Electronic Supplementary Material (ESI) for New Journal of Chemistry.

First Principle Quantum Chemical Studies on the Atmospheric Oxidation of HFC-C1436 with OH radical

R. Bhuvaneswari [a, b] and K. Senthilkumar*, [b]

[a] Department of Physics, Vellalar College For Women, Erode, India-638 012.

[b] Department of Physics, Bharathiar University, Coimbatore, India-641 046.

*Corresponding author: Fax No: +91-422-2422387, E-Mail: ksenthil@buc.edu.in

Supporting Information

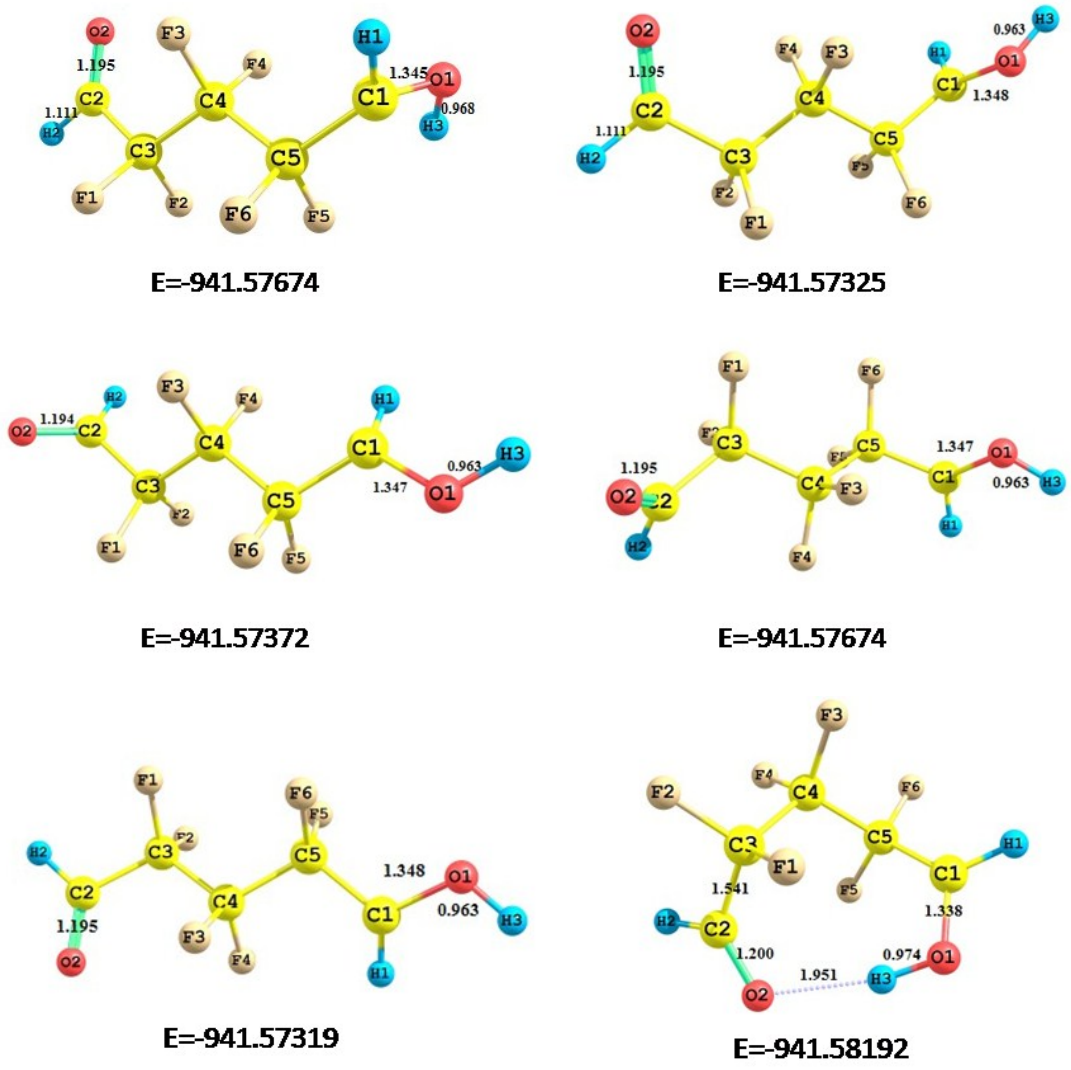


