

SUPPORTING INFORMATION

Syntheses and X-ray Crystal Structures of α - and β -[XeO₂F][SbF₆], [XeO₂F][AsF₆], [FO₂XeFXeO₂F][AsF₆], and [XeF₅][SbF₆]·XeOF₄ and Electronic Structure Calculations of the XeO₂F⁺ and FO₂XeFXeO₂F⁺ Cations and Related Species

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Thermochemistry; HF Solvation of XeO₂F⁺. Although reactions A-E (Table 3) are not spontaneous under standard conditions, their negative ΔS° values indicate that these reactions will tend toward spontaneity at the lower temperatures at which [XeO₂F][MF₆] and [FO₂XeFXeO₂F][AsF₆] have proven to be isolable from anhydrous HF. Apparently, the positive enthalpies of these reactions and their contributions to the Gibbs free energies are diminished by HF solvation of the reactants and products. The degree to which XeO₂F⁺ is stabilized and reaction spontaneity is promoted by HF solvation has been assessed by calculating the BSSE-corrected^{50,51} enthalpies and Gibbs free energies at the MP2/Stutt RLC ECP level for five successive solvation reactions (eq S1) at 298.15 and 195.15 K.



$$\Delta H^\circ(1) = -74.4 \quad \Delta H^\circ(2) = -143.9 \quad \Delta H^\circ(3) = -209.5 \text{ kJ mol}^{-1}$$

$$\Delta G^{298}(1) = -44.5 \quad \Delta G^{298}(2) = -82.8 \quad \Delta G^{298}(3) = -120.1 \text{ kJ mol}^{-1}$$

$$\Delta G^{195}(1) = -55.1 \quad \Delta G^{195}(2) = -104.4 \quad \Delta G^{195}(3) = -149.9 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ(4) = -261.1 \quad \Delta H^\circ(5) = -263.7 \text{ kJ mol}^{-1}$$

$$\Delta G^{298}(4) = -140.2 \quad \Delta G^{298}(5) = -111.3 \text{ kJ mol}^{-1}$$

$$\Delta G^{195}(4) = -183.5 \quad \Delta G^{195}(5) = -164.2 \text{ kJ mol}^{-1}$$

All geometries were fully optimized and all calculations resulted in stationary points with all frequencies real (Figure S2). For x = 1-3, the HF molecules are F-coordinated to xenon (Xe--F, 2.638–2.671 Å). For x = 4 and 5, three of the HF molecules are F-coordinated to xenon (Xe--F, 2.568–2.777 Å). For x = 4, the remaining HF molecule is F-coordinated, by means of H-bonding, to an HF molecule (H--F, 1.577 Å) that is coordinated to xenon, whereas for x = 5 one of the remaining HF molecules is also H-bonded (H--F, 1.599 Å) and the other is more weakly H-bonded (H--F, 2.262 Å). The enthalpy change corresponding to the addition of an HF solvent molecule to the coordination sphere of the xenon atom is significantly exothermic, increasing by approximately 50–70 kJ mol⁻¹ per solvated HF for x = 1–4 at 298 K and 50–80 kJ mol⁻¹ at 195 K with a significant break at ΔH°(5) (vide supra). The reversal in the Gibbs free energy at ΔG°(5) indicates that xenon is coordinately saturated at XeO₂F⁺·4HF and further coordination of HF is unfavorable.

The above thermodynamic properties were also calculated using x times single gaseous HF. As a starting point to the associated xHF(g) species, the same conformation as in $\text{XeO}_2\text{F}^+\cdot\text{xHF}_{(\text{g})}$ was used but with XeO_2F^+ removed. Similar trends and a break at x = 5 are exhibited with little change in the enthalpies but significantly more negative Gibbs free energies result.

