Prepared for PCCP

Supporting Information for

Atmospheric Chemistry of Hexa- and Penta-Fluorobenzene: UV Photolysis and Kinetics and Mechanisms of the reactions of Cl atoms and OH radicals

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Section S1: Calculated IR spectrum for oxidation products

All calculations at B3LYP/6-31+G(d,p) level using GAUSSIAN 09 Revision D.01.

S1.1 Molecule: *anti*-F(O)C-C(O)F

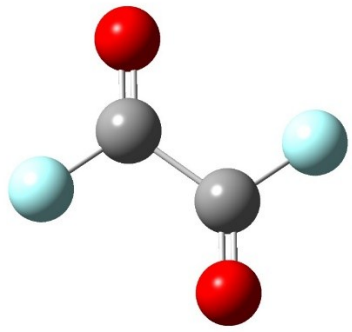

Table S1: Coordinates for the B3LYP/6-31+G(d,p) optimized structure of *anti*-F(O)C-C(O)F (Ångstrøm).

Atom	X	Y	Z
C	0.75346300	-0.14979200	-0.00063800
C	-0.75346300	0.14979200	-0.00070000
F	1.44371900	0.99952300	0.00038500
F	-1.44371900	-0.99952300	0.00039500
O	1.25894700	-1.22226200	0.00005600
O	-1.25894700	1.22226200	0.00007100

E = -426.329453 Hartree

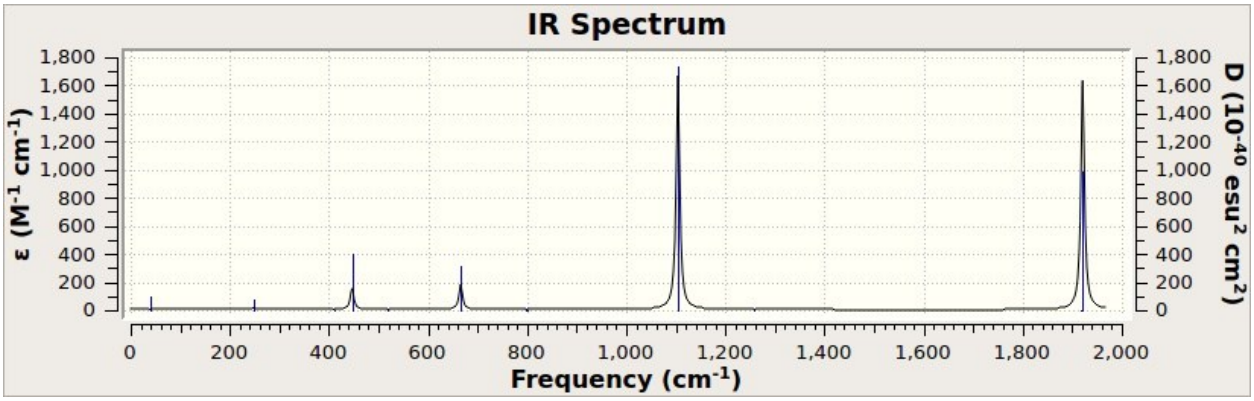

Figure S1: IR spectrum of *anti*-F(O)C-C(O)F calculated at the B3LYP/6-31+G(d,p)

S1.2 Molecule: *syn*-F(O)C-C(O)F

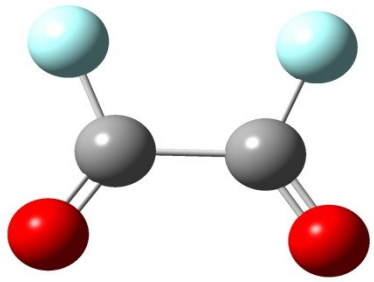

Table S2: Coordinates for the B3LYP/6-31+G(d,p) optimized structure of *syn*-F(O)C-C(O)F (Ångstrøm).