Fig S1: Optimized geometry of the conformers of I6 with the energy values

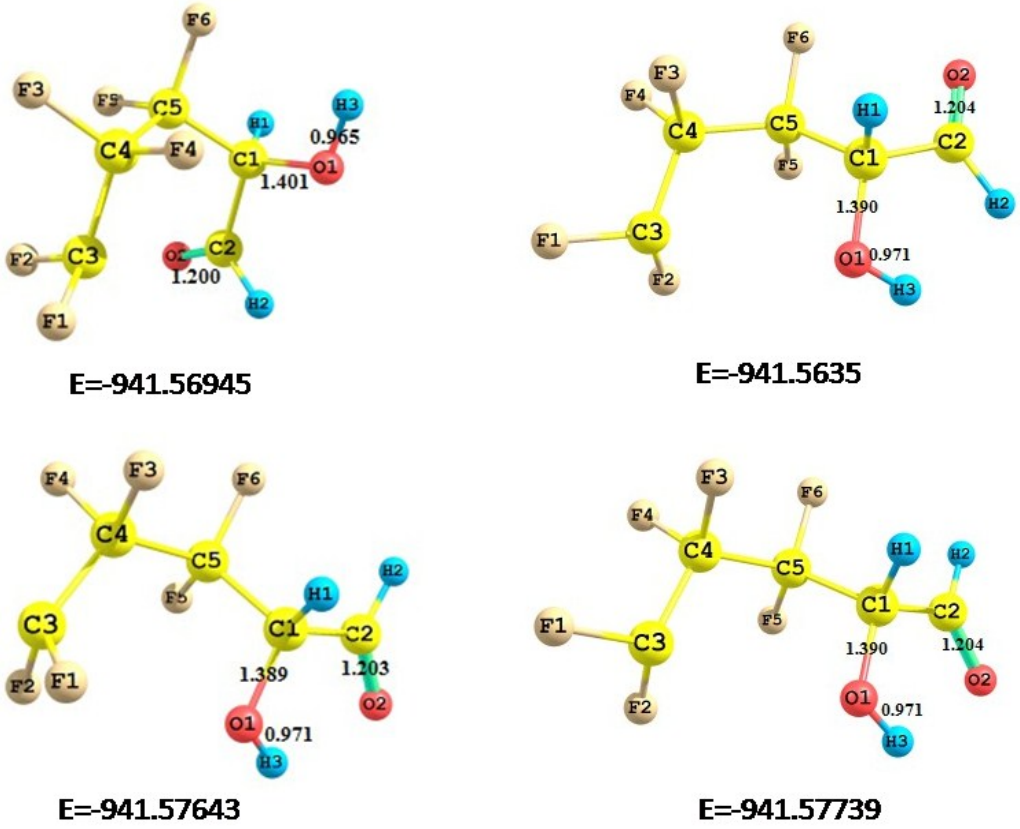
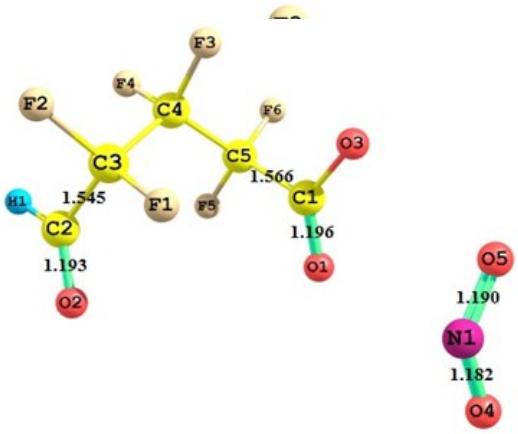


Fig S2: Optimized geometry of the conformers of I20 with the energy values

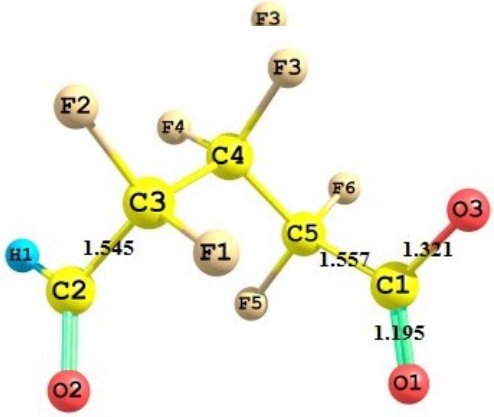
Table S1: Relative energies ΔE_{Tot} (kcal/mol), enthalpy ΔH_{298} (kcal/mol) and Gibbs free energy ΔG_{298} (kcal/mol) for the Unimolecular decomposition pathway-A of alkoxy radical, I4 calculated at M06-2X, ωB97XD and CCSD(T) levels of theory.