$$\begin{array}{lll}
 \Delta H^\circ(1) = -73.8 & \Delta H^\circ(2) = -152.1 & \Delta H^\circ(3) = -227.9 \text{ kJ mol}^{-1} \\
 \Delta G^{298}(1) = -43.8 & \Delta G^{298}(2) = -108.4 & \Delta G^{298}(3) = -179.8 \text{ kJ mol}^{-1} \\
 \Delta G^{195}(1) = -54.4 & \Delta G^{195}(2) = -123.0 & \Delta G^{195}(3) = -182.1 \text{ kJ mol}^{-1} \\
 \\
 \Delta H^\circ(4) = -270.7 & \Delta H^\circ(5) = -273.8 \text{ kJ mol}^{-1} \\
 \Delta G^{298}(4) = -230.7 & \Delta G^{298}(5) = -245.1 \text{ kJ mol}^{-1} \\
 \Delta G^{195}(4) = -242.2 & \Delta G^{195}(5) = -220.8 \text{ kJ mol}^{-1}
 \end{array}$$

Although the gas-phase solvation of XeO_2F^+ by HF molecules affords significant stabilization, it cannot overwhelm the highly endothermic gas-phase fluoride ion transfer reactions that give rise to XeO_2F^+ when AsF_5 , SbF_5 and Sb_2F_{10} are used as fluoride ion acceptors. Other factors such as Lewis acid and anion solvation would need to be accounted for in a fuller treatment of this problem.

Computational Results. Natural Resonance Theory (NRT). The NRT valencies of Xe (3.64), O (1.04) and F (0.78) suggest four single bonds in XeO_2F_2 . The most favored natural Lewis structures (Table 7) are the Xe-O single-bonded structure (3.0% non-Lewis type electrons) and the Xe-O single-bonded ion pair $[\text{FO}_2\text{Xe}^+][\text{F}^-]$ structure (3.1 % non-Lewis type electrons, see Table S8), the latter structure being consistent with the observed formation of XeO_2F^+ from XeO_2F_2 by removal of fluoride ion. Although the high terminal Xe–O bond order (0.87), which is about three times the single bond order (0.31 for Xe–F), supports significant double bond character for the terminal Xe–O bonds in this molecule, the Xe–O double-bonded Lewis structure is not as favorable (6.8% non-Lewis type electrons) as the Xe–O single-bonded and ion-pair Lewis structures as localized models of bonding. The Xe–O double-bonded structure results in very a low population (0.155) on the formal Xe–F bond NBO, which in this structure is composed 100% of fluorine orbitals. The other structures also show high contributions from O (88%) and F (86 – 77%) to the single Xe–O and Xe–F bonds. The low covalent part (0.19) of the total NRT valency (0.78) further reflects the highly ionic character of Xe–F bond.

The relative weighting of the natural resonance structures are given below.

XeO_2F_2 :

NRT analysis using 9 reference structures from totally ionic up to 2 double Xe–O + single Xe–F bonded structure results in 132 structures of which 24 structures have a weight $\geq 1.0\%$. The total weight of these 24 structures scaled to 100%.

Weight for structures with no Xe–O double bonds : 44.8%

Weight for structures with one Xe–O double bond: 44.0%

Weight for structures with two Xe–O double bond: 11.2%

XeO_2F^+ :

NRT analysis using 9 reference structures from totally ionic up to 2 double Xe–O + single Xe–F bonded structure results in 62 structures of which 19 structures have a weight $\geq 1.0\%$. The total weight of these 19 structures scaled to 100%.

Weight for structures with no Xe–O double bonds : 26.7%

Weight for structures with one Xe–O double bond: 60.7%

Weight for structures with two Xe–O double bond: 12.6%

IO₂F:

NRT analysis using 9 reference structures from totally ionic up to 2 double I-O + single I-F bonded structure results in 63 structures of which 15 structures have a weight $\geq 1.0\%$. The total weight of these 15 structures scaled to 100%.

Weight for structures with no I-O double bonds : 23.7%

Weight for structures with one I-O double bond: 61.6%

Weight for structures with two I-O double bond: 14.7%

TeO₂F⁻:

NRT analysis using 9 reference structures from totally ionic up to 2 double Te-O + single Te-F bonded structure results in 63 structures of which 14 structures have a weight $\geq 1.0\%$. The total weight of these 14 structures scaled to 100%.