Atom	X	Y	Z
C	0.00000000	0.76923400	0.14742200
C	0.00000000	-0.76923400	0.14742200
F	0.00000000	-1.27347800	-1.09824600
O	0.00000000	-1.43799600	1.12496100
F	0.00000000	1.27347800	-1.09824600
O	0.00000000	1.43799600	1.12496100

E = -426.328834 Hartree

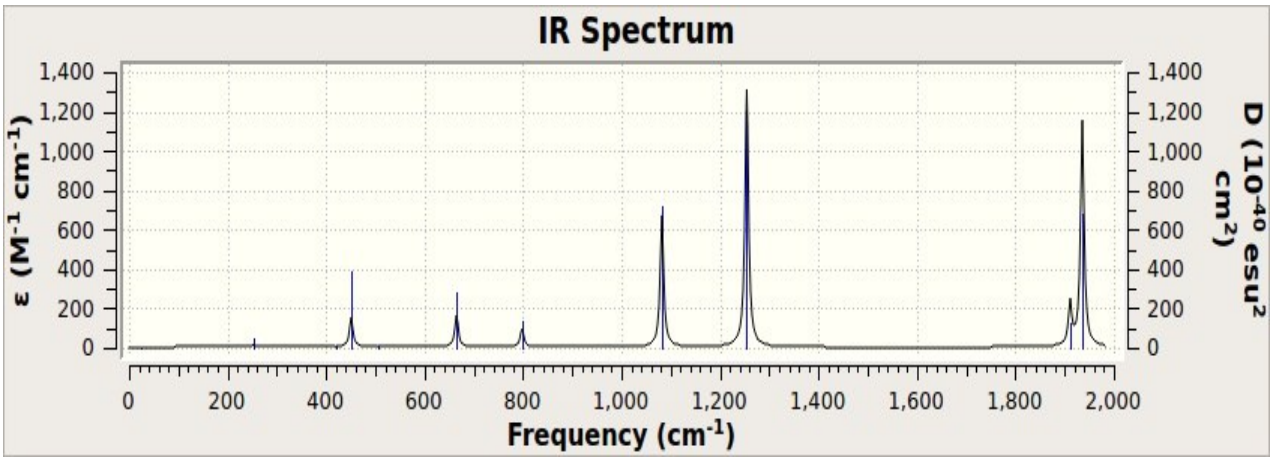

Figure S2: IR spectrum of *syn*-F(O)C-C(O)F calculated at the B3LYP/6-31+G(d,p) level.

S1.3 Molecule: *anti*-F(O)C-C(O)H

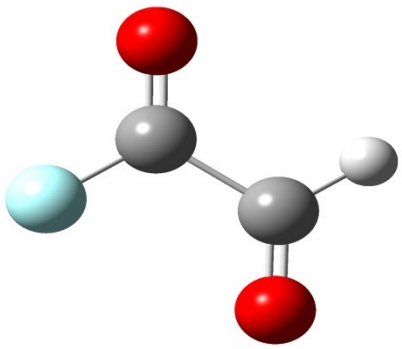

Table S3: Coordinates for the B3LYP/6-31+G(d,p) optimized structure of *anti*-F(O)C-C(O)H (Ångstrøm).

Atom	X	Y	Z
C	0.55255600	-0.09464900	0.00003600
C	-0.89608100	-0.59988000	-0.00005800
F	0.63776000	1.24698400	-0.00001200
O	1.51030100	-0.80392000	0.00000200
O	-1.84981900	0.13476700	0.00002400
H	-0.96254500	-1.70246400	0.00003700