Stationary points	M06-2X/ aug-cc-pvDZ			ωB97XD/ aug-cc-pvDZ			CCSD(T)/aug-cc-pvDZ// M06-2X/ aug-cc-pvDZ
	ΔE_{Tot}	ΔH_{298}	ΔG_{298}	ΔE_{Tot}	ΔH_{298}	ΔG_{298}	ΔE_{Tot}
I5	0	0	0	0	0	0	0
TS7	7.66	6.46	5.28	6.9	5.77	5.42	6.77
I6	-0.25	-2.2	0.55	-1.13	-2.88	-2.82	-1.04
I6+O_2	0	0	0	0	0	0	0
TS8	5.66	4.71	6.22	5.14	4.83	4.97	5.85
P4+HO_2	-13.24	-12.42	-8.47	-15.85	-14.72	-11.34	-13.57
P4+OH	0	0	0	0	0	0	0
TS9	4.64	2.38	2.66	0.88	0.19	0.26	-5.29
I7+H_2O	-25.29	-24.66	-24.00	-25.04	-24.35	-24.69	-24.26
I7+O_2	0	0	0	0	0	0	0
I8	-31.5	-28.87	-24.70	-29.30	-26.54	-23.27	-29.88
I8+NO	0	0	0	0	0	0	0
I9+NO_2	-14.23	-14.02	-12.11	-13.58	-13.17	-12.44	-14.46
I9	0	0	0	0	0	0	0
TS10	1.51	0.38	0.84	2.89	2.2	2.09	0.96
I10+CO_2	-26.79	-27.30	-30.72	-25.35	-25.6	-30.53	-27.55
I10+O_2	0	0	0	0	0	0	0
I11	-30.97	-30.14	-27.23	-31.21	-30.79	-28.85	-31.66
I11+NO	0	0	0	0	0	0	0
I12+NO_2	-13.37	-13.24	-12.08	-12.57	-12.11	-11.58	-13.32
I12	0	0	0	0	0	0	0
TS11	6.78	5.65	5.45	5.15	4.08	3.75	4.9

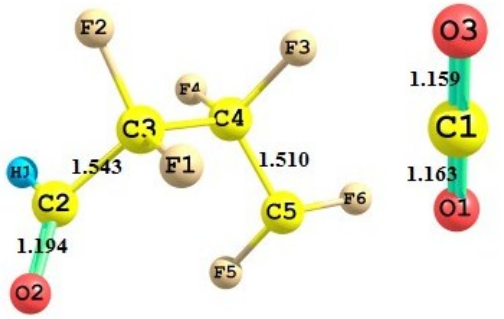
I13+COF_2	-7.59	-8.35	-4.22	-9.54	-10.35	-6.51	-9.28
I13+O_2	0	0	0	0	0	0	0
I14	-37.84	-35.39	-30.35	-33.63	-30.81	-26.81	-35.75
I14+NO	0	0	0	0	0	0	0
I15+NO_2	-11.61	-11.92	-11.17	-17.07	-16.5	-14.5	-13.06
I15	0	0	0	0	0	0	0
TS12	3.39	2.26	2.29	2.32	1.38	1.14	1.12
I16+COF_2	-20.08	-20.14	-18.85	-21.34	-21.46	-20.95	-21.78
I16+O_2	0	0	0	0	0	0	0
I17	-24.41	-22.59	-19.71	-21.39	-19.18	-19.04	-24.77
I17+NO	0	0	0	0	0	0	0
I18+NO_2	-19.14	-20.14	-20.10	-22.61	-22.92	-21.87	-18.69
I18	0	0	0	0	0	0	0
TS13	2.54	1.33	2.11	1.88	-0.06	-0.26	2.31
I19+COF_2	-7.4	-8.53	-5.40	-5.77	-7.78	-11.56	-6.57
I19+O_2	0	0	0	0	0	0	0
TS14	3.51	2.38	4.47	2.13	1.51	4.62	3.10
CO+HO_2	-35.89	-33.98	-33.62	-32.38	-30.18	-29.39	-35.21