Weight for structures with no Te-O double bonds : 37.0%

Weight for structures with one Te-O double bond: 41.8%

Weight for structures with two Te-O double bond: 21.2%

FO₂XeFXeO₂F⁺:

NRT analysis using 6 reference structures from singly bonded up to 4 double Xe-O + all Te-F single bonded structure results in 44 structures of which 20 structures have a weight $\geq 1.0\%$. The total weight of these 20 structures scaled to 100%.

Weight for structures with no Xe-O double bonds : 10.1%

Weight for structures with one Xe-O double bond: 58.5%

Natural Bond Orbital (NBO) and Electron Localization Function (ELF Analyses). The NBO program performs the analysis of the many-electron wavefunction in terms of localized electron-pair bonding units.⁵³⁻⁵⁶ The set of NBOs, each taken doubly occupied, is said to represent the "natural Lewis structure" of the molecule. The natural atomic charges are obtained by subtracting the sum of Natural Atomic Orbital (NAO) populations on one atom center from its nuclear charge. Natural charges can be used to estimate ionic character (polarity) of a bond. On the other hand, NAO overlap-weighted bond orders (BO's) represent the covalent character of a bond. For polar bonds, NAO's are usually much less than the expected formal BO's.

The electron localization function (ELF) analysis leads to a robust description of chemical bonding based on the topological analyses of HF or DFT total electron density related to the Pauli exclusion principle.⁶¹ ELF is a dimensionless function in three-space giving large values (0.5 – 1.0) for regions, so called basins, where electron density is localized. From ELF function values a volume and electron population (N_i) are calculated for each basin, either one-center core $C(A)$, two-center bonding $V(A,B)$ or one-center non-bonding (lone pair) $V(A)$ or $V(B)$ basins. Different basins overlap in space, so that part of the electron population (N_i) assigned to a particular basin comes, in part, from other basins. These contributions are treated as statistical variances and each basin contribution is given as a % of the total contribution (relative fluctuation, λ). Basin lobes can be graphically presented as isosurfaces at a particular ELF value, thus showing where the bonding and non-bonding electrons are most likely located in a molecule.

Although ELF analysis does not lead to bond orders or basin populations that are comparable with NBO properties, or even with those in different molecules, it complements the NBO analysis by visualizing the statistical electron distribution coming from a simple numerical integration of the total electron density.

XeO₂(OTeF₅)₂. At the ELF contour value 0.50, XeO₂(OTeF₅)₂ has bisynaptic bond basins V(Xe,O_{1,2}) to terminal O atoms (populations, 1.36 e; volume 15.7) and V(Xe,O_{3,4}) to bridging O atoms (populations, 0.70 e; volume 5.0). The V(Xe,O_{3,4}) and V(Xe,O_{1,2}) basins of XeO₂(OTeF₅)₂ are assigned to single and localized double bonds, respectively, based on their relative volumes and populations. Scaling of the single bond population (0.70) to 1 followed by application of this scaling factor (1.43) to the terminal Xe-O bond population (1.36) results in a value of 1.94, which is close to 2. Scaling of the basin volumes results in 1 for the single bond volume and ca. 3 for the double bond volume. The high λ -values for the single (0.83) and double (0.76) bond basins also reflect their localized characters. These highly localized bond basins are located closer to the oxygen ligands as can be seen from the isosurfaces depicted in Figure 5. Again, the non-bonding lone pair V₂(Xe) basin is shown to be more diffuse within the O₁-Xe-O₂ equatorial plane than along the O₃-Xe-O₄ axial plane and the bending of the O₃-Xe-O₄ angle towards the valence electron lone pair domain of xenon (Figure 5) is accounted for by the Robinson-Gillespie rationale and by arguments similar to those given above for the F-Xe-F angle in XeO₂F₂.

XeO₂(OTeF₅)⁺. Although the XeO₂(OTeF₅)⁺ cation has been characterized in SbF₅ solution by ¹⁹F and ¹²⁹Xe NMR spectroscopy [Inorg. Chem. 1992, 31, 3381], there are no experimental geometric parameters to compare with the calculated values given in Table S7. When compared with XeO₂F⁺, the calculated terminal Xe-O bond lengths are somewhat longer, but the geometry of the XeO₂O moiety of XeO₂(OTeF₅)⁺ is otherwise very similar to that of XeO₂F⁺ (Figure 5).

