Supplementary Materials: Lewis Acid Properties of Tetrel Tetrafluorides—The Coincidence of the σ-Hole Concept with the QTAIM Approach

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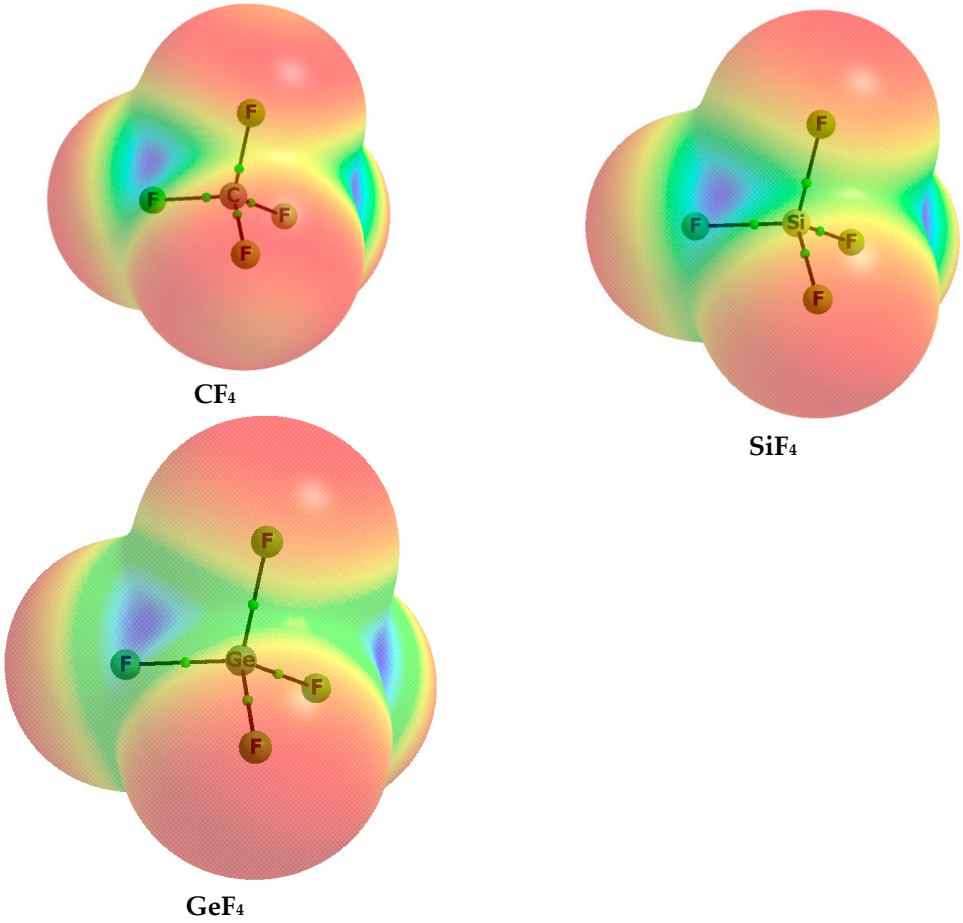

Figure S1. The maps of the electrostatic potential (EP) calculated at the 0.001 au molecular electron density surfaces for ZF_4; red and blue colors correspond to negative and positive EP, respectively; MP2/aug-cc-pVTZ level of calculations.

Table S1. The energetic parameters (in kcal/mol); the interaction energy, E_{int}, and the binding energy, E_{bin}, corrected for BSSE, the deformation energy, E_{def}. The tetrel—Lewis base centre distances are included, Z…B (i.e., Z…N or Z…As; Z = C, Si, Ge, in Å).