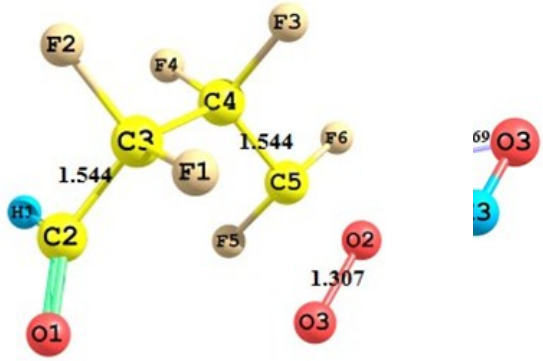
I9+NO_2



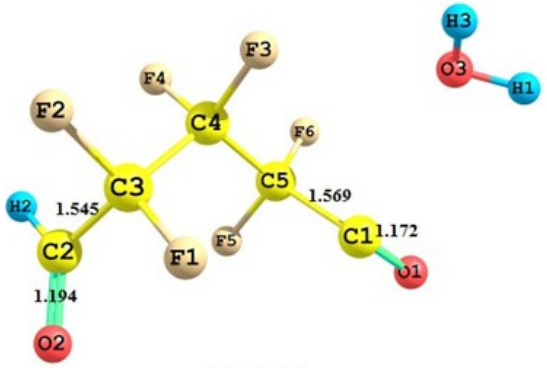
I9



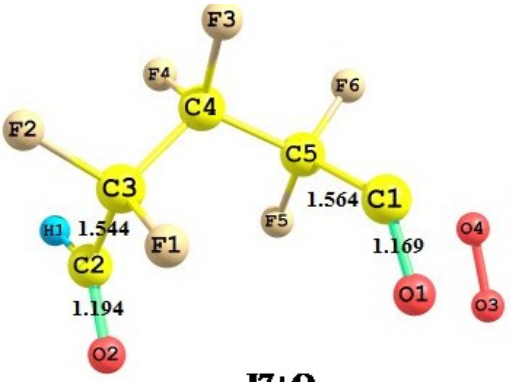
I10+CO_2



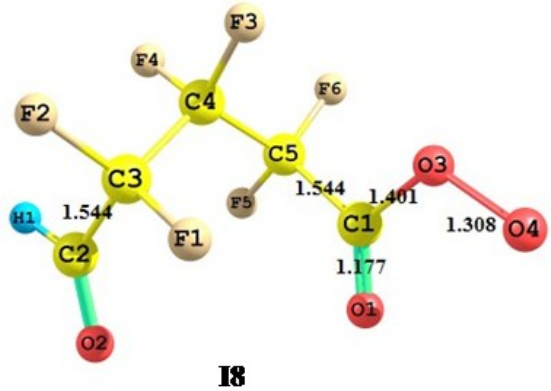
I10+O_2



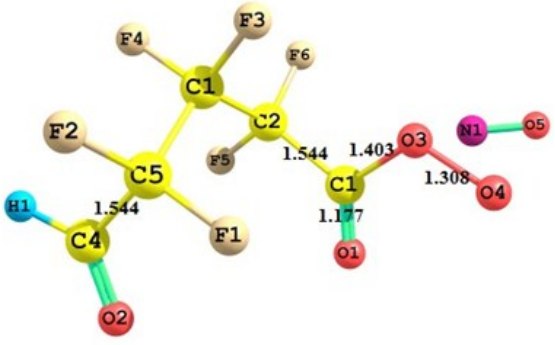
I7+H_2O



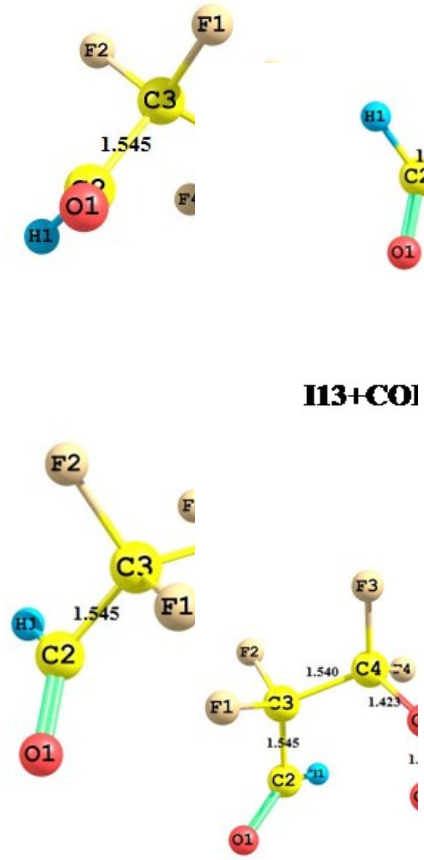
I7+O_2

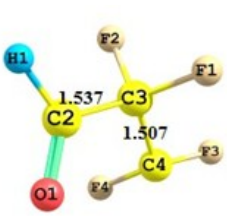


I8

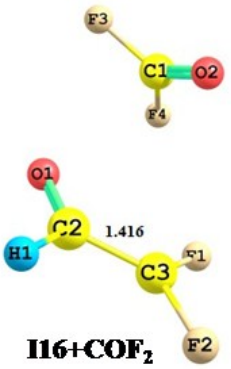


I8+NO

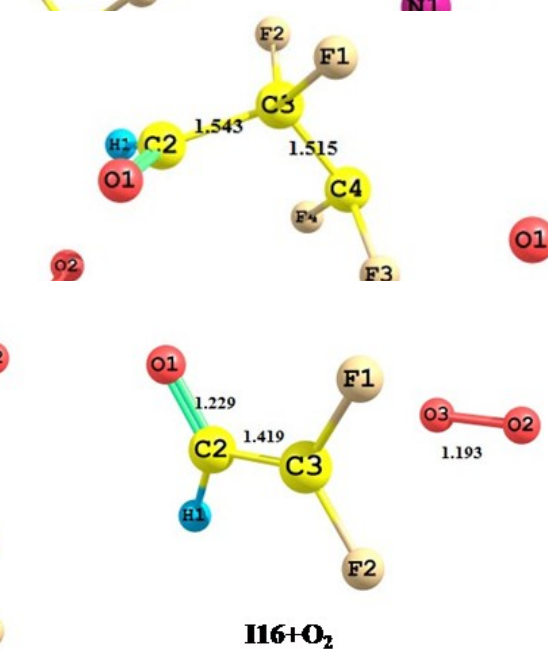




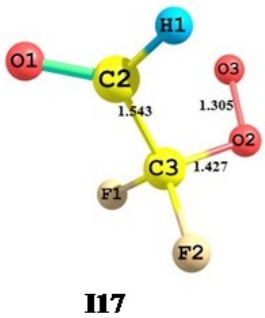
I13+COI



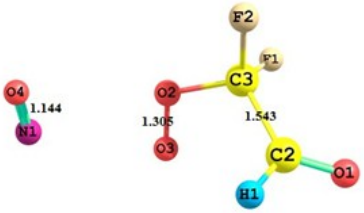
I16+COF_2



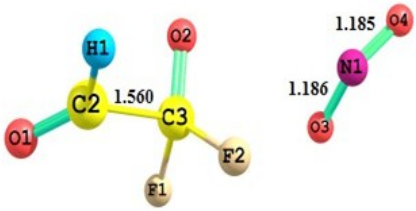