E = -327.065213 Hartree

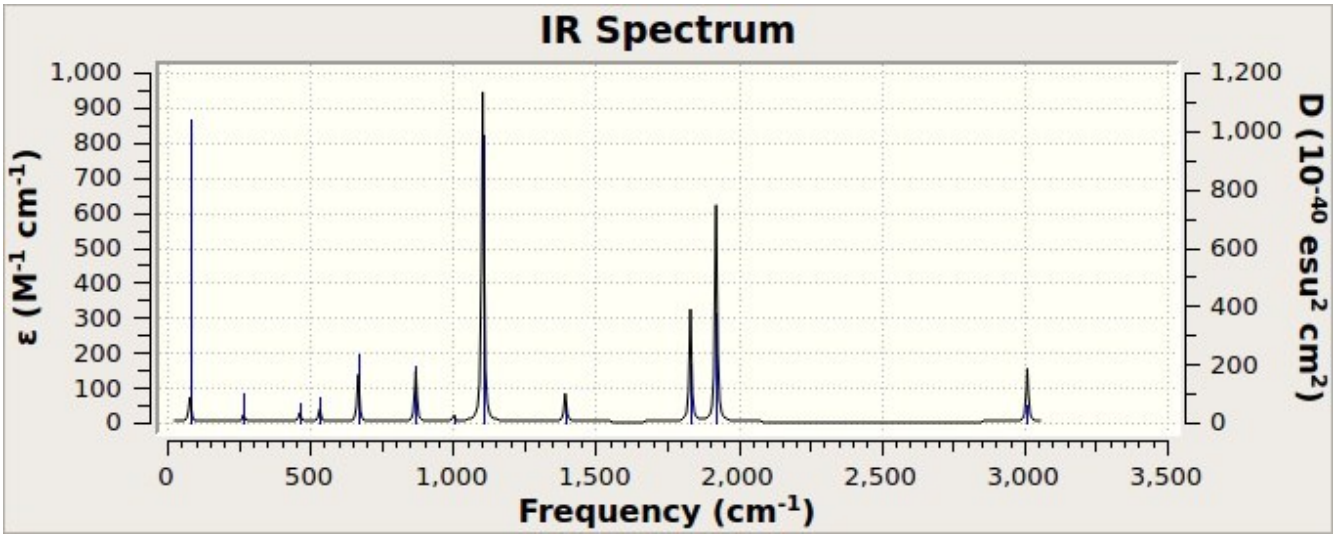

Figure S3: IR spectrum of *anti*-F(O)C-C(O)H calculated at the B3LYP/6-31+G(d,p) level.

S1.4 Molecule: *syn*-F(O)C-C(O)H

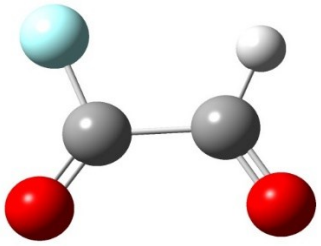

Table S4: Coordinates for the B3LYP/6-31+G(d,p) optimized structure of *syn*-F(O)C-C(O)H (Ångstrøm).

Atom	X	Y	Z
C	-0.47443100	0.14375500	-0.00002200
C	0.90475900	-0.54034400	0.00004200
F	-1.45006600	-0.81030100	-0.00018100
O	-0.71796500	1.30325300	0.00001500
O	1.91606200	0.11132900	0.00017800
H	0.88384700	-1.64440900	-0.00003400

E = -327.063767 Hartree

Figure S4: IR spectrum of *syn*-F(O)C-C(O)H calculated at the B3LYP/6-31+G(d,p) level.

S1.5 Molecule: F(O)C-CF=CF-C(O)F, isomer 1

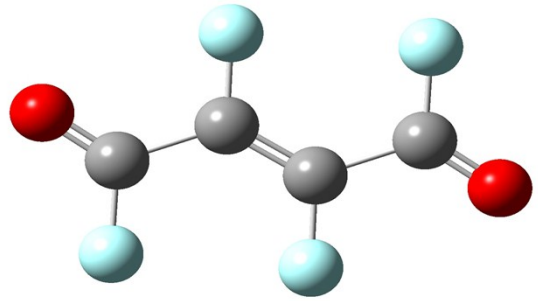

Table S5: Coordinates for the B3LYP/6-31+G(d,p) optimized structure of F(O)C-CF=CF-C(O)F, isomer 1 (Ångstrøm).

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.49016811
C	1.06516771	0.00000000	2.32211729
C	1.06516771	0.00000000	3.81228540
O	2.04170168	0.00000000	4.49139371
O	-0.97653396	-0.00000000	-0.67910831
F	1.24492999	0.00000000	-0.51698555
F	-1.23781271	-0.00000000	1.98252076
F	2.30298043	0.00000000	1.82976464
F	-0.17976227	0.00000000	4.32927096

