

[FAAF]⁻ (A = O, S, Se, Te) or How Electrostatic Interactions Influence the Nature of the Chemical Bond

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Supporting Information

A total of 5 pages

GEOMETRIES OF [FAAF]⁻

Table S1. Optimized geometry for [FSSF]⁻ (left) and [FSeSeF]⁻ (right) at the CCSD/6-31+G(d) (LANL2DZdp basis for A = Te) level of theory. Values in Å.

Atom	X	Y	Z	Atom	X	Y	Z
O	-0.811957	-0.547571	0.475646	S	-0.393703	0.892485	-0.179572
O	0.811957	0.547571	0.475646	S	0.393703	-0.892485	-0.179572
F	0.811957	1.724906	-0.422796	F	-0.393703	-2.573016	0.319239
F	-0.811957	-1.724906	-0.422796	F	0.393703	2.573016	0.319239
Se	-0.78814	-0.822939	-0.096201	Te	2.503787	0.537877	-0.125953
Se	0.78814	0.822939	-0.096201	Te	-2.505272	-0.540587	-0.12362
F	-0.78814	-2.72953	0.363425	F	-5.877483	1.33448	0.718734
F	0.78814	2.72953	0.363425	F	5.886063	-1.31882	0.72324

ASSESSMENT OF THE CASSCF METHOD

Table S2 shows the ELF analysis performed on [FSSF]⁻ and [FSeSeF]⁻ with CCSD/6-31+G(d) (LANL2DZdp for A = Te) compared to another obtained with a CASSCF(11,10) density. For A = O and S, the basis set is the Atomic Natural Orbital ANO-S[10s6p3d/6s5p3d] for oxygen and ANO-S[17s15p9d/7s6p3d] for sulphur, Dunning cc-aug-pVTZ for A = Se and ANO-RCC[22s19013d5f3g/9s8p7d4f1g] for A = Te. For A = Te scalar relativistic effect have been introduced through the Douglas-Kroll Hamiltonian. Both CCSD and CASSCF estimates agree reasonably well. Table S3 shows the same analysis but on A₂⁺ systems at different A—A distances. Again, the agreement between CCSD and CASSCF values is quite acceptable.

Table S2. ELF Analysis for [FAAF]⁻ (A=S, Se) with the CCSD (CASSCF) density. All values are in e. V(A) represents the population of the basin and $\delta(A,A')$ the delocalization index between both V(A) basin of different atoms.

	V(A)	V(A)	V'(F)	V'(F)	$\delta(A,A')$	$\delta(A,F)$
X = O	3.0006 (2.9944)	3.0286 (3.0208)	3.6333 (3.5754)	3.5446 (3.5658)	0.5458 (0.4150)	0.9580 (0.8650)
X = S	2.2875 (2.227)	3.4083 (3.5113)	3.6186 (3.7751)	3.8529 (3.8006)	1.6148 (1.5558)	0.5986 (0.5882)
X = Se	2.6398 (2.7684)	3.2471 (3.0697)	3.7426 (3.6695)	3.7426 (3.6695)	1.4444 (1.2710)	0.5932 (0.5898)
X = Te	2.8306 (2.7925)	2.8801 (2.8897)	3.6911 (3.6017)	3.9950 (4.0572)	1.2604 (0.9983)	0.5871 (0.4570)

EFFECT OF THE A—A BOND DISTANCE

Table S2 shows the ELF analysis performed on A_2^+ two different A—A distances. The first one (Eq.) corresponds to the equilibrium distance of the A_2^+ cation (1.133, 1.842, 2.126 and 2.519 Å for A = O, S, Se and Te, respectively, at the CCSD/6-31+G(d) level of theory –LANL2DZdp for Te-) while the second one (long) refers to the A—A bond length in the [FAAF]⁻ molecule (1.921, 1.963, 2.279 and 2.711 Å for A = O, S, Se and Te, respectively, at the CCSD/6-31+G(d) level of theory –LANL2DZdp for Te-). There is no significant difference between both bond distances and, consequently, both ELF analyses are rather similar.