I16+O_2



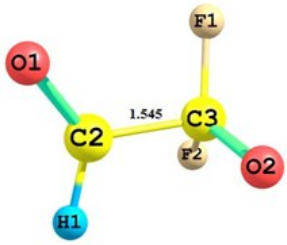
I17



I17+NO



I18+NO_2



I18

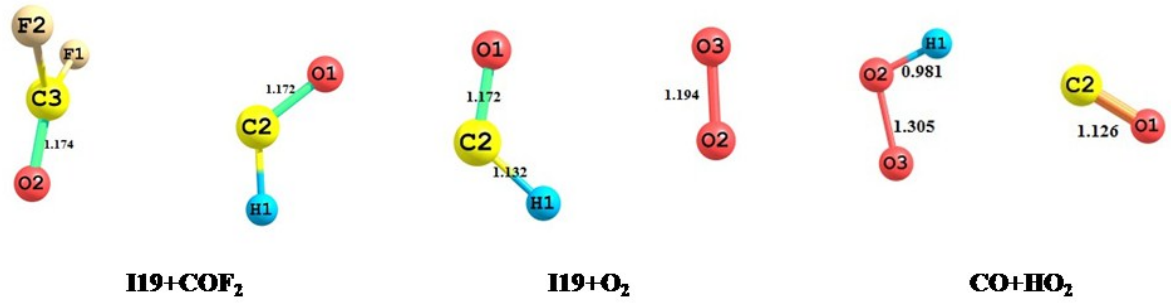
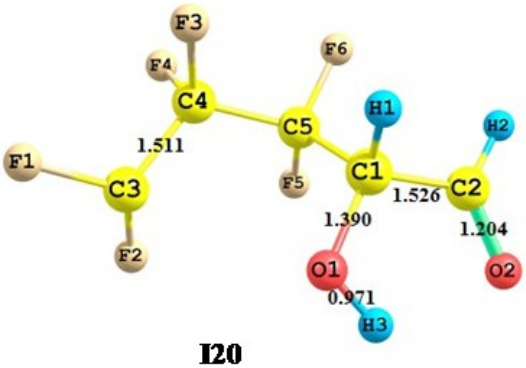


Fig. S3: Optimized structure of the intermediates and products involved in the first decomposition pathway of I4.

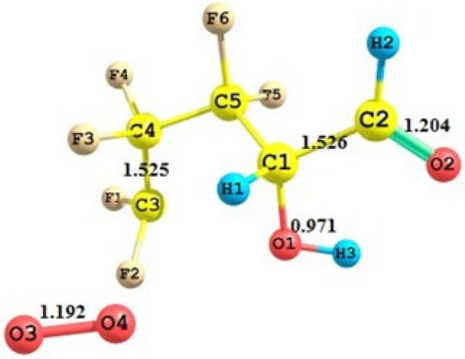
Table S2: Relative energies ΔE_{Tot} (kcal/mol), enthalpy ΔH_{298} (kcal/mol) and Gibbs free energy ΔG_{298} (kcal/mol) for the Unimolecular decomposition pathway-B of alkoxy radical, I4 calculated at M06-2X, ωB97XD and CCSD(T) levels of theory.

