

Relativistic DFT-NMR of ^{19}F in Tantalum(V) and Niobium(V) Fluorohalides

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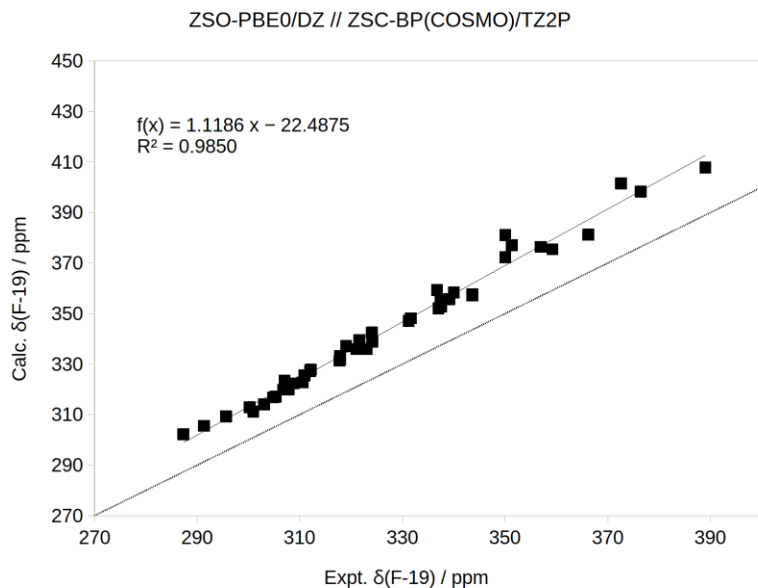


Figure S1. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **i**). Thick dotted line: $y = x$; thin black line: linear fit.

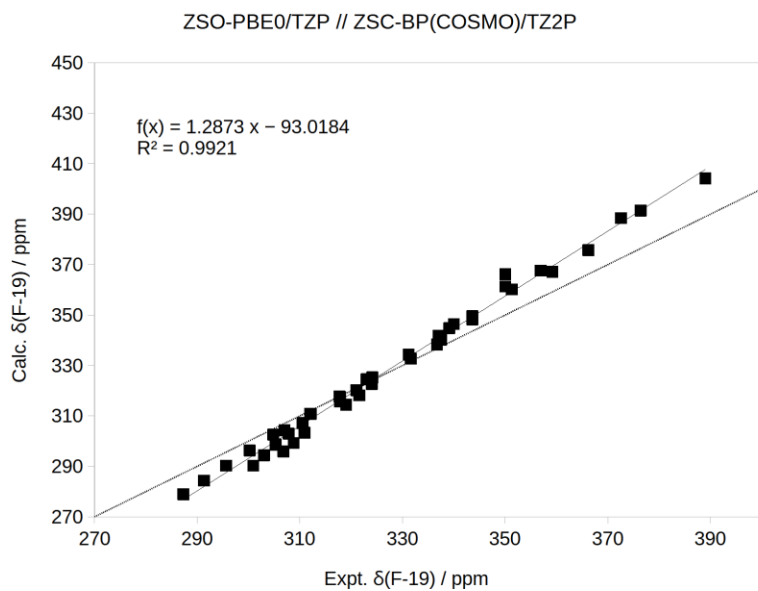


Figure S2. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **ii**). Thick dotted line: $y = x$; thin black line: linear fit.

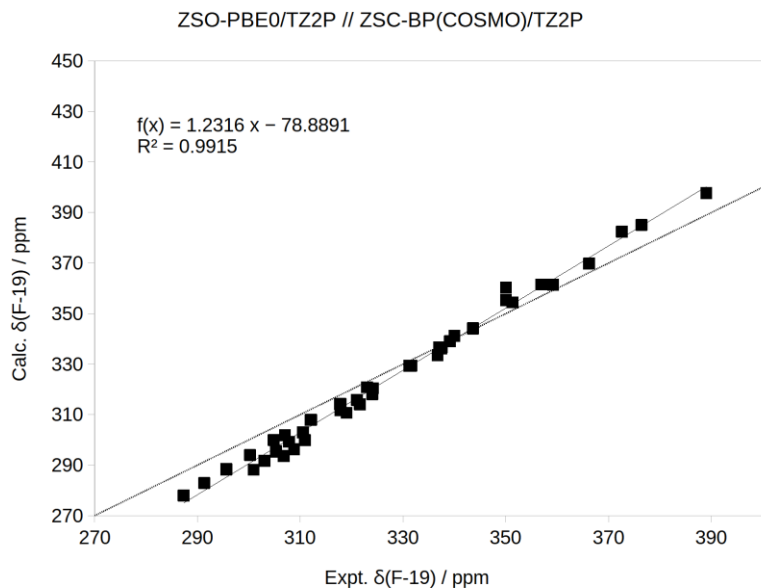


Figure S3. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **iii**). Thick dotted line: $y = x$; thin black line: linear fit.

