.36
F-C-F	108.68	108.78	108.57
	CH_2DBr		
H(D)-C-Br	107.61	107.77	107.64
H(D)-C-H	111.27	111.12	111.24
	CH_2CHF		
H(c)-C-H(t)[a]	119.15	119.39	119.70
H(g)-C-F	111.75	112.02	112.21
	CF_2CFCl		
F(c)-C-F(t)	112.45	112.58	112.68
F(g)-C-Cl	115.38	115.67	115.81
	cis-CHFCHBr		
H-C-F	113.22	113.44	113.73
H-C-Br	115.24	115.82	116.22
	cis-CHFCHI		
H-C-F	112.75	112.94	113.22
H-C-I	115.41	116.13	116.63
	overall MAEs[b]		
halo-methanes	0.14	0.20	0.00
halo-ethylenes	0.61	0.28	0.00
total[c]	0.34	0.23	0.00

[a] (c),(g) and (t) stand for cis-, geminal- and trans-, respectively.
[b] Overall MAEs are computed by averaging the errors of the angles over all the halo-methanes, halo-ethylenes, and the whole set of molecules (total).
[c] For each molecule, the MAE associated to both DFT methods is smaller than 1°.

TABLE IV. Harmonic and anharmonic (GVPT2) frequencies (cm^{-1}) for CH_2F_2.

modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ	CCSD(T)/ aug-cc-pCVQZ[b]	CCSD(T)/ REF			assignments[c]
				harmonic frequencies[a]				
ν_6	B_1	3143.2 (-16.6)	3158.1 (-1.7)	3160.0 (0.2)	3159.8			CH_2 (A) stretch.
ν_1	A_1	3067.5 (-17.2)	3082.8 (-1.9)	3085.0 (0.3)	3084.7			CH_2 (S) stretch.
ν_2	A_1	1518.2 (-33.8)	1555.3 (3.3)	1552.0 (0.0)	1552.0			CH_2 scissor
ν_8	B_2	1438.8 (-31.0)	1480.0 (10.2)	1470.0 (0.2)	1469.8			CH_2 wag
ν_5	A_2	1262.9 (-25.2)	1288.3 (0.2)	1289.0 (0.9)	1288.1			CH_2 twist
ν_7	B_1	1170.4 (-28.7)	1199.5 (0.4)	1200.0 (0.9)	1199.1			CH_2 rock
ν_3	A_1	1102.2 (-31.7)	1126.1 (-7.8)	1134.0 (0.1)	1133.9			CF_2 (S) stretch.
ν_9	B_2	1066.0 (-53.3)	1106.7 (-12.6)	1119.0 (-0.3)	1119.3			CF_2 (A) stretch.
ν_4	A_1	521.1 (-13.6)	531.1 (-3.6)	535.0 (0.3)	534.7			CF_2 bend
MAE		27.9	4.6	0.4	0.0			
				anharmonic frequencies[a]				
modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ	HYB^{B3D}[d]	HYB^{B2T}[e]	CCSD(T)/ Hyb1[bf]	exp.[b]	assignments[c]
ν_6	B_1	2995.7 (-18.7)	3019.2 (4.8)	3020.0 (5.6)	3020.2 (5.8)	3014.7 (0.3)	3014.4	CH_2 (A) stretch.
ν_1	A_1	2914.8[g] (-33.1)	2965.6[g] (17.7)	2961.7[g] (13.8)	2959.1[g] (11.2)	2955.0 (7.1)	2947.9	CH_2 (S) stretch.
ν_2	A_1	1479.3 (-30.3)	1515.4 (5.8)	1514.5 (4.9)	1512.1 (2.5)	1508.0 (-1.6)	1509.6	CH_2 scissor
ν_8	B_2	1407.3 (-28.2)	1445.5 (10.0)	1439.9 (4.4)	1435.4 (-0.1)	1435.7 (0.2)	1435.5	CH_2 wag
ν_5	A_2	1231.4 (-25.4)	1256.0 (-0.8)	1258.3 (1.5)	1256.0 (-0.8)	1256.4 (-0.4)	1256.8	CH_2 twist
ν_7	B_1	1151.3 (-27.4)	1179.4 (0.7)	1181.0 (2.3)	1179.1 (0.4)	1179.3 (0.6)	1178.7	CH_2 rock
ν_3	A_1	1080.1 (-31.5)	1104.0 (-7.6)	1115.3 (3.7)	1112.5 (0.9)	1111.5 (-0.1)	1111.6	CF_2 (S) stretch.
ν_9	B_2	1038.4 (-51.5)	1079.1 (-10.8)	1096.6 (6.7)	1092.8 (2.9)	1090.6 (0.7)	1089.9	CF_2 (A) stretch.
ν_4	A_1	515.1 (-13.2)	524.6 (-3.7)	529.4 (1.1)	528.3 (0.0)	528.7 (0.4)	528.3	CF_2 bend
MAE		28.8	6.9	4.9	2.7	1.3	0.0	

[a] In parenthesis the signed errors are reported. Errors of harmonic frequencies computed with respect to the CCSD(T)/REF harmonic frequencies, errors of anharmonic frequencies evaluated with respect to experimental fundamentals, and Mean Absolute Error (MAE) derived by averaging over the absolute errors of each mode.