Stationary points	M06-2X/ aug-cc-pvDZ			ωB97XD/ aug-cc-pvDZ			CCSD(T)/aug-cc-pvDZ// M06-2X/ aug-cc-pvDZ
	ΔE_{Tot}	ΔH_{298}	ΔG_{298}	ΔE_{Tot}	ΔH_{298}	ΔG_{298}	ΔE_{Tot}
I5	0	0	0	0	0	0	0
TS15	9.13	9.95	8.03	10.44	10.37	9.78	9.15
I20	-2.64	-3.14	-2.11	-3.45	-2.51	-1.11	-2.36
I20+O_2	0	0	0	0	0	0	0
I21	-35.45	-33.32	-29.94	-33.61	-33.26	-31.57	-30.74
I21+NO	0	0	0	0	0	0	0
I22+NO_2	-11.92	-11.8	-11.48	-14.95	-15.07	-15.60	-13.34
I22	0	0	0	0	0	0	0
TS16	5.21	4.14	3.77	5.13	4.88	4.62	3.88
I23+COF_2	-6.28	-6.90	-9.27	-9.29	-9.91	-11.56	-8.27
I23+O_2	0	0	0	0	0	0	0
I24	-36.52	-34.39	-30.70	-33.26	-30.94	-28.34	-35.79
I24+NO	0	0	0	0	0	0	0
I25+NO_2	-11.57	-11.13	-10.79	-14.57	-14.14	-13.66	-11.58
I25	0	0	0	0	0	0	0
TS17	4.33	3.26	3.07	2.82	2.20	2.11	3.12
I26+COF_2	-9.09	-9.66	-10.95	-9.85	-10.10	-14.99	-10.83
I26+O_2	0	0	0	0	0	0	0
I27	-36.91	-36.11	-34.32	-33.92	-33.22	-30.67	-35.54
I27+NO	0	0	0	0	0	0	0
I28+NO_2	-13.05	-13.30	-12.95	-16.53	-16.13	-15.79	-12.82
I28	0	0	0	0	0	0	0
TS18	0.6	-0.4	0.2	1.17	-0.94	0.73	0.3

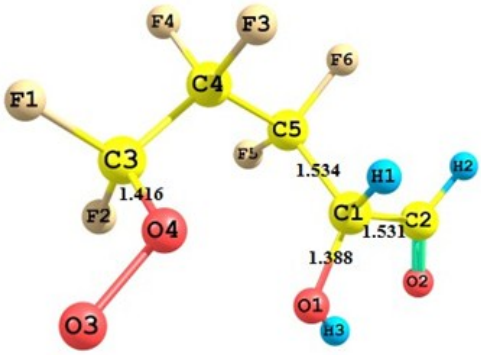
I29+COF_2	-25.29	-24.91	-27.64	-22.67	-22.15	-20.23	-25.76
I29+O_2	0	0	0	0	0	0	0
TS19	5.15	4.21	7.67	4.65	4.01	5.74	4.55
P8+HO_2	-23.59	-24.41	-24.52	-18.16	-18.09	-19.87	-22.98
P8+OH	0	0	0	0	0	0	0
TS20	4.33	2.5	3.08	4.11	2.39	2.96	3.56
I30+H_2O	-38.59	-37.84	-37.91	-35.42	-34.57	-34.22	-38.31
I30+O_2	0	0	0	0	0	0	0
I31	-23.16	-20.77	-17.61	-22.28	-19.45	-17.99	-22.67
I31+NO	0	0	0	0	0	0	0
I32+NO_2	-11.20	-10.89	-9.91	-14.60	-14.66	-14.18	-12.58
I32	0	0	0	0	0	0	0
TS21	5.23	4.11	2.79	2.26	1.44	7.29	5.04
I19+CO_2	-17.29	-16.86	-15.99	-20.06	-21.88	-29.23	-16.84
I19+O_2	0	0	0	0	0	0	0
TS14	3.51	2.38	4.47	1.69	1.26	5.6	3.11
CO+HO_2	-35.89	-33.98	-33.62	-33.45	-30.50	-28.48	-35.07