E = -702.188633 Hartree

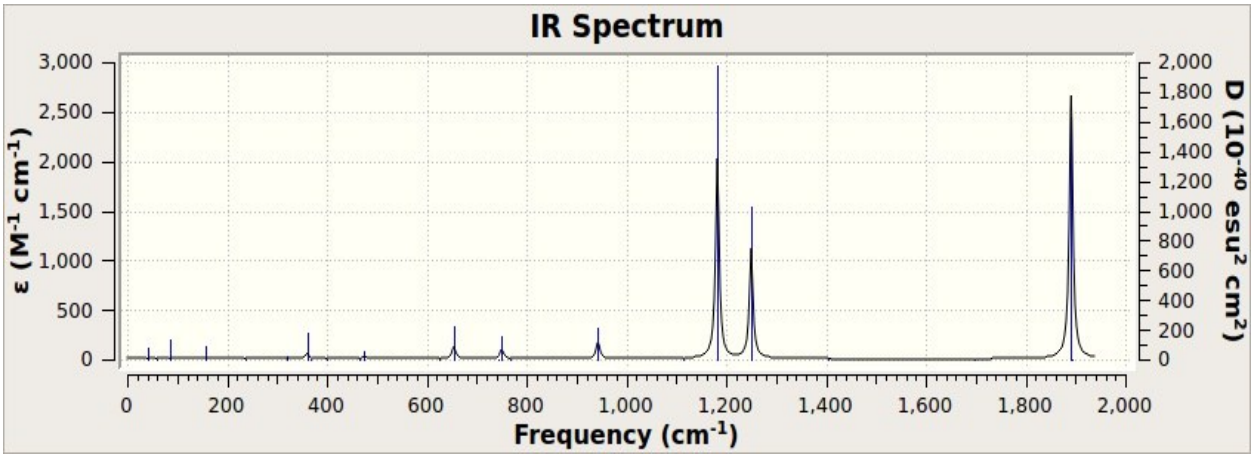

Figure S5: IR spectrum of F(O)C-CF=CF-C(O)F, isomer 1, calculated at the B3LYP/6-31+G(d,p) level.

S1.6 Molecule: F(O)C-CF=CF-C(O)F, isomer 2

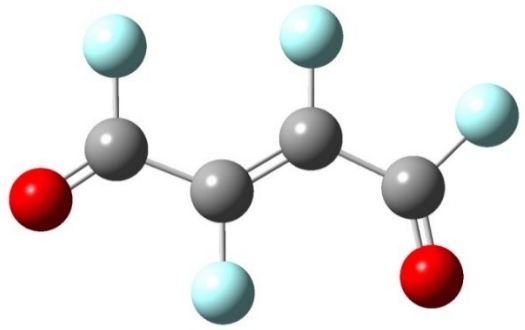

Table S6: Coordinates for the B3LYP/6-31+G(d,p) optimized structure of F(O)C-CF=CF-C(O)F, isomer 2 (Ångstrøm).

Atom	X	Y	Z
C	-1.99702000	-0.02041300	0.00000500
C	-0.57907300	0.43313500	0.00001300
C	0.53916300	-0.32680700	-0.00000300
C	1.92211900	0.22374300	-0.00001100
F	-2.10855100	-1.36534300	0.00005600
F	-0.47557400	1.75882500	0.00000200
F	0.45687800	-1.65770400	-0.00002300
F	2.82549500	-0.78264200	-0.00002300
O	-2.94261600	0.70100600	-0.00005600
O	2.24319600	1.36947300	0.00003900