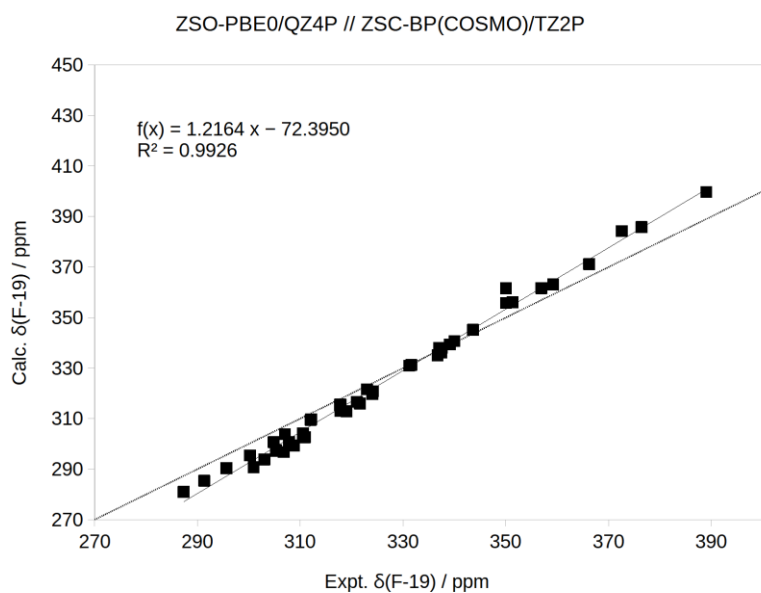


Figure S4. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **iv**). Thick dotted line: $y = x$; thin black line: linear fit.

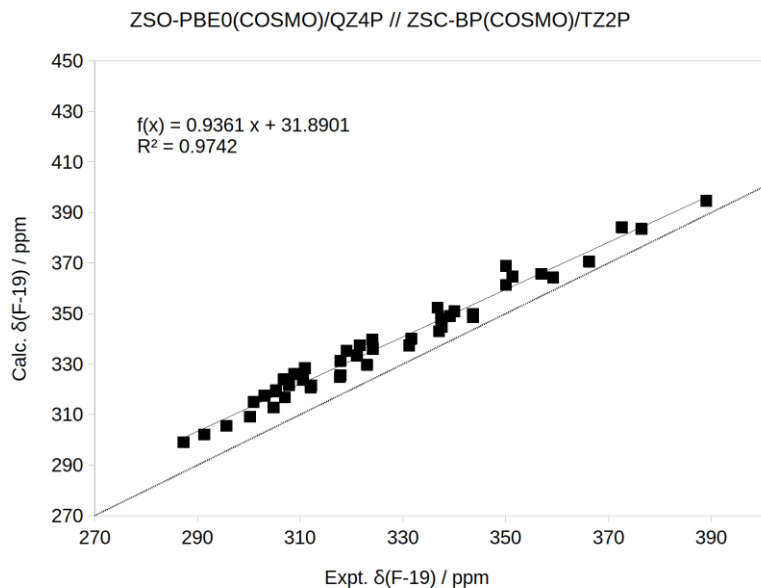


Figure S5. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory v. Thick dotted line: $y = x$; thin black line: linear fit.

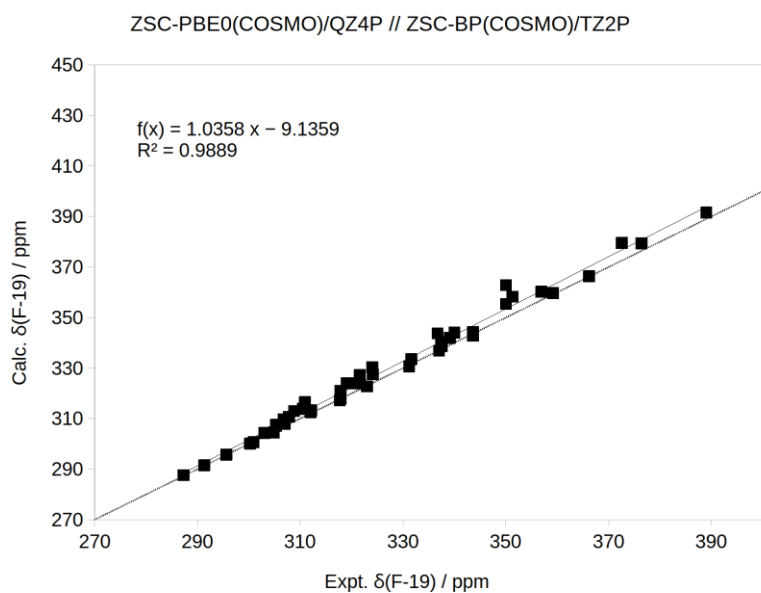


Figure S6. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory vi). Thick dotted line: $y = x$; thin black line: linear fit.