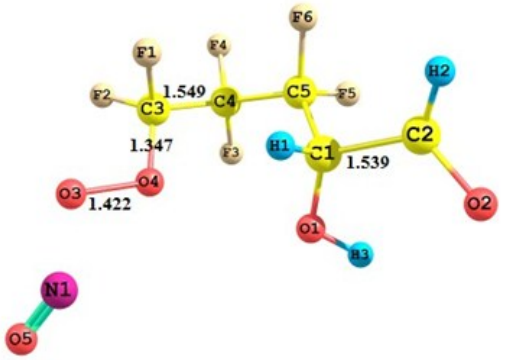
I20



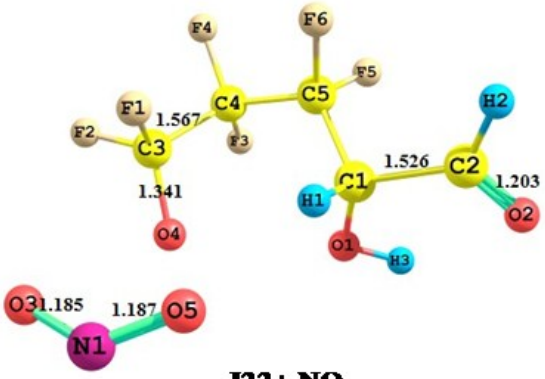
I20+ O_2



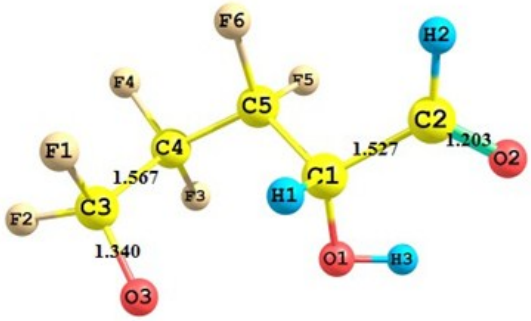
I21



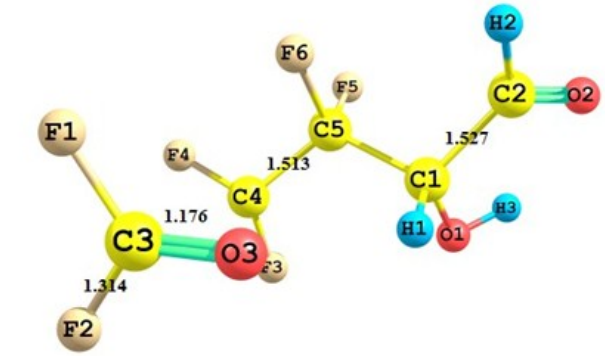
I21+NO



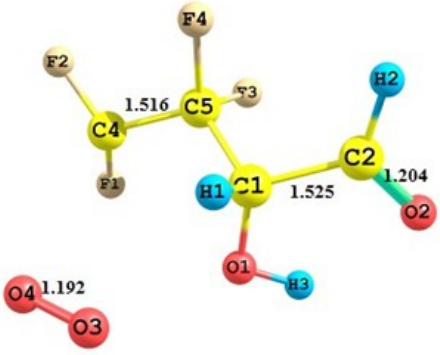
I22+ NO_2



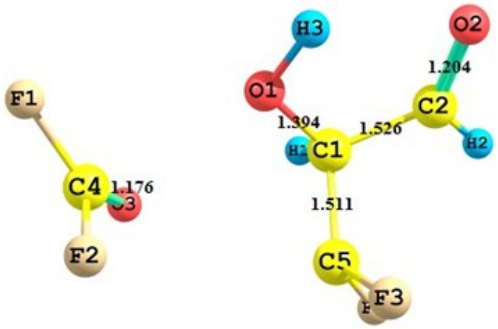
I22



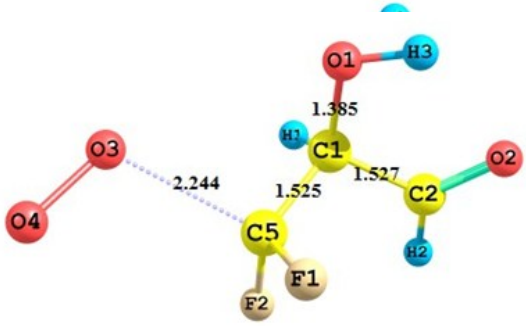