The Xe charge of 2.93 in XeO₂(OTeF₅)⁺ is similar to that in XeO₂F⁺. The Xe-O bond order (0.93) is higher than the bridging Xe-O single bond order (0.52) and higher than that of XeO₂F⁺. The double- and single-bonded Lewis structures are almost equally weighted, i.e., 2.3 and 2.6% non-Lewis type electrons, respectively, with similar bond polarities in both Lewis structure models. The OTeF₅ group has a high charge on Te (3.54) while F atoms have natural charges of about -0.57, so that the Te-F single bonds (average bond order, 0.45) are highly polar (NBO composition of 13% Te and 87% F).

The ELF basin composition of XeO₂(OTeF₅)⁺ is very similar to that of XeO₂F⁺, but replacement of F with a OTeF₅ group results in a description having bisynaptic bond basins V(Xe,O_{1,2}) (population, 0.85; volume 10.5) to the terminal oxygen atoms and V(Xe,O₃) to the bridging oxygen (population, 0.43; volume 3.24). Scaling the population of V(Xe,O₃) to 1 gives a scaled population value of 1.98 for V(Xe,O_{1,2}), which, like XeO₂(OTeF₅)₂, is close to 2. Again, the basin volumes scale close to 1:3 and the basin lobes in Figure 5 are similar in appearance to those of other species that have been discussed.

Figure S1. Thermochemical cycles that describe the reactions of XeO_2F_2 with MF_5 ($\text{M} = \text{As, Sb}$) and lead to the formation of $[\text{XeO}_2\text{F}][\text{MF}_6]$, $[\text{XeO}_2\text{F}][\text{Sb}_2\text{F}_{11}]$ and $[\text{FO}_2\text{XeF}\text{XeO}_2\text{F}][\text{MF}_6]$