E = -702.188782 Hartree

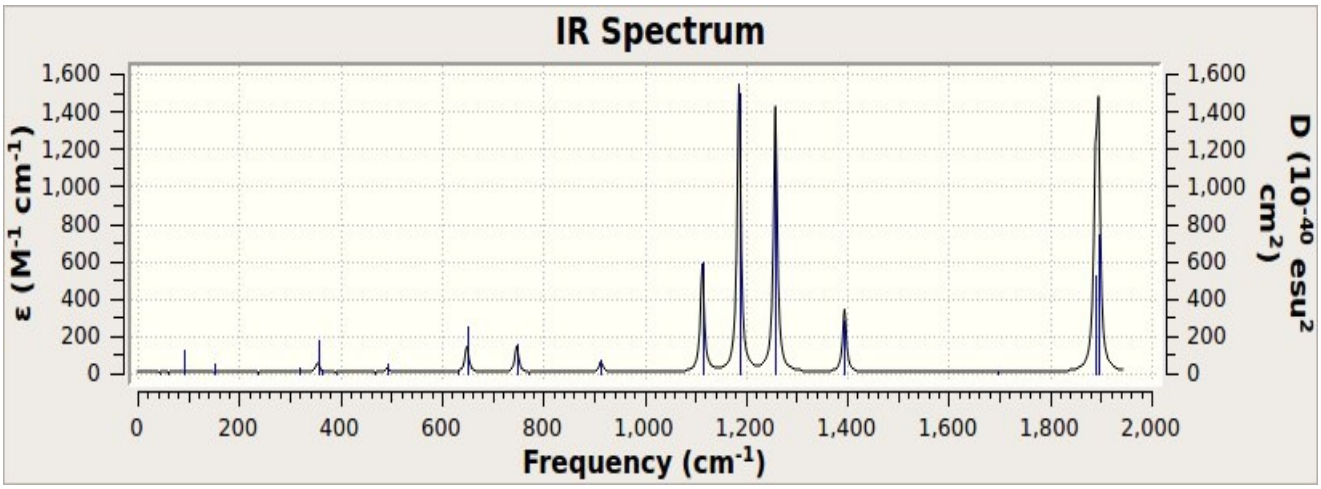

Figure S6: IR spectrum of F(O)C-CF=CF-C(O)F, isomer 2, calculated at the B3LYP/6-31+G(d,p) level.

S1.7 Molecule: F(O)C-CF=CF-C(O)F, isomer 3

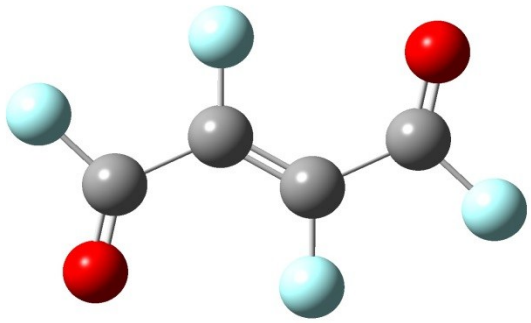

Table S7: Coordinates for the B3LYP/6-31+G(d,p) optimized structure of F(O)C-CF=CF-C(O)F, isomer 3 (Ångstrøm).

Atom	X	Y	Z
C	-1.93310600	0.25397200	0.00000500
C	-0.57569700	-0.35456500	-0.00000400
C	0.57570600	0.35456700	-0.00001500
C	1.93310300	-0.25397500	-0.00003000
F	-2.87920200	-0.71159800	0.00001600
F	-0.53976300	-1.68508800	-0.00000500
F	0.53978400	1.68509000	-0.00001900
F	2.87919400	0.71159900	0.00003800
O	-2.20291900	1.41316300	0.00000200
O	2.20289900	-1.41316700	-0.00000200

E = -702.188919 Hartree

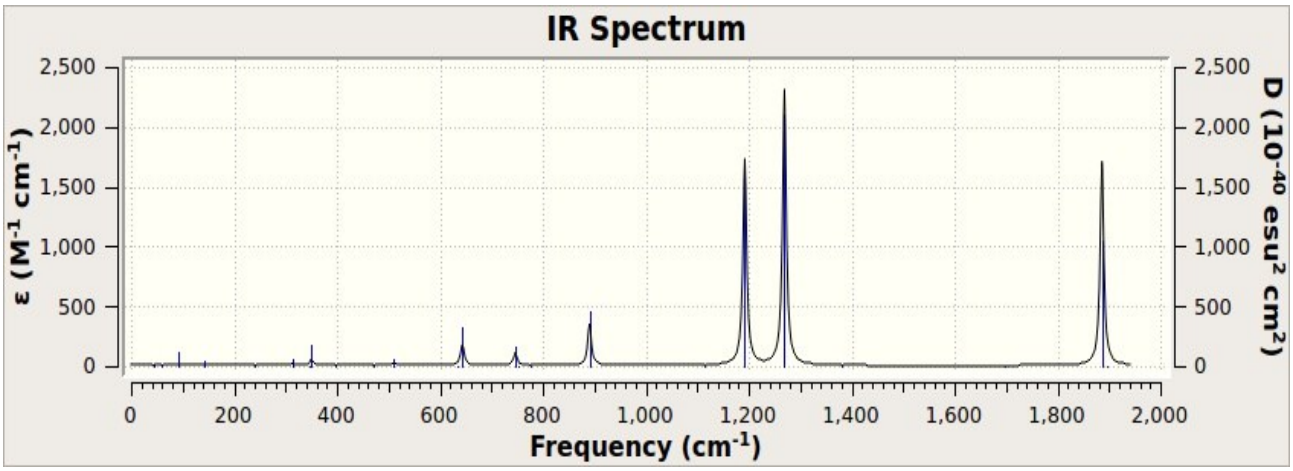

Figure S7: IR spectrum of F(O)C-CF=CF-C(O)F, isomer 3, calculated at the B3LYP/6-31+G(d,p) level.