[b] Tasinato et al.[1].

[c] (A) and (S) refer to Asymmetric and Symmetric modes, respectively.

[d] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B3LYP/SNSD level.

[e] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B2PLYP/cc-pVTZ level.

[f] Geometry and quadratic force constants at the CCSD(T)/aug-cc-pCVQZ level; cubic and semi-diagonal force constants at the CCSD(T) level, employing the aug-cc-pCVQZ basis set for F atoms, and aug-cc-pCVTZ for C and H atoms.

[g] Deperturbed values (from the first to the fourth column): 2910.1, 2932.2, 2932.5, 2934.3 cm^{-1}.

TABLE V. Harmonic and anharmonic (GVPT2) frequencies (cm^{-1}) for CF_3Br.

modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ-PP	CCSD(T)/ REF			assignments
				harmonic frequencies[a]			
ν_4	E	1183.8 (-46.7)	1219.9 (-10.6)	1230.5			CF_3 (A) stretch
ν_1	A_1	1059.6 (-43.9)	1084.8 (-18.7)	1103.5			CF_3 (S) stretch
ν_2	A_1	750.5 (-12.1)	763.7 (1.1)	762.6			CF_3 (S) bend
ν_5	E	541.1 (-7.1)	549.5 (1.3)	548.2			CF_3 (A) bend
ν_3	A_1	337.0 (-16.5)	348.0 (-5.5)	353.5			CBr stretch
ν_6	E	297.8 (-6.2)	302.3 (-1.7)	304.0			CF_3 rock
MAE		22.1	6.5	0.0			
				anharmonic frequencies[a]			
modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ-PP	HYB^{B3D}[b]	HYB^{B2T}[c]	exp.[d]	assignments
ν_4	E	1157.6 (-51.4)	1194.2 (-14.8)	1208.1 (-0.9)	1205.7 (-3.3)	1209	CF_3 (A) stretch
ν_1	A_1	1038.8 (-46.2)	1063.1 (-21.9)	1088.2 (3.2)	1085.7 (0.7)	1085	CF_3 (S) stretch
ν_2	A_1	743.3 (-17.7)	756.4 (-4.6)	756.5 (-4.5)	755.7 (-5.3)	761	CF_3 (S) bend
ν_5	E	534.7 (-15.3)	543.2 (-6.8)	542.4 (-7.6)	542.1 (-7.9)	550	CF_3 (A) bend
ν_3	A_1	334.1 (-15.9)	344.6 (-5.4)	351.1 (1.1)	350.2 (0.2)	350	CBr stretch
ν_6	E	295.3 (-9.7)	299.8 (-5.2)	301.6 (-3.4)	301.5 (-3.5)	305	CF_3 rock
MAE		26.0	9.8	3.5	3.5	0.0	

[a] In parenthesis the signed errors are reported. Errors of harmonic frequencies computed with respect to the CCSD(T)/REF harmonic frequencies, errors of anharmonic frequencies evaluated with respect to experimental fundamentals, and Mean Absolute Error (MAE) derived by averaging over the absolute errors of each mode. In the case of modes affected by Fermi resonances, differences smaller than 10 cm^{-1} have been found between GVPT2 and deperturbed values.

[b] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B3LYP/SNSD level.

[c] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B2PLYP/cc-pVTZ-PP level.

[d] Refs.[2,3].

TABLE VI. Harmonic and anharmonic (GVPT2) frequencies (cm^{-1}) for CH_2DBr.