Table S3. ELF analysis for the A_2^+ cation at the equilibrium bond distance (Eq.) and the A–A bond distance in $[FAAF]^-$ (long). All values are in e. $V(A)$ represents the population of the basin and $\delta(A,A')$ the delocalization index between both $V(A)$ basin of different atoms.

		Eq.		Long	
		CASSCF	CCSD	CASSCF	CCSD
$V(A,A)$	O	1.6904	1.7688	-	-
	S	2.1819	1.9695	1.8177	1.6717
	Se	1.8988	1.9764	1.4003	1.4856
	Te	2.3606	2.0658	1.7542	1.6201
$V(A)$	O	4.5518	4.3942	5.3919	5.4184
	S	4.3291	4.4299	4.5272	4.6053
	Se	4.6173	4.6390	4.8950	4.8754
	Te	4.4689	4.9665	4.7038	5.1881
$\delta(A,A')$	O	0.9034	0.3046	0.6608	0.7718
	S	0.3692	0.4904	0.4283	0.5467
	Se	0.3941	0.4750	0.4989	0.5451
	Te	0.3690	0.4743	0.4413	0.4770

RESULTS OF THIS COMPUTATIONAL EXPERIMENT FOR A = O

The characteristics of the neutral $[FOOF]$ deviate significantly from those of the heavier chalcogen analogues, and therefore, as expected, the behavior of O_2^+ under an external electric field. Actually, as shown below the population of the $V(O,O)$ disynaptic basin goes through a minimum as the intensity of the negative electric field increases. The O–O bond in the neutral $[FOOF]$ shows already a significant CS character, while in the anion it should be better regarded as weak interaction. Consequently, it should be expected that the results of this computational experiment obtained for oxygen deviate significantly when $A = S, Se$ or Te . The O–O distance in $[FOOF]^-$ is much larger (1.921 Å) with respect to that of O_2^+ (1.133 Å). O_2^+ , with a bond length of 1.921 Å, presents no disynaptic basin, so to study the interaction between O_2^+ and an external field, the optimized bond distance of the cation will be employed.

Due to the high electronegativity of oxygen, O_2^+ is less sensitive to the external field (see Table S4). The orbitals of oxygen are more contracted than those of sulfur, selenium or tellurium and, hence, less polarizable. When interacting with a negative field, the disynaptic $V(O,O)$ reaches its

minimum population of 1.4823 e when the charge is -3.5. For higher negative charges the population increases because the electric field created by these charges is highly repulsive and forces the outer valence electrons to be polarized away from them (see Fig. S1) with a consequent increase of the electronic density in the bonding region. The strong attractive field created by the oxygen atoms is not surpassed however by an external positive field and only polarization of the electron density towards the internuclear region takes place, with the subsequent increase of the population of the V(O,O) disynaptic basin.

Table S4. Basin population and delocalization indexes between the lone pair monosynaptic V(O) basins of the ELF analysis for O_2^+ in the presence of different point charges. All values in e.

Charge		0	+0.5	+1.0	+1.5	+2.5	-0.5	-1.0	-1.5	-2.5
V(A,A)	O	1.6904	1.6883	1.7184	1.7535	1.9340	1.6887	1.6742	1.6634	1.5855
V(A)	O	4.5196	4.5381	4.5224	4.1823	4.4167	4.5439	4.5506	4.5465	4.5863
$\delta(A,A')$	O	0.9040	0.9354	0.8800	0.7754	0.7428	0.9120	0.9152	0.9162	0.9420

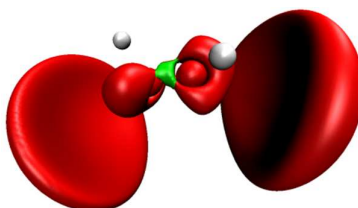


Figure S1. Localization domains of the ELF (ELF=0.80) for O_2^+ interacting with two point charges of -5.0 e. The two outer basins (with a population of ca. 0.50 e) represent electron density expelled from the molecule due to the highly repulsive external electric field. The white balls represent the point charges.