Complex	Z…B	E_{int}	E_{bin}	BSSE	E_{def}
CF_4…NH_3	3.658	−1.1	−1.1	0.3	0.0
CF_4…$(NH_3)_2$	1.658	−29.1	90.1	3.0	119.2
CF_4…$(NH_3)_2$ *	1.658	−76.8	91.9	6.5	168.7
SiF_4…NH_3	2.072	−29.6	−8.5	2.5	21.1
SiF_4…$(NH_3)_2$	1.940	−44.4	−14.7	2.4	29.7
SiF_4…$(NH_3)_2$ *	1.940	−93.9	−23.7	4.4	70.2
GeF_4…NH_3 [a]	2.084	−34.2	−16.7	4.7	17.5
GeF_4…NH_3	2.080	−33.8	−16.2	4.7	17.6
GeF_4…$(NH_3)_2$ [a]	2.001	−43.1	−19.8	4.7	23.3
GeF_4…$(NH_3)_2$	1.997	−42.4	−19.2	4.9	23.2
GeF_4…$(NH_3)_2$ *,[a]	2.001	−91.9	−35.1	10.8	56.8

$GeF_4…(NH_3)_2$ *	1.997	−90.5	−34.2	10.9	56.3
$GeF_4…AsH_3$ [a]	3.381	−3.1	−1.9	2.1	1.2
$GeF_4…AsH_3$	3.399	−2.8	−1.8	1.9	1.0
$GeF_4…(AsH_3)_2$ [a]	2.550	−23.3	8.6	5.3	31.9
$GeF_4…(AsH_3)_2$	2.543	−22.3	10.3	5.1	32.6
$GeF_4…(AsH_3)_2$ *,[a]	2.550	−50.3	9.8	10.5	60.1
$GeF_4…(AsH_3)_2$ *	2.543	−48.1	11.5	10.1	59.6

* Interaction and binding energies are related to three components (see text for explanation). [a] Relativistic effects not taken into account (MP2/aug-cc-pVTZ level).

Table S2. Electrostatic potential local maxima and minima for ZF_4, $ZF_4…NH_3$ and $GeF_4…AsH_3$ species (in au); for the species containing Ge and As centres these values are the same if relativistic effects are taken into account; in a case of $ZF_4…NH_3$ complexes the local maximum is indicated since the global EP maximum corresponds to H-centres, in a case of the $GeF_4…AsH_3$ complex that is the global EP maximum; the EP results for the surfaces of the electron density of 0.001 au are presented.

ZF_4 or ZF_4-BH_3	Max	Max Localization	Min	Min Localization
CF_4	+0.034	F-C extension	−0.002	F-centre
SiF_4	+0.072	F-Si extension	−0.012	F-centre
GeF_4	+0.086	F-Ge extension	−0.012	F-centre
$CF_4…NH_3$	+0.025	F-C extension	−0.031	F…N area
$SiF_4…NH_3$	+0.018	F-Si extension	−0.053	F-centre
$GeF_4…NH_3$	+0.021	F-Ge extension	−0.053	F-centre
$GeF_4…AsH_3$	+0.069	F-Ge extension	−0.023	F-centre

Table S3. The QTAIM characteristics (in au) of the Z-F bond critical point; electron density at BCP, ρ_{BCP}, its laplacian, $\nabla^2\rho_{BCP}$, the total electron energy density at BCP, H_{BCP}, the potential electron energy density at BCP, V_{BCP}, the kinetic electron energy density at BCP, G_{BCP}.

Complex	ρ_{BCP}	V_{BCP}	G_{BCP}	H_{BCP}	$\nabla^2\rho_{BCP}$
$CF_4…NH_3$	0.305	−0.908	0.410	−0.498	−0.354
$CF_4…NH_3$ *	0.299	−0.879	0.393	−0.486	−0.369
$CF_4…(NH_3)_2$	0.177	−0.274	0.110	−0.164	−0.217
$SiF_4…NH_3$	0.134	−0.356	0.316	−0.040	1.103
$SiF_4…NH_3$ *	0.135	−0.361	0.317	−0.045	1.087
$SiF_4…(NH_3)_2$	0.114	−0.278	0.244	−0.033	0.844
$GeF_4…NH_3$	0.149	−0.354	0.283	−0.071	0.846
$GeF_4…NH_3$ *	0.153	−0.365	0.289	−0.076	0.853
$GeF_4…(NH_3)_2$	0.131	−0.290	0.231	−0.058	0.692
$GeF_4…AsH_3$	0.163	−0.405	0.321	−0.084	0.949
$GeF_4…AsH_3$ *	0.162	−0.400	0.318	−0.083	0.940
$GeF_4…(AsH_3)_2$	0.134	−0.297	0.236	−0.060	0.704

* for the Z-F bond located at the opposite side of the NH_3 or AsH_3 ligand.