				harmonic frequencies[a]				
modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ-PP	CCSD(T)/ cc-pVTZ[b]	CCSD(T)/ REF			assignments[c]
ν_7	A"	3201.7 (8.1)	3210.9 (17.3)	3195.0 (1.4)	3193.6			CH_2 (A) stretch.
ν_1	A'	3132.1 (8.0)	3143.5 (19.4)	3128.0 (3.9)	3124.1			CH_2 (S) stretch.
ν_2	A'	2317.0 (8.8)	2324.6 (16.4)	2313.0 (4.8)	2308.2			CD stretch.
ν_3	A'	1451.2 (-17.8)	1468.8 (-0.2)	1463.0 (-6.0)	1469.0			CH_2 deformation
ν_8	A"	1270.3 (-17.2)	1287.1 (-0.4)	1284.0 (-3.5)	1287.5			CH_2 twist
ν_4	A'	1243.8 (-11.8)	1256.1 (0.5)	1252.0 (-3.6)	1255.6			CH_2 wag
ν_9	A"	939.1 (-7.4)	945.8 (-0.7)	942.0 (-4.5)	946.5			CH_2 rock
ν_5	A'	770.6 (-9.7)	779.0 (-1.3)	779.0 (-1.3)	780.3			DCBr deformation
ν_6	A'	574.1 (-28.2)	598.2 (-4.1)	605.0 (2.7)	602.3			CBr stretch.
MAE		13.0	6.7	3.5	0.0			
				anharmonic frequencies[a]				
modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ-PP	HYB^{B3D} [d]	HYB^{B2T} [e]	CCSD(T)/ cc-pVTZ[b]	exp.[b]	assignments[c]
ν_7	A"	3051.0 (-2.0)	3066.6 (13.6)	3043.0 (-10.0)	3046.5 (-6.5)	3045.0 (-8.0)	3053.0	CH_2 (A) stretch.
ν_1	A'	3001.0 (0.0)	3018.3 (17.3)	2999.8[f] (-1.2)	3001.8[f] (0.8)	2997.0 (-4.0)	3001.0	CH_2 (S) stretch.
ν_2	A'	2240.9 (-2.9)	2252.9 (9.1)	2233.1 (-10.7)	2235.4 (-8.4)	2239.0 (-4.8)	2243.8	CD stretch.
ν_3	A'	1411.6 (-13.3)	1430.3 (5.4)	1430.1 (5.2)	1430.4 (5.5)	1425.0 (0.1)	1424.9	CH_2 deformation
ν_8	A"	1238.7 (-13.8)	1256.2 (3.7)	1256.6 (4.1)	1256.5 (4.0)	1254.0 (1.5)	1252.5	CH_2 twist
ν_4	A'	1217.4 (-7.8)	1230.7 (5.5)	1230.1 (4.9)	1230.2 (5.0)	1228.0 (2.8)	1225.2	CH_2 wag
ν_9	A"	923.5 (-6.8)	931.4 (1.1)	931.5 (1.2)	932.1 (1.8)	927.0 (-3.3)	930.3	CH_2 rock
ν_5	A'	758.5 (-10.3)	767.5 (-1.3)	768.9 (0.1)	768.8 (0.0)	766.0 (-2.8)	768.8	DCBr deformation
ν_6	A'	562.5 (-32.5)	586.4 (-8.6)	593.1 (-1.9)	590.9 (-4.1)	593.0 (-2.0)	595.0	CBr stretch.
MAE		9.9	7.3	4.4	4.0	3.3	0.0	

[a] In parenthesis the signed errors are reported. Errors of harmonic frequencies computed with respect to the CCSD(T)/REF harmonic frequencies, errors of anharmonic frequencies evaluated with respect to experimental fundamentals, and Mean Absolute Error (MAE) derived by averaging over the absolute errors of each mode.
[b] Baldacci et al.[4].
[c] (A) and (S) refer to Asymmetric and Symmetric modes, respectively.
[d] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B3LYP/SNSD level.
[e] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B2PLYP/cc-pVTZ-PP level.
[f] Deperturbed values (from the second to the third column): 2980.3, 2983.2 cm^{-1}.

TABLE VII. Harmonic and anharmonic (GVPT2) frequencies (cm^{-1}) for CH_2CHF.

modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ	CCSD(T)/ cc-pVQZ[b]	CCSD(T)/ REF			assignments[c]
				harmonic frequencies[a]				
ν_1	A'	3272.0 (-12.9)	3291.7 (6.8)	3282.1 (-2.8)	3284.9			CH_2 (A) stretch
ν_2	A'	3216.3 (-8.6)	3226.8 (1.9)	3220.7 (-4.2)	3224.9			CH stretch
ν_3	A'	3174.9 (-5.7)	3191.5 (10.9)	3178.4 (-2.2)	3180.6			CH_2 (S) stretch
ν_4	A'	1706.6 (5.4)	1713.6 (12.4)	1700.2 (-1.0)	1701.2			CC stretch
ν_5	A'	1400.6 (-15.4)	1427.3 (11.3)	1416.5 (0.5)	1416.0			CH_2 bend
ν_6	A'	1327.2 (-6.8)	1344.0 (10.0)	1332.7 (-1.3)	1334.0			CHF bend
ν_7	A'	1158.1 (-21.3)	1181.2 (1.8)	1180.7 (1.3)	1179.4			CF stretch
ν_{10}	A"	955.8 (1.1)	974.6 (19.9)	953.1 (-1.6)	954.7			(oop) torsion
ν_8	A'	931.2 (-10.7)	945.9 (4.0)	941.3 (-0.6)	941.9			CH_2 rock
ν_{11}	A"	887.5 (8.3)	893.3 (14.1)	873.1 (-6.1)	879.2			(oop) CH_2 (S) bend
ν_{12}	A"	723.9 (-4.1)	737.8 (9.8)	726.7 (-1.3)	728.0			(oop) CH_2 (A) bend
ν_9	A'	484.2 (0.8)	487.3 (3.9)	482.2 (-1.2)	483.4			CCF bend
MAE		8.4	8.9	2.0	0.0			
				anharmonic frequencies[a]				
modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ	HYB^{B3D}[d]	HYB^{B2T}[e]	CCSD(T)/ cc-pVQZ(TZ)[fg]	exp.[f]	assignments[c]
ν_1	A'	3127.7 (-13.0)	3151.9 (11.2)	3142.0 (1.3)	3143.2 (2.5)	3136.7 (-4.0)	3140.7	CH_2 (A) stretch
ν_2	A'	3084.0 (-10.5)	3100.3 (5.8)	3093.5 (-1.0)	3094.3 (-0.2)	3084.9 (-9.6)	3094.5	CH stretch
ν_3	A'	3068.9[h] (6.8)	3093.9[h] (31.8)	3078.9[h] (16.8)	3076.4[h] (14.3)	3073.1 (11.0)	3062.1	CH_2 (S) stretch
ν_4	A'	1666.1 (10.5)	1670.1 (14.5)	1661.1 (5.5)	1656.2 (0.6)	1653.9 (-1.7)	1655.6	CC stretch
ν_5	A'	1363.1 (-16.4)	1386.9 (7.4)	1380.5 (1.0)	1374.7 (-4.8)	1375.5 (-4.0)	1379.5	CH_2 bend
ν_6	A'	1300.2 (-5.0)	1316.8 (11.6)	1307.4 (2.2)	1306.4 (1.2)	1304.0 (-1.2)	1305.2	CHF bend
ν_7	A'	1135.0 (-20.4)	1157.1 (1.7)	1157.6 (2.2)	1155.0 (-0.4)	1155.7 (0.3)	1155.4	CF stretch
ν_{10}	A"	930.9 (1.8)	951.9 (22.8)	930.1 (1.0)	931.5 (2.4)	930.2 (1.1)	929.1	(oop) torsion
ν_8	A'	916.4 (-11.4)	930.2 (2.4)	927.9 (0.1)	925.9 (-1.9)	927.5 (-0.3)	927.8	CH_2 rock
ν_{11}	A"	866.4 (3.3)	875.5 (12.4)	858.3 (-4.8)	860.9 (-2.3)	854.6 (-8.5)	863.1	(oop) CH_2 (S) bend
ν_{12}	A"	710.1 (-2.3)	725.9 (13.5)	714.6 (2.2)	715.7 (3.3)	712.9 (0.5)	712.4	(oop) CH_2 (A) bend
ν_9	A'	483.5 (0.6)	486.4 (3.5)	482.8 (-0.1)	482.4 (-0.5)	480.4 (-2.5)	482.9	CCF bend
MAE		8.5	11.6	3.2	2.9	3.7	0.0	

[a] In parenthesis the signed errors are reported. Errors of harmonic frequencies computed with respect to the CCSD(T)/REF harmonic frequencies, errors of anharmonic frequencies evaluated with respect to experimental fundamentals, and Mean Absolute Error (MAE) derived by averaging over the absolute errors of each mode.

[b] The agreement between our calculations and the frequencies reported by Stoppa et al.[5] at the same computational level is within 2 cm^{-1}.

[c] (A) and (S) refer to Asymmetric and Symmetric modes, respectively, (oop) refers to out of plane bending modes.

[d] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B3LYP/SNSD level.

[e] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B2PLYP/cc-pVTZ level.

[f] Stoppa et al.[5].

[g] Geometry and second-order force constants at the CCSD(T)/cc-pVQZ level, third- and fourth-order force constants at the CCSD(T)/cc-pVTZ level.

[h] Deperturbed values (from the first to the fourth column): 3038.6, 3059.3, 3045.8, 3046.5 cm^{-1}.

TABLE VIII. Harmonic and anharmonic (GVPT2) frequencies (cm^{-1}) for cis-CHFCHBr.