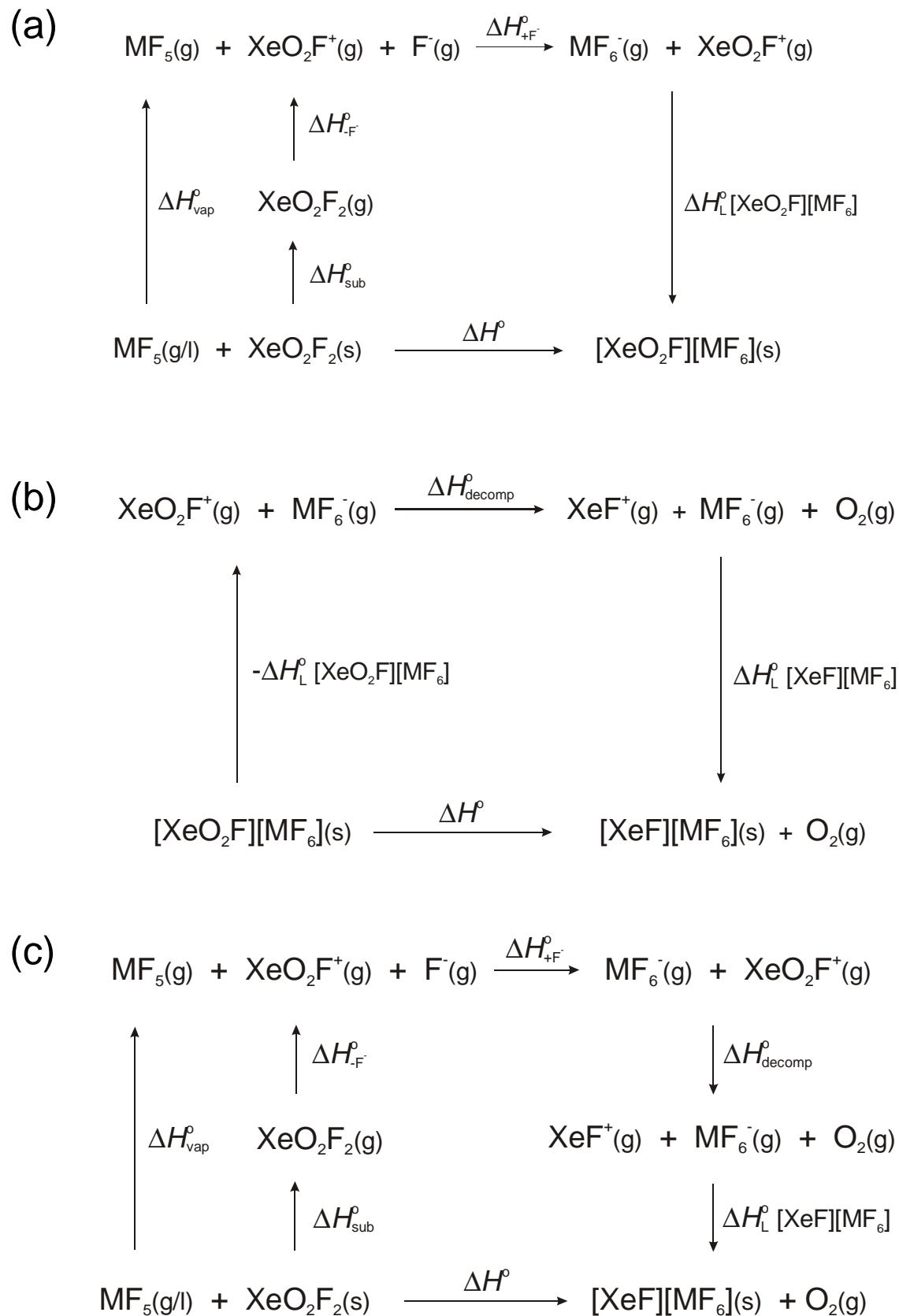
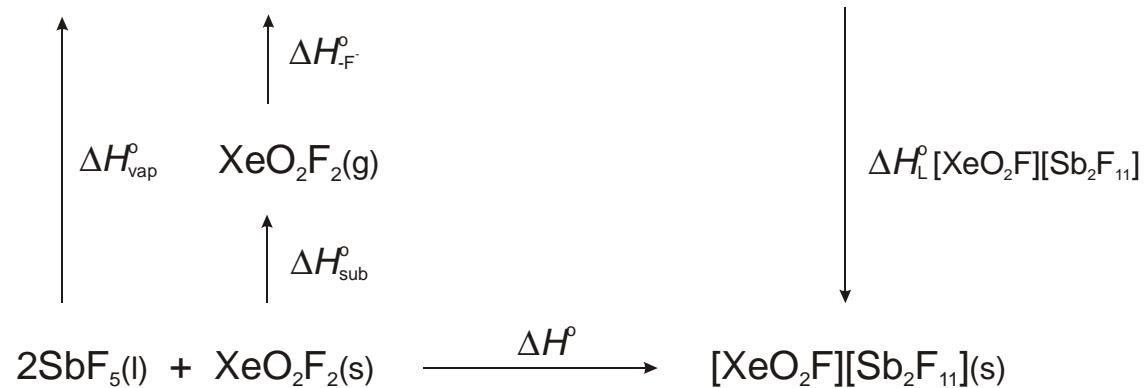
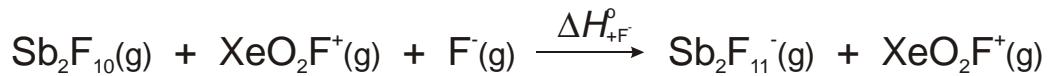


Figure S1. (continued...)

