

Electronic Supplementary Information for Paper B202865D :

Anharmonic force field, structure, and thermochemistry of CF₂ and CCl₂.

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Table S1. Quadratic, cubic, and quartic force constants of CF₂ in dimensionless normal coordinates (all values in cm⁻¹)

Constant	Value	Constant	Value
ω_1	1251.68	1111	32.69
ω_2	677.99	1112	32.61
ω_3	1146.32	1122	-0.13
111	-258.35	1133	109.71
112	-75.41	1222	5.41
122	-30.01	1233	27.72
133	-391.25	2222	21.77
222	-111.16	2233	-18.48
233	-61.46	3333	114.82

^a CCSD(T)(ae)/cc-pwCVQZ for the quadratic and cubic constants
CCSD(T)(ae)/cc-pCVTZ for the quartic constants

Table S2. Quadratic, cubic, and quartic force constants of CCl₂ in dimensionless normal coordinates (all values in cm⁻¹)

Constant	MP2 ^a	CCSD(T) ^b	Constant	MP2 ^a	CCSD(T) ^b
ω_1	760.96	735.33	1111	-1.73	-2.77
ω_2	350.44	335.93	1112	19.03	18.25
ω_3	799.76	769.62	1122	1.17	1.87
111	-92.88	-91.75	1133	61.07	60.03
112	-51.94	-49.28	1222	-0.80	-0.49
122	-9.02	-9.76	1233	12.85	11.62
133	-248.51	-234.57	2222	6.79	6.92
222	-40.73	-41.82	2233	-10.10	-10.26
233	-33.61	-36.69	3333	61.52	9.15

^a MP2(fc)/cc-pVQZ+1

^b Harmonic wavenumbers from CCSD(T)(ae)/cc-pCVTZ+aug(Cl) and anharmonic constants from CCSD(T)(ae)/cc-pCVTZ

Table S3. Thermochemical properties of CF₂.

T K	$H(T) - H(0)$ kJ mol ⁻¹	C_p J mol ⁻¹ K ⁻¹	S J mol ⁻¹ K ⁻¹
180	6.03	34.55	222.47
200	6.73	35.14	226.14
220	7.43	35.81	229.52
250	8.53	36.93	234.17
298.15	10.35	38.92	240.84
400	14.53	43.11	252.87
500	19.02	46.58	262.88
600	23.82	49.25	271.62
800	34.06	52.81	286.32
1000	44.85	54.92	298.35
1200	55.98	56.29	308.49
1500	73.08	57.63	321.21
2000	102.27	59.04	337.99
2500	132.06	60.09	351.28
3000	162.34	61.05	362.32

Table S4. Thermochemical properties of CCl₂.

T K	$H(T) - H(0)$ kJ mol ⁻¹	C_p J mol ⁻¹ K ⁻¹	S J mol ⁻¹ K ⁻¹
180	6.34	39.68	243.57
200	7.14	40.96	247.82
220	7.98	42.21	251.78
250	9.27	44.01	257.29
298.15	11.45	46.58	265.27
400	16.42	50.62	279.56
500	21.62	53.17	291.15
600	27.02	54.87	301.01
800	38.23	56.94	317.11
1000	49.75	58.18	329.96
1200	61.47	59.05	340.64
1500	79.35	60.06	353.93
2000	109.74	61.46	371.41
2500	140.86	62.89	385.29
3000	172.65	64.32	396.89