I23+ COF_2



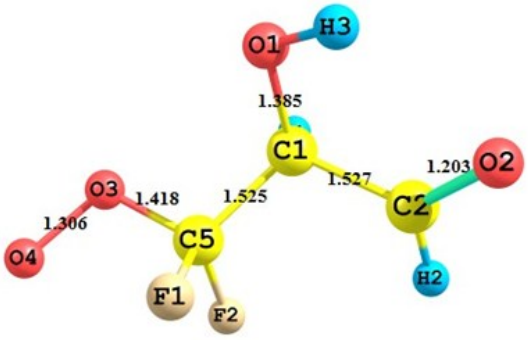
I23+ O_2



I26+ COF_2

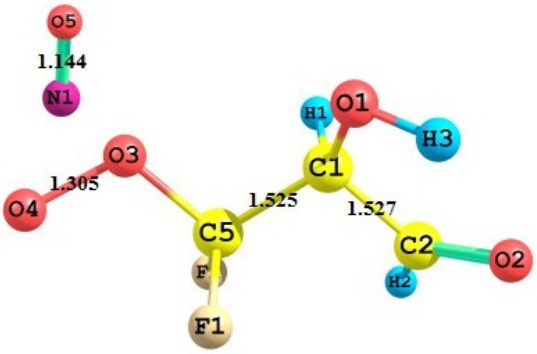


I26+ O_2



I27

I25+ NO_2



I27+ NO

I25

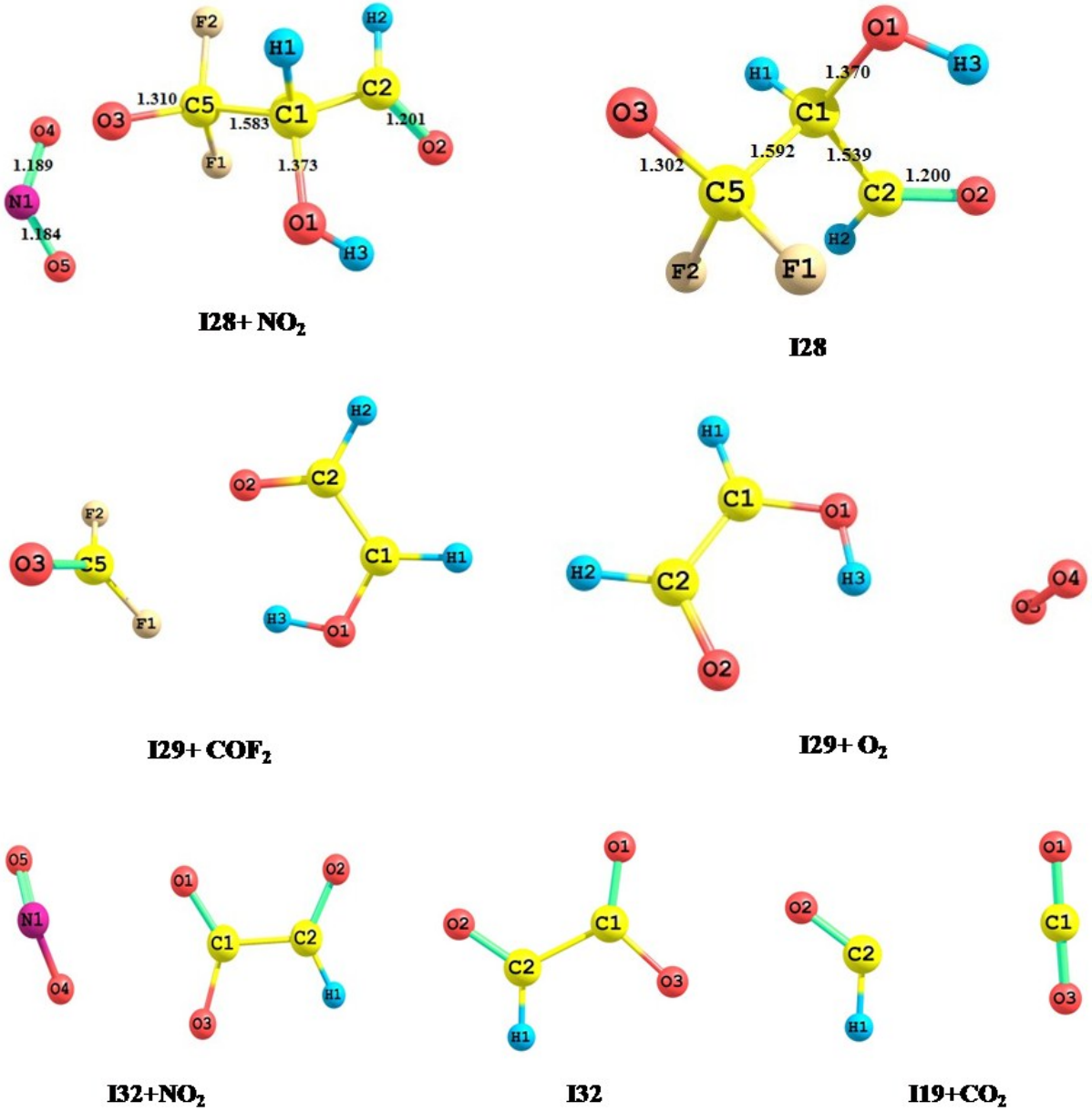


Fig. S4: Optimized structure of the intermediates and products involved in the seconddecomposition pathway of I4.