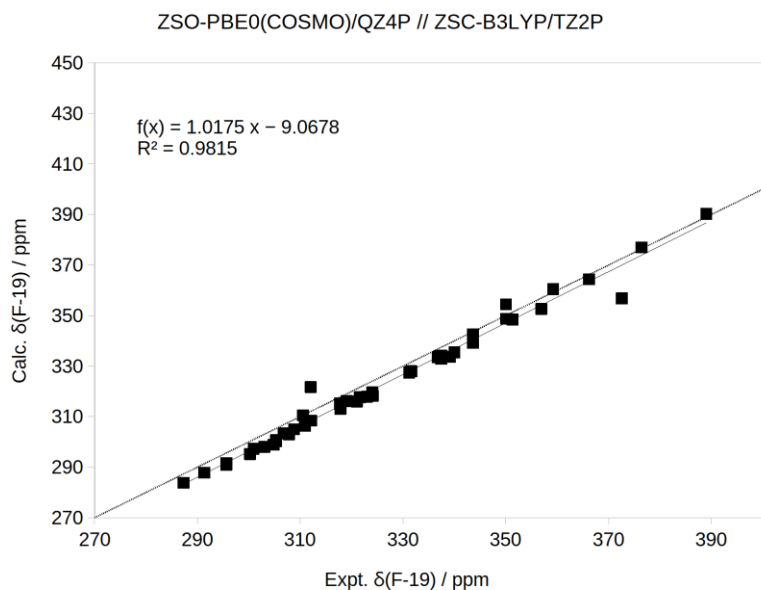


Figure S7. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **vii**). Thick dotted line: $y = x$; thin black line: linear fit.

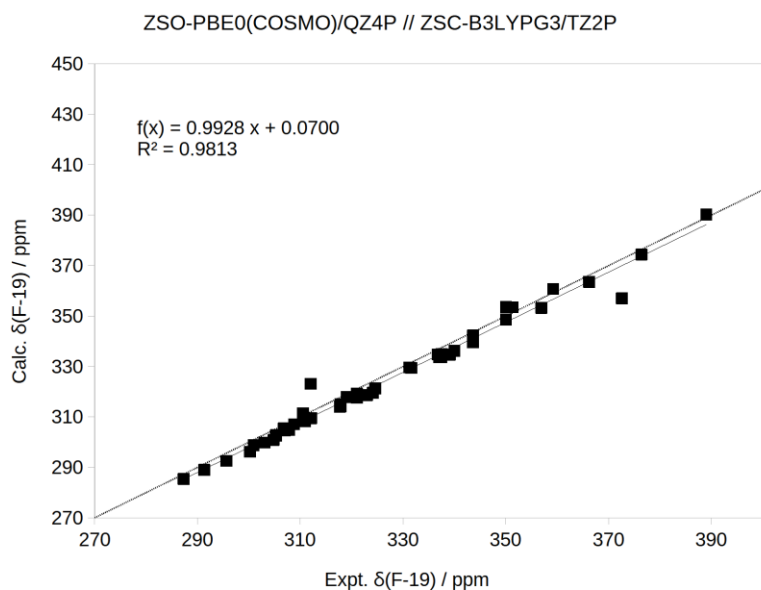


Figure S8. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **viii**). Thick dotted line: $y = x$; thin black line: linear fit.

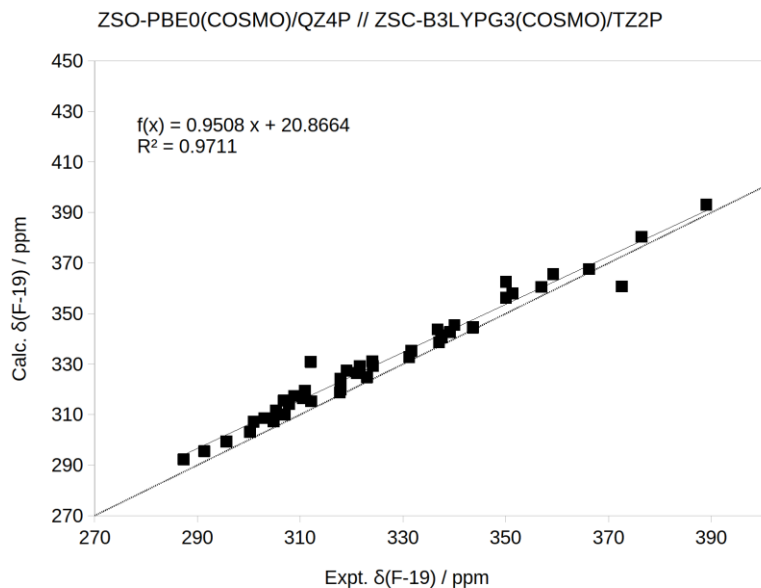


Figure S9. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xi**). Thick dotted line: $y = x$; thin black line: linear fit.