				harmonic frequencies[a]				
modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ-PP	CCSD(T)/ REF	CCSD(T)/ cc-pVTZ[b]			assignments[c]
ν_1	A'	3250.3 (-7.7)	3263.4 (5.4)	3252.9 (-5.1)	3258.0			CH(Br) stretch
ν_2	A'	3211.5 (2.5)	3222.1 (13.1)	3213.4 (4.4)	3209.0			CH(F) stretch
ν_3	A'	1701.2 (6.2)	1704.9 (9.9)	1698.5 (3.5)	1695.0			CC stretch
ν_4	A'	1335.9 (-16.1)	1355.3 (3.3)	1353.6 (1.6)	1352.0			(ip) CHBr/CHF (A) bend
ν_5	A'	1235.4 (-6.6)	1250.0 (8.0)	1250.1 (8.1)	1242.0			(ip) CHBr/CHF (S) bend
ν_6	A'	1054.8 (-7.2)	1067.4 (5.4)	1068.3 (6.3)	1062.0			CF stretch
ν_{10}	A"	887.5 (5.5)	898.0 (16.0)	875.9 (-6.1)	882.0			(oop) CHBr (A) bend
ν_7	A'	745.4 (-12.6)	756.2 (-1.8)	754.4 (-3.6)	758.0			CCF bend
ν_{11}	A"	744.9 (-6.1)	755.2 (4.2)	747.7 (-3.3)	751.0			(oop) CCH (S) bend
ν_8	A'	559.0 (-17.0)	572.3 (-3.7)	572.3 (-3.7)	576.0			CBr stretch
ν_{12}	A"	429.5 (6.5)	432.7 (9.7)	419.8 (-3.2)	423.0			(oop) torsion
ν_9	A'	166.9 (-1.1)	167.0 (-1.0)	166.4 (-1.6)	168.0			CCBr bend
MAE		7.9	6.8	4.2	0.0			
				anharmonic frequencies[a]				
modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ-PP	HYB^{B3D}[d]	HYB^{B2T}[e]	CCSD(T)+MP2[bf]	exp.[b]	assignments[c]
ν_1	A'	3113.9 (-4.2)	3132.1 (14.0)	3117.4 (-0.7)	3120.1 (2.0)	3117.0 (-1.1)	3118.1	CH(Br) stretch
ν_2	A'	3087.3[g] (-4.5)	3105.5[g] (13.7)	3091.9[g] (0.1)	3095.2[g] (3.4)	3091.0 (-0.8)	3091.8	CH(F) stretch
ν_3	A'	1662.2 (10.4)	1664.4 (12.6)	1659.7 (7.9)	1656.0 (4.2)	1654.0 (2.2)	1651.8	CH(F) stretch
ν_4	A'	1308.0 (-19.5)	1329.7 (2.2)	1326.4 (-1.1)	1327.5 (0.0)	1327.0 (-0.5)	1327.5	CC stretch
ν_5	A'	1214.8 (-7.2)	1228.3 (6.3)	1229.9 (7.9)	1228.1 (6.1)	1222.0 (0.0)	1222.0	(ip) CHBr/CHF (A) bend
ν_6	A'	1035.6 (-9.8)	1048.9 (3.5)	1049.9 (4.5)	1049.5 (4.1)	1045.0 (-0.4)	1045.4	(ip) CHBr/CHF (S) bend
ν_{10}	A"	855.9 (-2.0)	874.1 (16.2)	844.2 (-13.7)	851.3 (-6.6)	859.0 (1.1)	857.9	CF stretch
ν_7	A'	736.6 (-13.5)	747.1 (-3.0)	746.2 (-3.9)	745.2 (-4.9)	751.0 (0.9)	750.1	(oop) CHBr (A) bend
ν_{11}	A"	729.0 (-1.1)	741.7 (11.6)	731.9 (1.8)	733.7 (3.6)	730.0 (-0.1)	730.1	CCF bend
ν_8	A'	550.4 (-17.8)	563.9 (-4.3)	564.4 (-3.8)	563.8 (-4.4)	568.0 (-0.2)	568.2	(oop) CCH (S) bend
ν_{12}	A"	421.4 (5.3)	426.2 (10.1)	411.5 (-4.6)	413.0 (-3.1)	416.0 (-0.1)	416.1	CBr stretch
ν_9	A'	166.6 (-0.9)	166.4 (-1.1)	166.0 (-1.5)	165.7 (-1.8)	167.0 (-0.5)	167.5	(oop) torsion
MAE		8.0	8.2	4.3	3.7	0.7	0.0	CCBr bend

[a] In parenthesis the signed errors are reported. Errors of harmonic frequencies computed with respect to the CCSD(T)/REF harmonic frequencies, errors of anharmonic frequencies evaluated with respect to experimental fundamentals, and Mean Absolute Error (MAE) derived by averaging over the absolute errors of each mode.

[b] Baldacci et al.[6].

[c] (A) and (S) refer to Asymmetric and Symmetric modes, respectively, (ip) and (oop) refer to in plane and out of plane bending modes, respectively.

[d] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B3LYP/SNSD level.

[e] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B2PLYP/cc-pVTZ-PP level.

[f] Geometry and second-order force constants at the CCSD(T)/cc-pVTZ level, third- and fourth-order force constants at the MP2/SV level (see original work for details).

[g] Deperturbed values (from the first to the fourth column): 3065.4, 3082.3, 3068.1, 3071.9 cm^{-1}.