Section S2: Calculated IR spectrum for reactants

All calculations at B3LYP/6-31+G(d,p) level using GAUSSIAN 09 Revision D.01.

S2.1 Molecule: Hexafluorobenzene

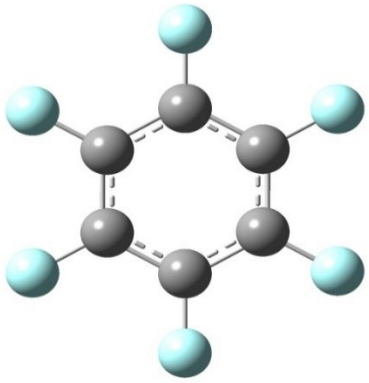

Table S8: Coordinates for the B3LYP/6-31+G(d,p) optimized structure of hexafluorobenzene (Ångstrøm).

Atom	X	Y	Z
C	-1.37806900	-0.20945600	-0.00000400
C	-0.50763100	-1.29829800	0.00001100
C	0.87053600	-1.08879800	0.00001600
C	1.37806900	0.20945600	0.00000400
C	0.50763100	1.29829800	-0.00001100
C	-0.87053600	1.08879800	-0.00001600
F	-2.70112900	-0.41054000	-0.00000900
F	-0.99531500	-2.54462900	0.00002200
F	1.70655400	-2.13385400	0.00003100
F	2.70112900	0.41054000	0.00000800
F	0.99531500	2.54462900	-0.00002200
F	-1.70655400	2.13385400	-0.00003100

E = -827.604288 Hartree

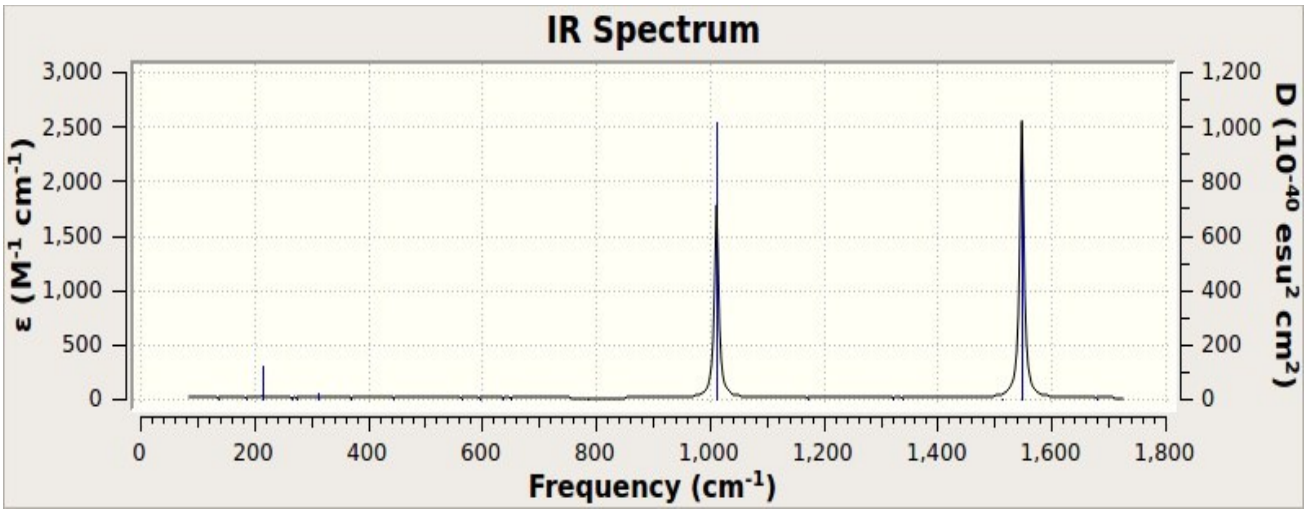

Figure S8: IR spectrum of hexafluorobenzene calculated at the B3LYP/6-31+G(d,p) level.