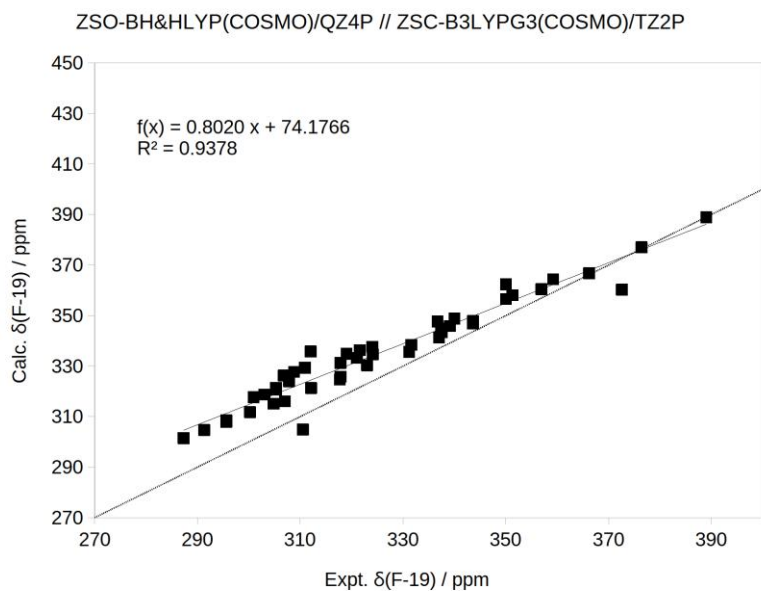


Figure S10. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **x**). Thick dotted line: $y = x$; thin black line: linear fit.

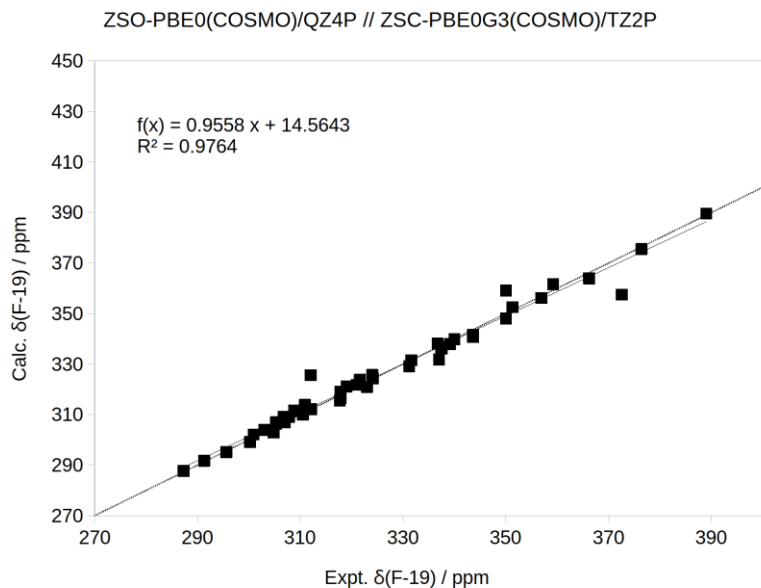


Figure S11. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xi**). Thick dotted line: $y = x$; thin black line: linear fit.

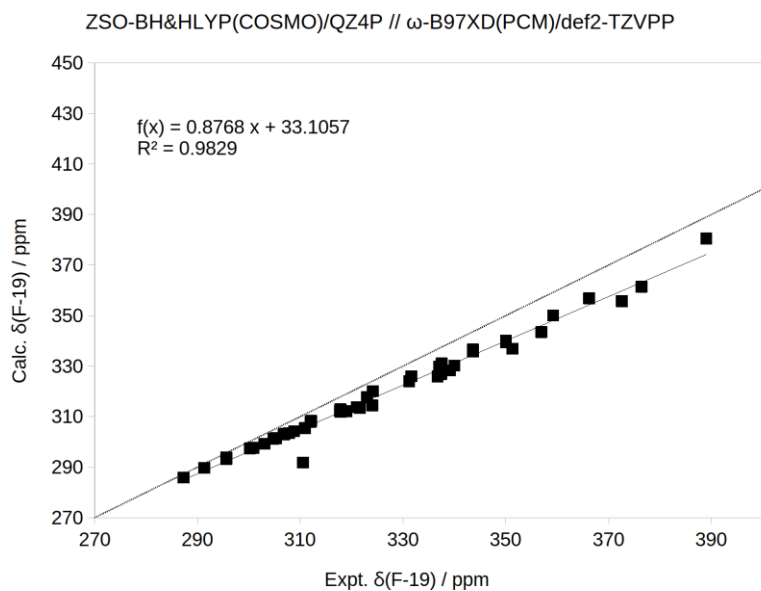


Figure S12. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xii**). Thick dotted line: $y = x$; thin black line: linear fit.