TABLE IX. Harmonic and anharmonic (GVPT2) frequencies (cm^{-1}) for cis-CHFCHI.

modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ-PP	CCSD(T)/ REF	CCSD(T)/ cc-pVTZ-PP[b]			assignments[c]
				harmonic frequencies[a]				
ν_1	A'	3248.8 (3.8)	3257.9 (12.9)	3245.4 (0.4)	3245.0			CH(I) stretch
ν_2	A'	3203.0 (-1.0)	3213.0 (9.0)	3204.7 (0.7)	3204.0			CH(F) stretch
ν_3	A'	1691.3 (6.3)	1691.3 (6.3)	1684.7 (-0.3)	1685.0			CC stretch
ν_4	A'	1328.5 (-16.5)	1347.1 (2.1)	1345.5 (0.5)	1345.0			(ip) CHI/CHF (A) bend
ν_5	A'	1217.9 (-19.1)	1234.8 (-2.2)	1237.3 (0.3)	1237.0			(ip) CHI/CHF (S) bend
ν_6	A'	1040.4 (-12.6)	1052.3 (-0.7)	1053.0 (0.0)	1053.0			CF stretch
ν_{10}	A"	890.0 (8.0)	902.4 (20.4)	882.9 (0.9)	882.0			(oop) CHI (A) bend
ν_{11}	A"	742.0 (-5.0)	752.5 (5.5)	746.4 (-0.6)	747.0			(oop) CHI (S) bend
ν_7	A'	712.4 (-5.6)	721.3 (3.3)	717.6 (-0.4)	718.0			CCF bend
ν_8	A'	496.7 (-17.3)	514.0 (0.0)	513.1 (-0.9)	514.0			CI stretch
ν_{12}	A"	400.2 (8.2)	403.9 (11.9)	391.5 (-0.5)	392.0			(oop) torsion
ν_9	A'	150.4 (1.4)	150.3 (1.3)	149.9 (0.9)	149.0			CCI bend
MAE		8.7	6.3	0.5	0.0			
				anharmonic frequencies[a]				
modes	symm.	B3LYP/ SNSD	B2PLYP/ cc-pVTZ-PP	HYB^{B3D}[d]	HYB^{B2T}[e]	CCSD(T)-B3LYP[b,f]	exp.[b]	assignments[c]
ν_1	A'	3111.9 (3.6)	3125.5 (17.2)	3108.9 (0.6)	3111.6 (3.3)	3108.6 (0.3)	3108.3	CH(I) stretch
ν_2	A'	3075.2[g] (-6.3)	3092.6[g] (11.1)	3078.8[g] (-2.7)	3082.8[g] (1.3)	3084.5 (3.0)	3081.5	CH(F) stretch
ν_3	A'	1651.5 (14.2)	1651.0 (13.7)	1645.9 (8.6)	1643.2 (5.9)	1645.4 (8.1)	1637.3	CC stretch
ν_4	A'	1298.4 (-14.8)	1318.9 (5.7)	1315.8 (2.6)	1316.9 (3.7)	1318.4 (5.2)	1313.2	(ip) CHI/CHF (A) bend
ν_5	A'	1197.7 (-7.9)	1210.3 (4.7)	1217.7 (12.1)	1213.7 (8.1)	1213.9 (8.3)	1205.6	(ip) CHI/CHF (S) bend
ν_6	A'	1023.4 (-8.1)	1036.2 (4.7)	1037.3 (5.8)	1036.4 (4.9)	1036.9 (5.4)	1031.5	CF stretch
ν_{10}	A"	857.4 (-5.6)	878.1 (15.1)	850.4 (-12.6)	858.0 (-5.0)	859.3 (-3.7)	863.0	(oop) CHI (A) bend
ν_{11}	A"	727.6 (-1.2)	740.1 (11.3)	731.9 (3.1)	733.4 (4.6)	733.3 (4.5)	728.8	(oop) CHI (S) bend
ν_7	A'	704.0 (-8.3)	713.1 (0.8)	709.5 (-2.8)	709.2 (-3.1)	709.4 (-2.9)	712.3	CCF bend
ν_8	A'	488.5 (-18.6)	506.7 (-0.4)	505.8 (-1.3)	505.7 (-1.4)	506.0 (-1.1)	507.1	CI stretch
ν_{12}	A"	393.5 (6.5)	398.5 (11.5)	384.6 (-2.4)	385.9 (-1.1)	386.7 (-0.3)	387.0	(oop) torsion
ν_9	A'	149.7 (-0.3)	150.2 (0.2)	149.2 (-0.8)	149.8 (-0.2)	149.5 (-0.5)	150.0	CCI bend
MAE		8.0	8.0	4.6	3.6	3.6	0.0	

[a] In parenthesis the signed errors are reported. Errors of harmonic frequencies computed with respect to the CCSD(T)/REF harmonic frequencies, errors of anharmonic frequencies evaluated with respect to experimental fundamentals, and Mean Absolute Error (MAE) derived by averaging over the absolute errors of each mode.

[b] Baldacci et al.[7].

[c] (A) and (S) refer to Asymmetric and Symmetric modes, respectively, (oop) refers to out of plane bending modes.

