Supporting Information

Density Functional and Spin-Orbit *Ab Initio* Study of CF_3Br: Molecular Properties and Electronic Curve-Crossing

Joonghan Kim,[1] Tae Kyu Kim,[2,*] and Hyotcherl Ihee[1,*]

[1]*Center for Time-Resolved Diffraction, Department of Chemistry, Graduate School of Nanoscience & Technology (WCU), KAIST, Daejeon, 305-701, Republic of Korea*

[2]*Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan, 609-735, Republic of Korea*

* Corresponding author. E-mail : hyotcherl.ihee@kaist.ac.kr and tkkim@pusan.ac.kr

Table S1. The performance of methods for various molecular properties.[a]

	HF	MP2	CCSD(T)	B3LYP	B3PW91	PBE0	mPW1PW91	B97-2	ωB97X	B1B95	TPSSh	BMK	M05-2X	M06-2X
r(C–F)[b]	X	O	O	◎	O	□	□	O	O	□	O	□	O	□
∠(F–C–F)[b]	□	O	O	□	□	□	□	□	O	O	O	O	□	O
Vib. Freq.[b]	X	□	□	□	◎	□	□	◎	O	□	□	X	□	X
r(C–F)[c]	X	◎	◎	◎	O	□	□	O	◎	□	◎	□	O	□
r(C–Br)[c]	O	X	O	X	□	□	□	□	O	◎	X	□	◎	□
∠(F–C–F)[c]	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎
Vib. Freq.[c]	X	□	□	□	◎	O	O	O	□	O	□	□	□	□
μ[c]	X	X	X	□	X	X	X	X	◎	X	X	O	O	O
D_0[c]	X	X	◎	X	□	O	□	O	□	O	□	□	◎	□

a: (Best) ◎(4) → O(3) → □(2) → X(1) (Worst)

b: molecular structure and property of CF_3 radical.

c: molecular structure and properties of CF_3Br.

Figure S1. The active orbitals of CF_3Br for CAS(6,6) calculations.

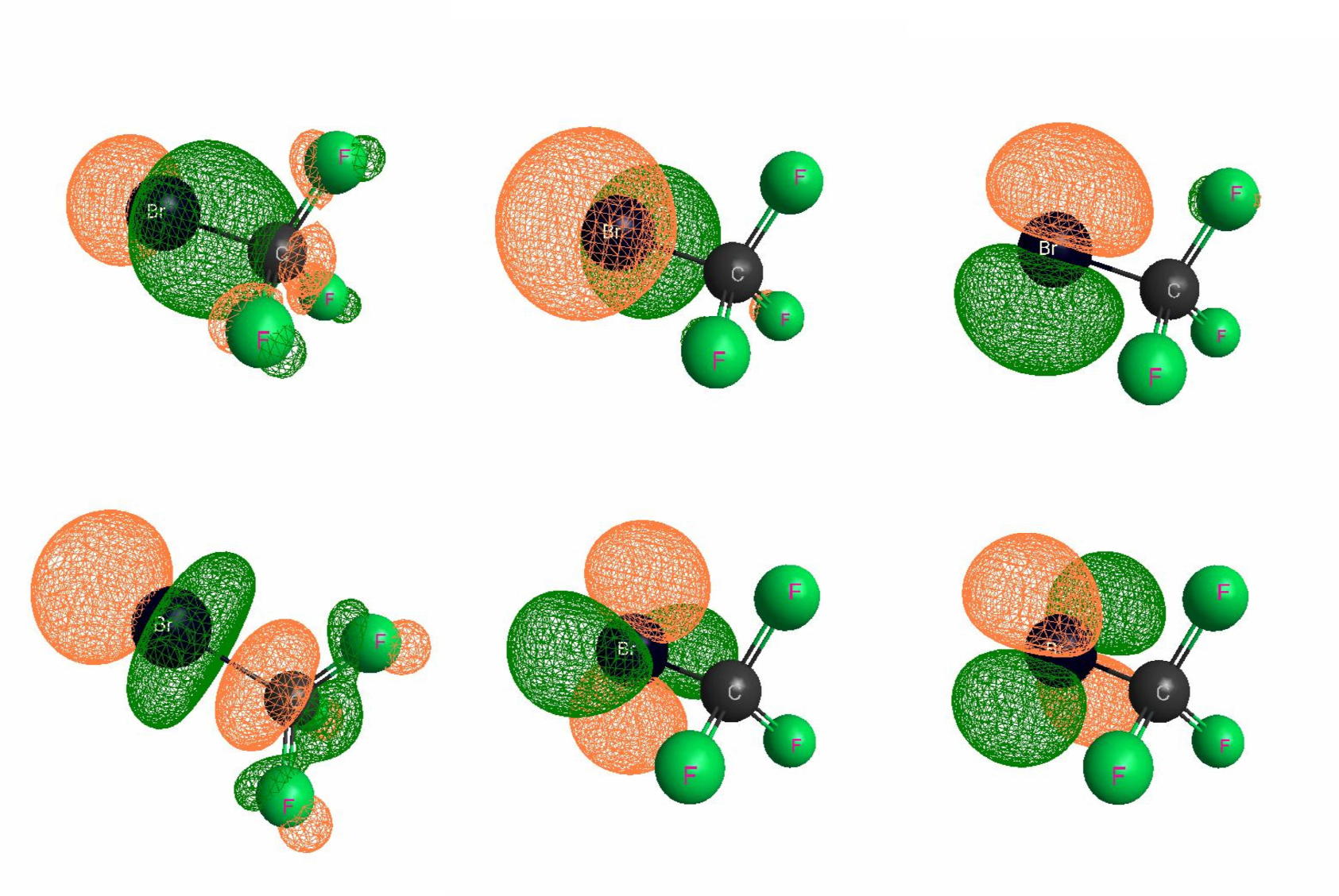

Figure S2. The scatter plot of the percentage error of the C–Br bond length (x-axis) *vs.* MAEs of T_v values (y-axis). The correlation coefficient is 0.909.