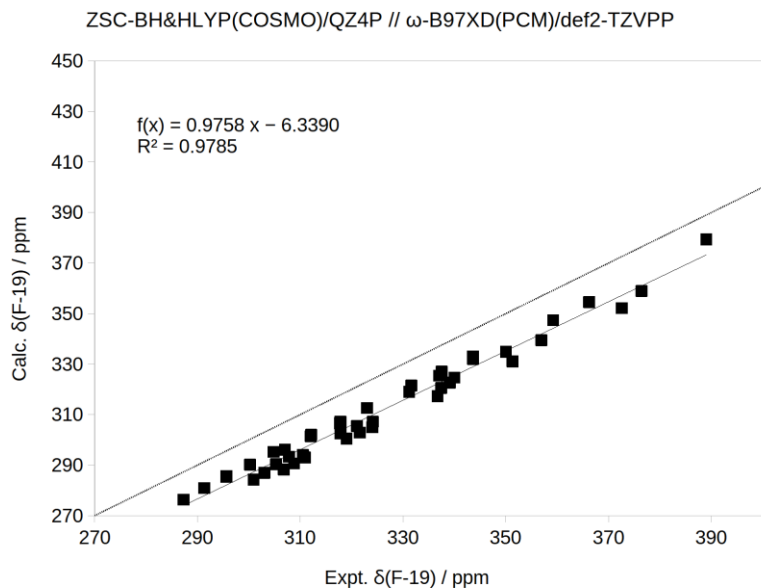


Figure S13. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xiii**). Thick dotted line: $y = x$; thin black line: linear fit.

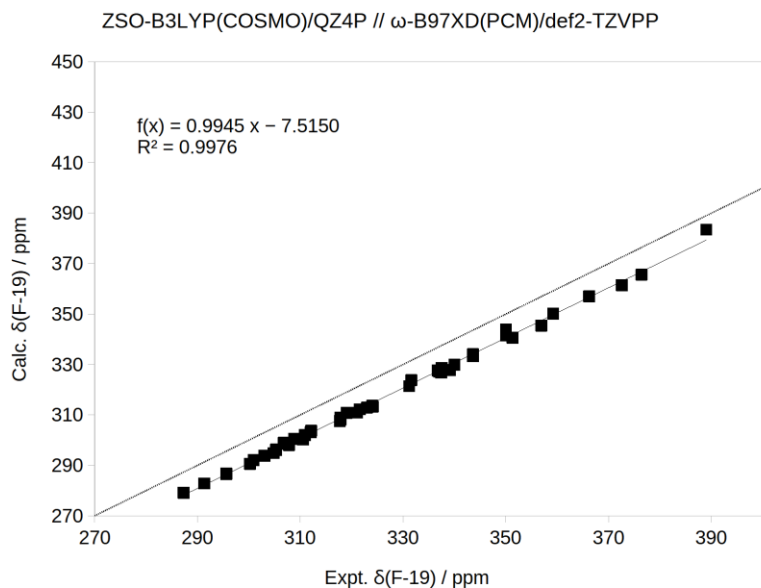


Figure S14. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xiv**). Thick dotted line: $y = x$; thin black line: linear fit.

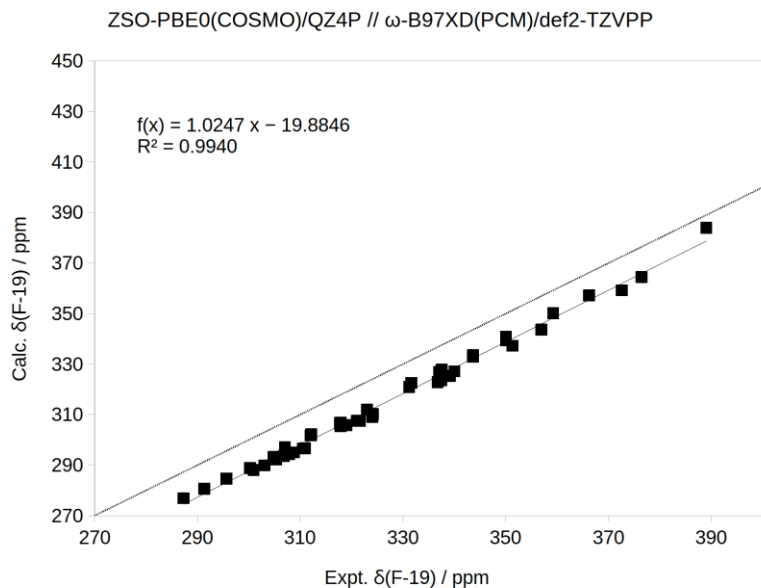


Figure S15. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xv**). Thick dotted line: $y = x$; thin black line: linear fit.