[d] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B3LYP/SNSD level.

[e] Harmonic frequencies at the CCSD(T)/REF level, cubic and semi-diagonal quartic force constants at the B2PLYP/cc-pVTZ-PP level.

[f] Geometry and second-order force constants at the CCSD(T)/cc-pVTZ-PP level, third- and fourth-order force constants at the B3LYP/cc-pVTZ level.

[g] Deperturbed values (from the first column to the fourth): 3054.8, 3071.2, 3057.2, 3061.2 cm^{-1}.

TABLE X. Integrated cross section (km/mol) of CH_2F_2.

range (cm^{-1})	main transition	B3LYP/ SNSD	B2PLYP/ cc-pVTZ	CCSD(T)/ REF		
		harmonic integrated cross section				
425-625	ν_4	4.65	4.63	5.20		
850-945	$\nu_8+\nu_4$	-	-	-		
945-1250	ν_9,ν_3,ν_7	378.46	355.99	359.24		
1250-1290	ν_5	0.00	0.00	0.00		
1371-1475	ν_8	10.04	17.87	13.54		
1478-1550	ν_2	0.12	0.88	0.23		
1580-1690	$\nu_4+\nu_3$	-	-	-		
2060-2300	$\nu_9+\nu_3$	-	-	-		
2400-2580	$\nu_9+\nu_8$	-	-	-		
2580-2737	$\nu_5+\nu_8$	-	-	-		
2737-3151	ν_1,ν_6	67.21	86.97	64.66		
3151-3320	$3\nu_9$	-	-	-		
3850-4286	$\nu_3+\nu_6$	-	-	-		
4286-4600	$\nu_2+\nu_6$	-	-	-		
5100-5400	not available	-	-	-		
5725-5925	$\nu_1+\nu_6,2\nu_6$	-	-	-		
MAE[a]		4.32	5.19	0.00		
		anharmonic integrated cross section				
range (cm^{-1})	main transition	B3LYP/ SNSD	B2PLYP/ cc-pVTZ	HYB^{B3D}[b]	HYB^{B2T}[c]	exp.[d]
425-625	ν_4	4.36	4.38	4.90	4.95	4.97
850-945	$\nu_8+\nu_4$	0.00	0.00	0.00	0.00	0.17
945-1250	ν_9,ν_3,ν_7	377.35	355.08	358.12	358.32	337
1250-1290	ν_5	0.00	0.00	0.00	0.00	0.149
1371-1475	ν_8	7.96	14.80	11.46	10.47	10.03
1478-1550	ν_2	0.24	0.81	0.14	0.15	0.38
1580-1690	$\nu_4+\nu_3$	0.37	0.56	0.37	0.56	0.56
2060-2300	$\nu_9+\nu_3$	5.74	5.30	5.74	5.30	5.37
2400-2580	$\nu_9+\nu_8$	0.36	0.48	0.36	0.48	0.64
2580-2737	$\nu_5+\nu_8$	0.10	0.90	0.10	0.90	0.46
2737-3151	ν_1,ν_6	75.03	92.50	72.48	70.20	67.3
3151-3320	$3\nu_9$	0.00	0.00	0.00	0.00	0.30
3850-4286	$\nu_3+\nu_6$	2.18	2.13	2.18	2.13	2.4
4286-4600	$\nu_2+\nu_6$	1.62	1.77	1.62	1.77	2.1
5100-5400	not available	0.00	0.00	0.00	0.00	0.5
5725-5925	$\nu_1+\nu_6,2\nu_6$	1.15	0.60	1.15	0.60	0.6
MAE[f]		3.40	3.22	1.98	5.58	0.0

[a] MAE of harmonic calculations evaluated with respect to the CCSD(T)/REF data.
[b] Harmonic intensities of fundamental modes empirically corrected at the CCSD(T)/AVQZ+CV level, B3LYP/SNSD intensities for all other modes.
[c] Harmonic intensities of fundamental modes empirically corrected at the CCSD(T)/AVQZ+CV level, B2PLYP/cc-pVTZ intensities for all other modes.
[d] Tasinato et al.[1].
[f] MAE of anharmonic calculations evaluated with respect to the experimental data.