Tabel S9: IR intensities of hexafluorobenzene calculated at the B3LYP/6-31+G(d,p) level.

Wavenumber region	Integrated Cross Section (cm/molecule)[a]
950-1050 cm^{-1}	8.6×10^{-17}
1500-1580 cm^{-1}	1.2×10^{-16}

[a] Sum of all transitions in the given region, calculated in km/mol and converted.

S2.2 Molecule: Pentafluorobenzene

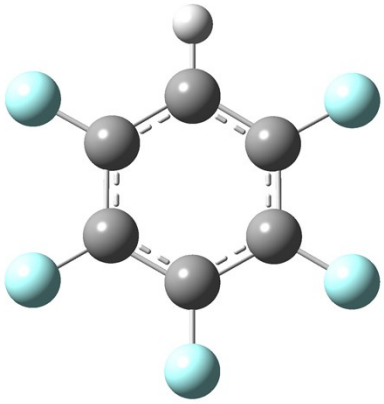

Table S10: Coordinates for the B3LYP/6-31+G(d,p) optimized structure of pentafluorobenzene (Ångstrøm).

Atom	X	Y	Z
C	-1.19383700	-0.96826000	-0.00001100
C	-1.20954000	0.42516300	-0.00002700
C	0.00000000	1.11961000	0.00000100
C	1.20955800	0.42512300	-0.00001600
C	1.19383600	-0.96826200	-0.00003100
C	-0.00002100	-1.67969100	0.00000700
H	0.00000800	-2.76293500	0.00003100
F	-2.36707900	-1.62592000	0.00001400
F	-2.36769200	1.09948700	0.00000200
F	0.00005400	2.45748000	0.00001400
F	2.36768200	1.09949600	0.00000700
F	2.36703600	-1.62600600	0.00001200

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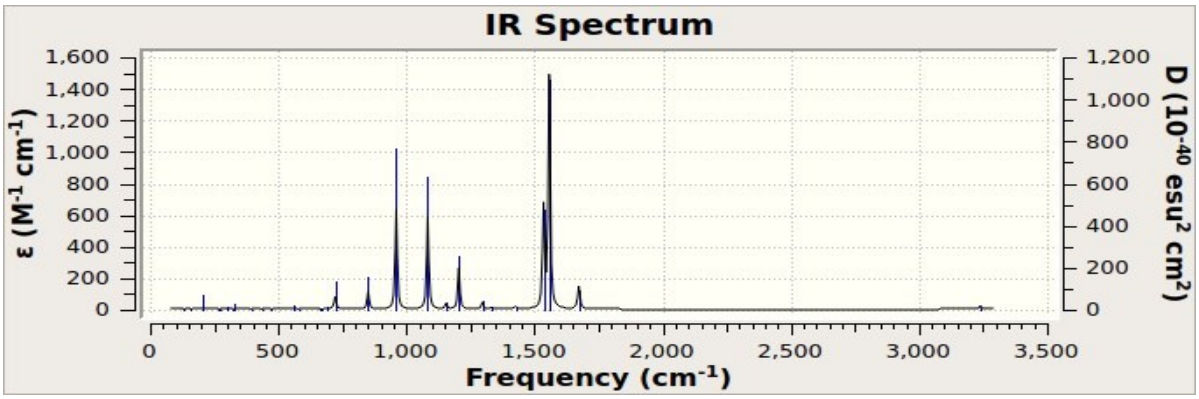

Figure S9: IR spectrum of pentafluorobenzene calculated at the B3LYP/6-31+G(d,p) level.

Tabel S11: IR intensities of pentafluorobenzene calculated at the B3LYP/6-31+G(d,p) level.

Wavenumber region	Integrated Cross Section (cm/molecule)[a]
650-1350 cm^{-1}	8.7×10^{-17}
1450-1600 cm^{-1}	1.0×10^{-16}
1600-1700 cm^{-1}	7.4×10^{-18}

[a] Sum of all transitions in the given region, calculated in km/mol and converted.