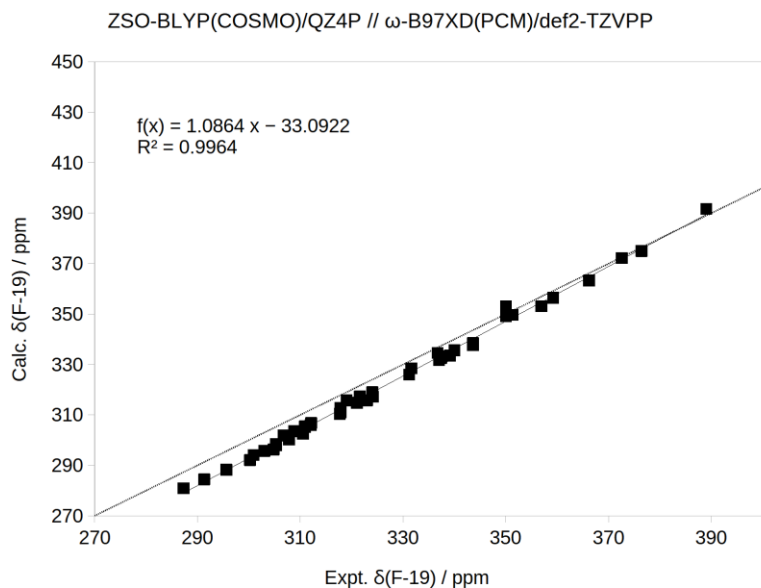


Figure S16. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xvi**). Thick dotted line: $y = x$; thin black line: linear fit.

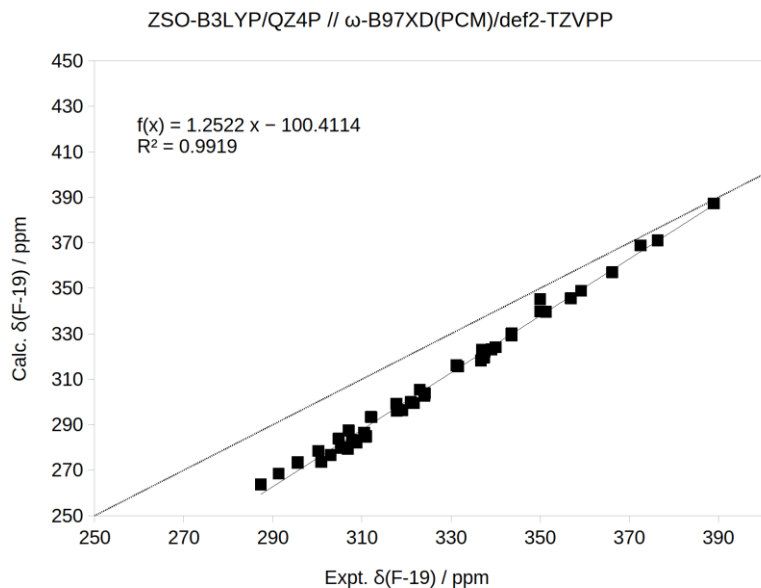


Figure S17. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xvii**). Thick dotted line: $y = x$; thin black line: linear fit.

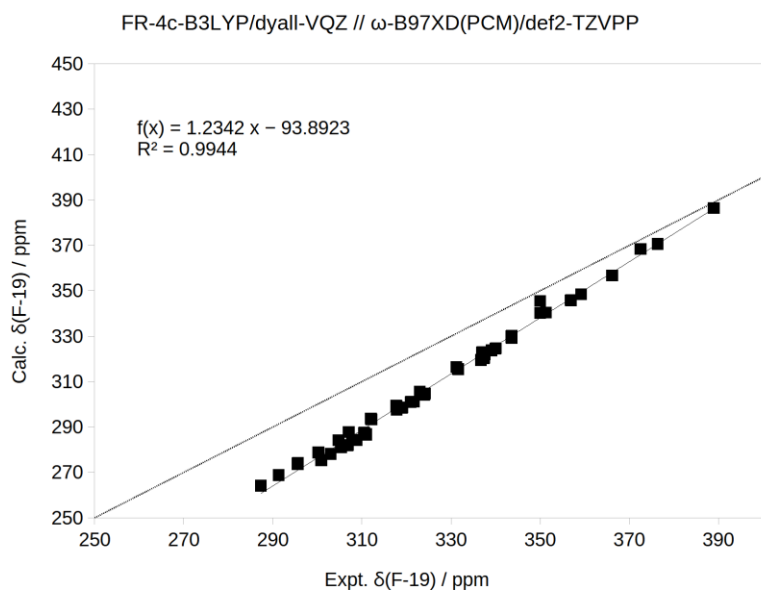


Figure S18. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xviii**). Thick dotted line: $y = x$; thin black line: linear fit.

