Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

New Insight into the Electronic Structure of SiF_4: Synergistic Back-Donation and Eighteen-Electron Rule

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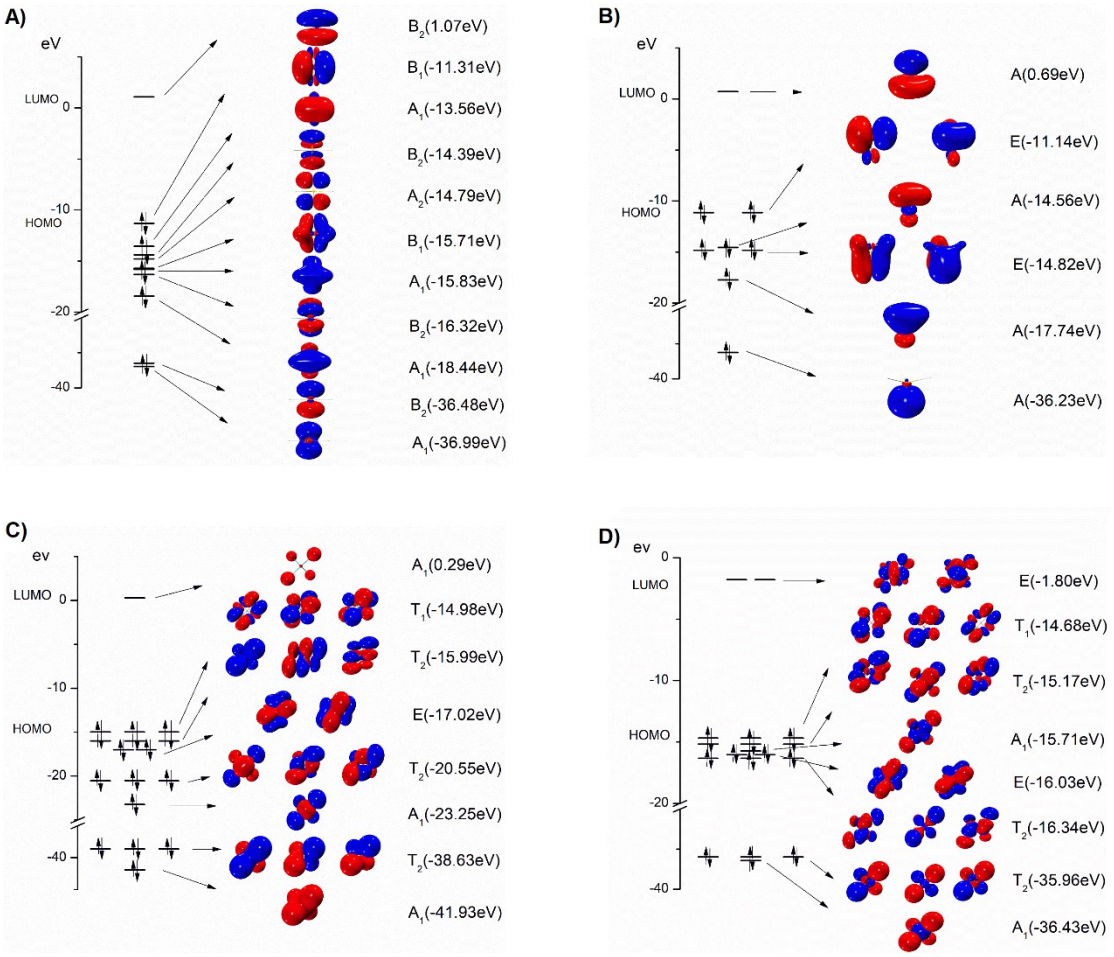

Figure S1. The canonical molecular orbitals (CMOs) of A) SiH_2F_2 with C_{2v} symmetry, B) SiH_3F with C_{3v} symmetry, C) CF_4 with *Td* symmetry, D) TiF_4 with *Td* symmetry. The isovalue is 0.03.

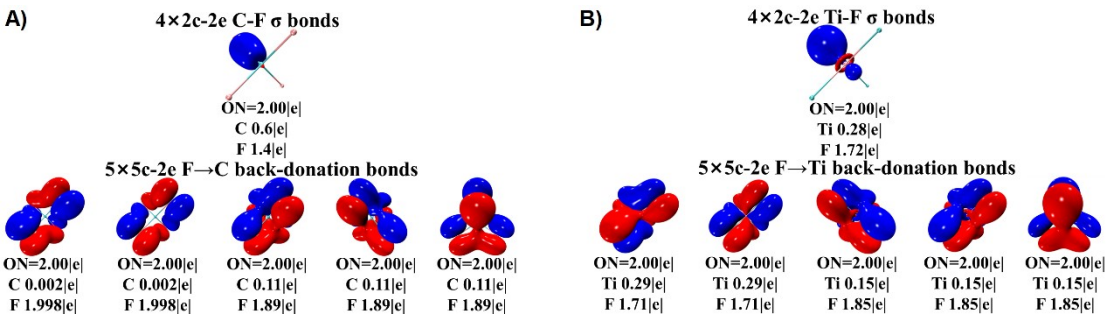

Figure S2. AdNDP localized natural bonding orbitals of A) CF_4 and B) TiF_4. ON gives the occupation numbers.

