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JA9506521-3-a-64

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Supplementary Material

Hybridizations and VALBOND parameters used around hypervalent centers.

molecule	bond	hybridization	$K_{VALBOND}$
XeF2	Xe-F	sp10.0	220.0
ClF3	Cl-F	sp10.0	220.0
ClF2H	Cl-F	sp10.0	220.0
	Cl-H	sp3.0	220.0
ClF2CH3	Cl-F	sp10.0	220.0
	Cl-C	sp3.0	220.0
ClF2SiH3	Cl-F	sp10.0	220.0
	Cl-Si	sp3.0	220.0
SF4	S-F	sp5.0	220.0
SF6	S-F	sp50.0	220.0
XeF4	Xe-F	sp10.0	220.0
XeF6	Xe-F	sp10.0	220.0
PF5	P-F	sp10.0	220.0
PF4H	P-F	sp10.0	220.0
	P-H	sp3.5	220.0
PF4Me	P-F	sp10.0	220.0
	P-C	sp4.0	220.0
PF3Me2	P-F	sp10.0	220.0
	P-C	sp4.0	220.0
PF2Me3	P-F	sp10.0	220.0
	P-C	sp4.0	220.0
PNPOSI	Si-N	sp3.591	220.0
	Si-O	sp3.591	220.0
	Si-C	sp6.772	220.0
CINLIU	Si-F	sp5.122	220.0
	Si-C	sp2.922	220.0
DALFOL	Si-O	sp3.591	220.0
	Si-C	sp6.772	220.0
ADSBOP	P-O	sp2.410	220.0
	P-C	sp2.516	220.0

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MSPBZP	P-O	sp1.410	220.0
	P-C	sp2.516	220.0
MPHLPA	P-C	sp3.000	220.0
DULDIX	I-O	sp4.0	220.0
	I-C	sp4.0	220.0
BENICL	I-Cl	sp4.0	220.0
	I-C	sp4.0	220.0
JAGCUP	I-O	sp4.0	220.0
IBZDAC	I-O	sp4.0	220.0
	I-C	sp4.0	220.0
DUCCAF	I-O	sp5.0	220.0
	I-C	sp4.0	220.0
CESFEL	P-O	sp4.0	220.0
	P-N	sp4.0	220.0

nonstandard bond stretch parameters
Atom type, Atom type, force constant(kcal/mol Å), equilibruim distance (Å)

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XCL   XF    300.0    1.698
XI    XCL   300.0    2.465
XE    XF    210.0    2.029
ST    XF    300.0    1.5467
PT    XF    300.0    1.55
PT    H     443.0    1.4
H     OT    505.0    0.948
H     ST    281.0    1.35
PT    OT    455.0    1.580
CF3   CT    208.0    1.520
CF3   XF    275.0    1.320
OE    XI    350.0    2.11
OS    XI    350.0    2.11
OT    XI    350.0    2.11
OS    PT    300.0    1.810
PT    NP    300.0    1.700
C6R   XI    300.0    2.09
MSI   XCL   300.0    2.07
MSI   HA    500.0    1.475
MSI   OE    390.0    1.64
MSI   NT    300.0    2.34
MSI   CT    295.0    1.874
MSI   C6R   295.0    1.853
MSI   XF    300.0    1.68
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Results from selected NRT and NBO analyses. All calculations done at HF/6-311G** or HF/LANL1DZ

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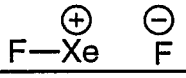
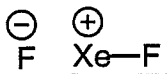
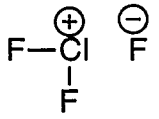
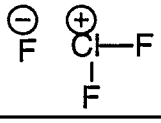
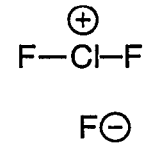
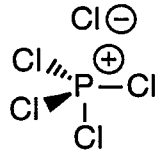
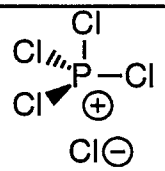
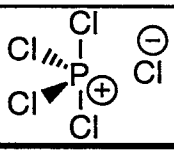
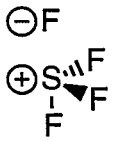
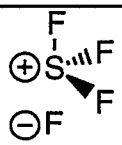
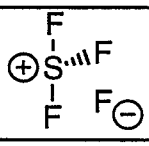
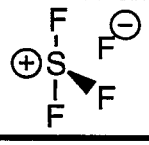
Molecule	Resonance structure	Weight (%)	Hybridizations
XeF_2		50	Xe–F: $sp^{99.99}$
		50	
ClF_3		40.22	$Cl–F_{ax}$: $sp^{11.34}$ $Cl–F_{eq}$: $sp^{9.61}$
		40.22	
		19.08	
PCl_5		33.63	$P–Cl_{ax}$: $sp^{2.86}d^{1.86}$ $P–Cl_{eq}$: $sp^{3.00}d^{0.61}$
		33.63	
		3x(6.38)	
SF_4		29.84	$S–F_{ax}$: $sp^{7.57}$ $S–F_{eq}$: $sp^{5.95}$
		29.84	
		17.68	
		17.68	