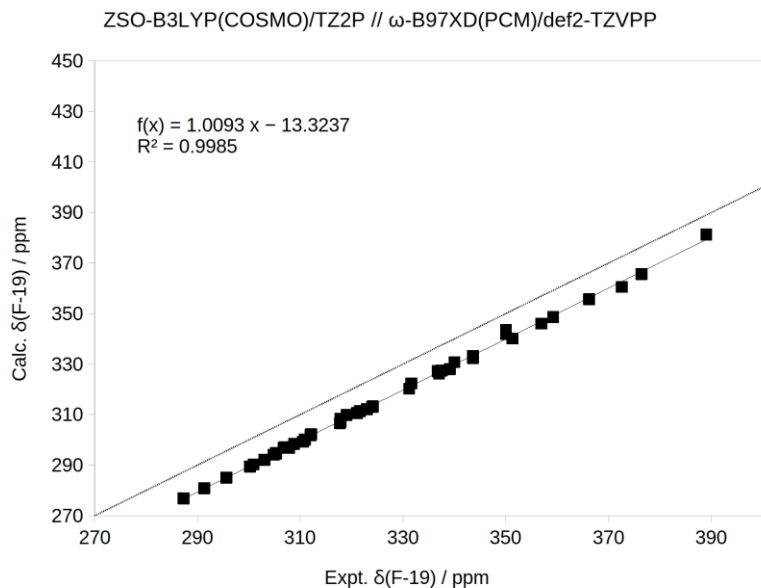


Figure S19. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xix**). Thick dotted line: $y = x$; thin black line: linear fit.

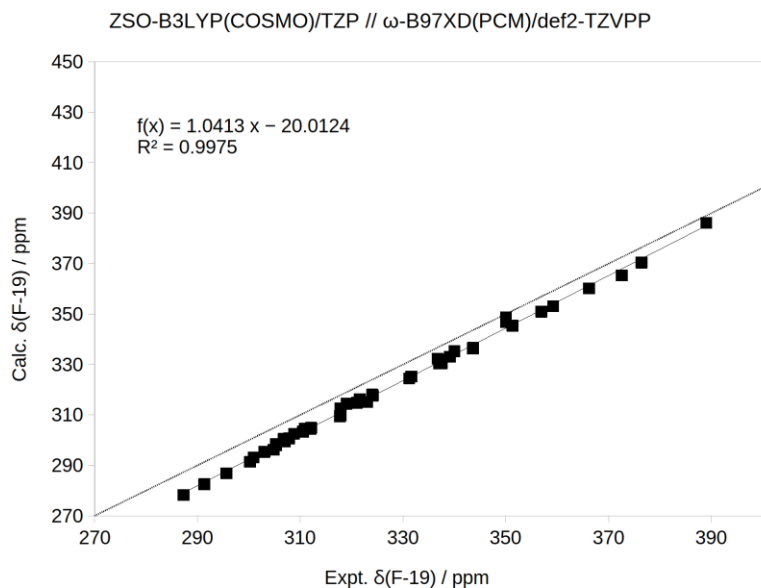


Figure S20. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xx**). Thick dotted line: $y = x$; thin black line: linear fit.

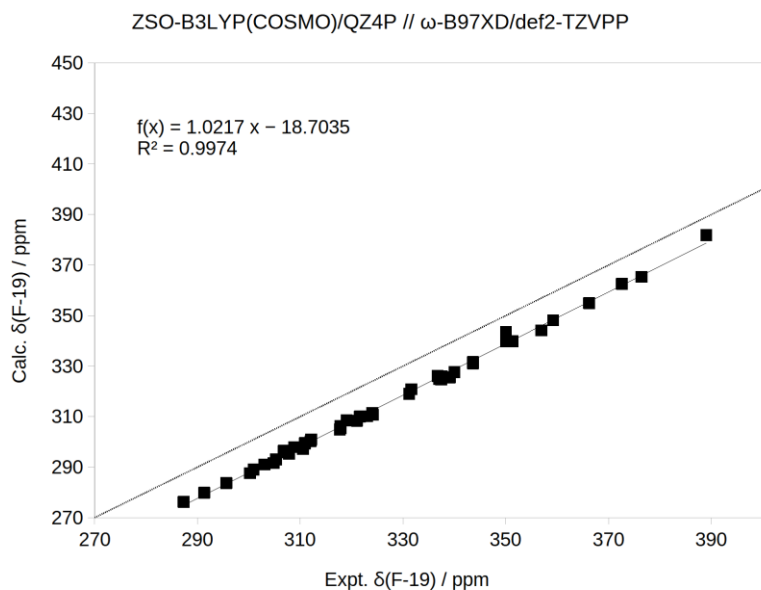


Figure S21. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Tantalum(V) fluorohalides at level of theory **xxi**). Thick dotted line: $y = x$; thin black line: linear fit.