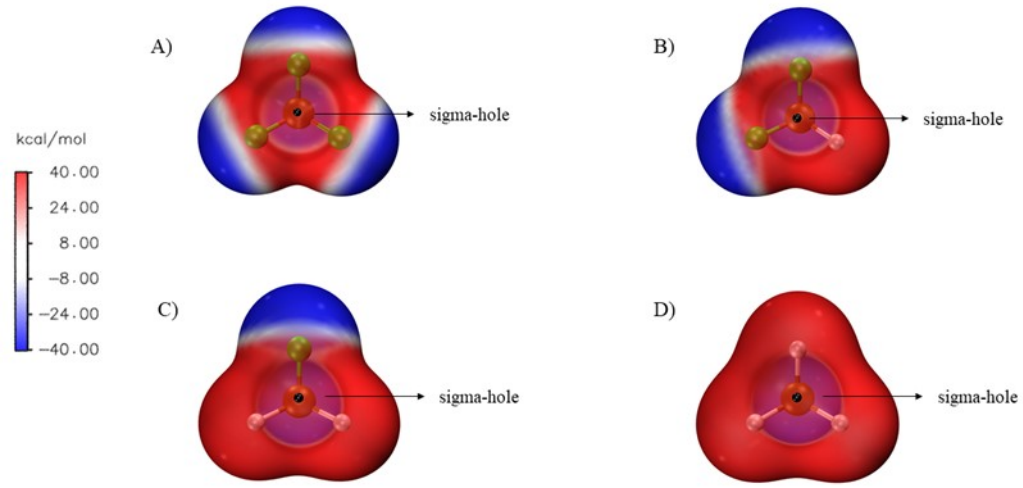

Figure S3. Molecular electrostatic potentials drawn over the electronic density surface with an isovalue of 0.001 a.u. for A) SiF_4 (with four sigma-holes), B) $SiHF_3$ (with three sigma-holes), C) SiH_2F_2 (with two sigma-holes), D) SiH_3F (with one sigma-hole). The black dot is the sigma-hole. The green represents atom F and the pink represents atom H.

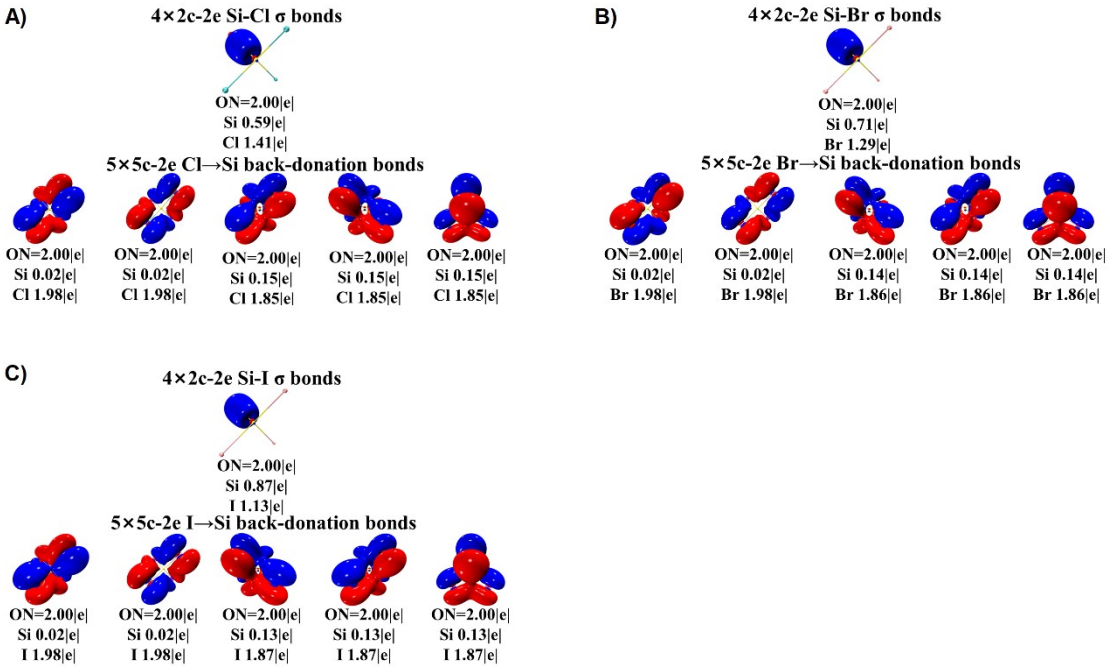

Figure S4. AdNDP localized natural bonding orbitals of A) $SiCl_4$, B) $SiBr_4$, C) SiI_4. ON gives the occupation numbers.

Table S1. The calculated and experimental C-F, Si-F and Ti-F average bond energies (kcal/mol) of CF_4, SiF_4 and TiF_4.

molecules	theory	experiment*
CF_4	118.60	122.80±2.39[1]
SiF_4	142.44	137.76±4.06[1]
TiF_4	136.17	135.99±7.89[1]

* The experimental values are average bond energies. They were calaculated by this formula: $BE=(4E_F+E_A-E_{AF4})/4$ (A=C, Si, Ti) at M06-2X/def2-TZVPP level of theory.

Table S2. The total feedback electron number (N_e) in 5c-2e bonds for molecules SiX_4 (X=F, Cl, Br, I), CF_4 and TiF_4.

molecules	CF_4	SiF_4	$SiCl_4$	$SiBr_4$	SiI_4	TiF_4
N_e	0.334	0.450	0.490	0.460	0.430	1.030

Reference

1. Y.-R. Luo, *Comprehensive handbook of chemical bond energies*, CRC press, 2007, pp 4.