TABLE XI. Integrated cross sections (km/mol) of CF_3Br.

range (cm^{-1})	main transitions	B3LYP/ SNSD	B2PLYP/ cc-pVTZ-PP	CCSD(T)/ REF		
		harmonic integrated cross sections				
500-600	ν_5	1.45	2.49	2.49		
670-715	$2\nu_3$	-	-	-		
720-790	ν_2	44.33	44.96	37.23		
810-880	$\nu_5+\nu_6$	-	-	-		
1040-1150	ν_1	508.92	521.06	482.37		
1150-1250	ν_4	531.32	537.22	498.24		
1250-1360	$\nu_5+\nu_2$	-	-	-		
1360-1800	$\nu_1+\nu_2$	-	-	-		
1800-1910	$\nu_4+\nu_2$	-	-	-		
1940-2000	not available	-	-	-		
2120-2480	$\nu_4+\nu_1$	-	-	-		
MAE[a]		16.94	21.35	0.00		
		anharmonic integrated cross sections				
range (cm^{-1})	main transitions	B3LYP/ SNSD	B2PLYP/ cc-pVTZ-PP	HYB^{B3D} [b]	HYB^{B2T} [c]	exp.[d]
500-600	ν_5	1.59	2.30	2.63	2.30	2.29
670-715	$2\nu_3$	1.43	1.82	1.43	1.82	2.28
720-790	ν_2	39.39	39.89	32.29	32.16	33.72
810-880	$\nu_5+\nu_6$	0.76	0.75	0.76	0.75	0.90
1040-1150	ν_1	506.24	517.57	479.68	478.88	468.52
1150-1250	ν_4	515.50	522.56	482.42	483.57	473.94
1250-1360	$\nu_5+\nu_2$	6.49	7.90	6.49	7.90	7.52
1360-1800	$\nu_1+\nu_3$	3.33	3.19	3.33	3.19	3.76
1800-1910	$\nu_1+\nu_2$	0.61	0.93	0.61	0.93	1.07
1940-2000	$\nu_4+\nu_2$	0.00	0.64	0.00	0.64	0.79
2120-2480	$\nu_4+\nu_1$	9.97	10.81	9.97	10.81	8.98[e]
MAE[f]		8.21	9.78	2.37	2.29	0.00

[a] MAE of harmonic calculations evaluated with respect to the CCSD(T)/REF data.
[b] Harmonic intensities of fundamental modes empirically corrected at the CCSD(T)/AVTZ-PP level, B3LYP/SNSD intensities for all other modes.
[c] Harmonic intensities of fundamental modes empirically corrected at the CCSD(T)/AVTZ-PP level, B2PLYP/cc-pVTZ intensities for all other modes.
[d] Pietropolli Charmet et al.[8].
[e] Experimental intensities in the [2120-2240] cm^{-1} (0.75 km/mol), [2240-2340] cm^{-1} (4.32 km/mol), and [2340-2480] cm^{-1} (3.91 km/mol) ranges have been summed in order to facilitate the assignment of the transitions.
[f] MAE of anharmonic calculations evaluated with respect to the experimental data.

TABLE XII. Integrated cross section (km/mol) of CH_2CHF.

range (cm^{-1})	main transition	B3LYP/ SNSD	B2PLYP/ cc-pVTZ	CCSD(T)/ REF		
		harmonic integrated cross section				
420-580	ν_9	3.90	4.14	4.10		
610-1050	ν_{11},ν_8,ν_{10}	134.80	122.50	118.61		
1050-1250	ν_7	104.12	94.53	91.88		
1250-1480	$\nu_9+\nu_8,\nu_5,\nu_6$	6.64	6.95	7.87		
1520-1720	ν_4	109.26	103.05	96.15		
2000-2200	$\nu_8+\nu_7$	0.00	0.00	0.00		
2900-3420	ν_2,ν_1	7.06	9.74	6.60		
MAE[a]		7.24	2.92	0.00		
		anharmonic integrated cross section				
range (cm^{-1})	main transition	B3LYP/ SNSD	B2PLYP/ cc-pVTZ	CCSD(T)/ cc-pVTZ[b]	HYB^{B3D} [c]	HYB^{B2T} [d]	exp.[e]
420-580	ν_9	3.98	4.21	4.33	4.18	4.17	4.30
610-1050	ν_{11},ν_8,ν_{10}	135.84	122.02	113.55	119.64	118.13	110.4
1050-1250	ν_7	103.54	94.75	84.86	91.31	92.10	77.9
1250-1480	$\nu_9+\nu_8,\nu_5,\nu_6$	6.02	6.54	10.25	8.54	7.46	7.48
1520-1720	ν_4	107.81	103.42	80.85	94.70	96.53	83.7
2000-2200	$\nu_8+\nu_7$	2.03	1.86	0.00	2.03	1.86	2.14
2900-3420	ν_2,ν_1	9.83	13.03	10.91	9.37	9.89	9.57
MAE[f]		11.05	7.57	2.57	5.02	5.07	0.00

[a] MAE of harmonic calculations evaluated with respect to the CCSD(T)/REF data.
[b] Fundamental modes only.
[c] Harmonic intensities of fundamental modes empirically corrected at the CCSD(T)/REF level, B3LYP/SNSD intensities for all other modes.
[d] Harmonic intensities of fundamental modes empirically corrected at the CCSD(T)/REF level, B2PLYP/cc-pVTZ intensities for all other modes.
[e] Stoppa et al.[5].
[f] MAE of anharmonic calculations evaluated with respect to the experimental data.

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