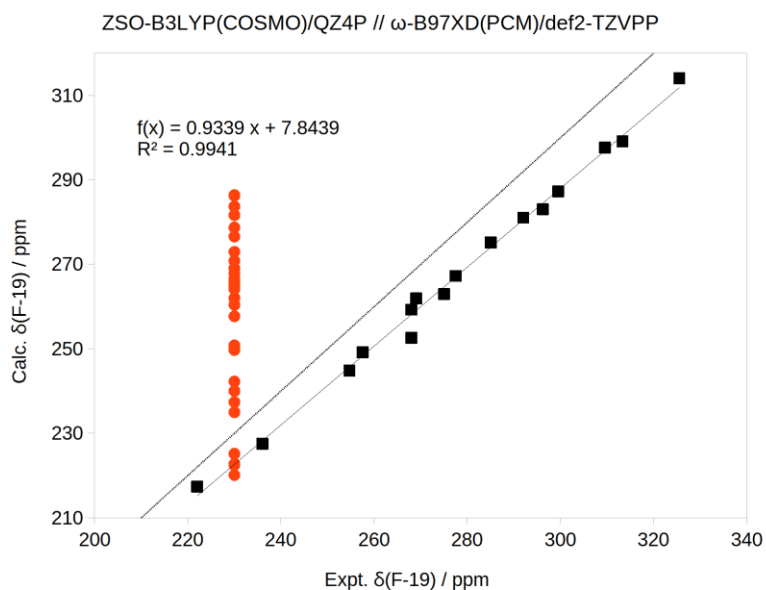


Figure S22. Correlation between calculated and experimental ^{19}F chemical shifts (w.r.t. F_2) for Niobium(V) fluorohalides at level of theory **ii**). Thick dotted line: $y = x$; thin black line: linear fit.

Red points: calculated values for the remaining Nb complexes not experimentally reported by Buslaev and Ylyin and correlated with the of 230 ppm assigned to *cis*-NbF₄Br₂⁻ (IV).

Table S1: Statistical parameters of the calculated vs. experimental chemical shifts of the Tantalum(V) fluorhalides at the various levels of theory.

Level of theory	R ²	Slope	Intercept / ppm	MAE / ppm	MaxErr / ppm
i)	0.9850	1.1186	-22.4	16.1	31.1
ii)	0.9921	1.2873	-93.0	5.9	16.1
iii)	0.9915	1.2316	-78.9	5.9	13.2
iv)	0.9926	1.2164	-72.39499	5.0	11.7
v)	0.9742	0.9361	31.9	11.1	18.8
vi)	0.9889	1.0358	-9.1	2.7	12.8
vii)	0.9815	1.0175	-9.1	4.1	15.8
viii)	0.9812	0.9928	0.1	3.2	15.6
ix)	0.9711	0.9508	20.9	5.4	18.9
x)	0.9378	0.8020	74.2	10.4	23.8
xi)	0.9764	0.9558	14.6	2.1	15.1
xii)	0.9829	0.8768	33.1	7.0	18.7
xiii)	0.9785	0.9758	-6.3	14.2	20.4
xiv)	0.9976	0.9945	-7.5	9.3	11.5

xv)	0.9940	1.0247	-19.9	11.8	14.9
xvi)	0.9964	1.0864	-33.1	5.2	8.5
xvii)	0.9919	1.2522	-100.4	18.2	27.5
xviii)	0.9944	1.2342	-93.9	17.6	25.6
xix)	0.9985	1.0093	-13.3	10.3	12.1
xx)	0.9975	1.0413	-20.0	6.6	9.0
xxi)	0.9974	1.0217	-18.7	11.6	13.6

Table S2: SO correction (obtained as the difference between the shielding constant at the ZORA-SO- and ZORA-SC-B3LYP(COSMO)/QZ4P levels for the compounds reported in Figure 5 of the main text.

mol		Ta complexes	Nb complexes
		$\sigma_{\text{SO}} - \sigma_{\text{SC}} / \text{ppm}$	$\sigma_{\text{SO}} - \sigma_{\text{SC}} / \text{ppm}$
I	F1	7.3	5.4
II	F1	8.6	5.8
II	F2	9.1	5.5
III	F1	10.3	7.1
IV	F1	10.7	6.9
IV	F2	10.6	6.0
VI	F1	14.8	10.3

XXXII	F1	8.4	5.6
XXXII	F2	8.4	5.4
XXXIII	F1	9.5	5.9
XXXIV	F1	9.9	6.0
XXXIV	F2	9.7	5.8
XXXV	F1	11.0	6.5
XXXV	F2	10.9	6.2
XXXVI	F1	12.3	7.1
XXXVII	F2	12.6	6.9
XXXVIII	F2	14.0	7.6