(d)



(e)

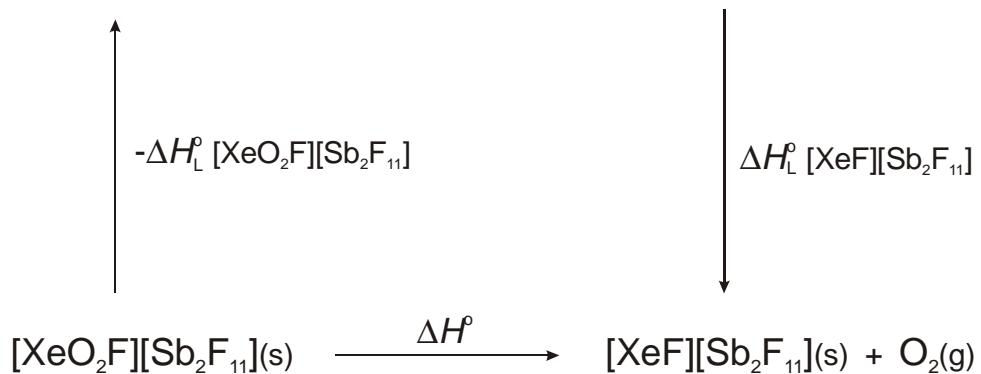
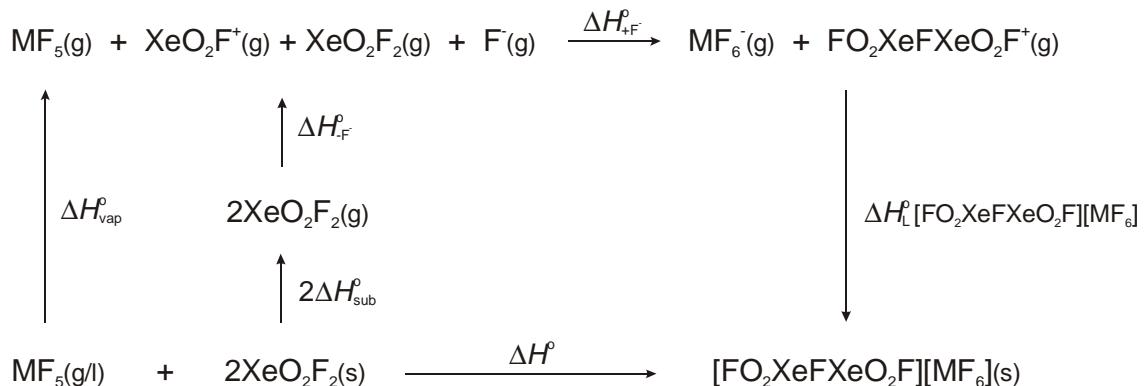


Figure S1. (continued...)

(f)



(g)

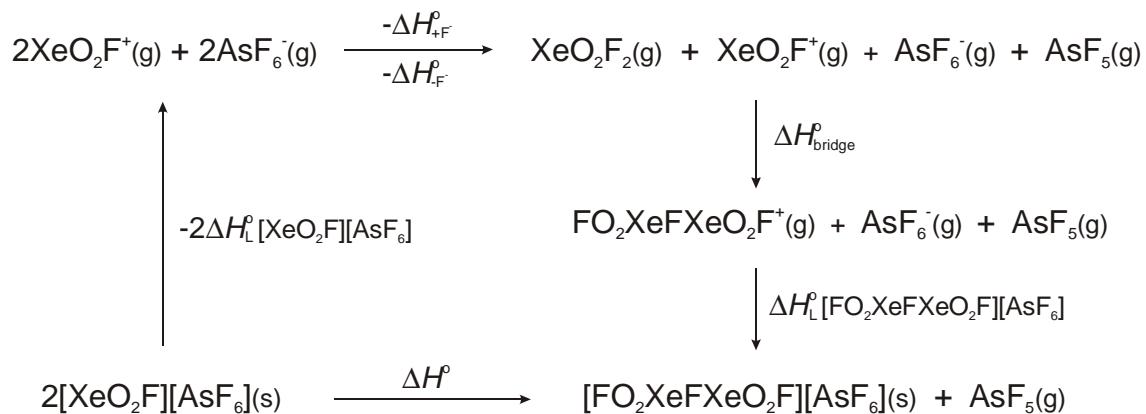


Figure S2. Calculated geometries of the XeO_2F^+ HFadducts.

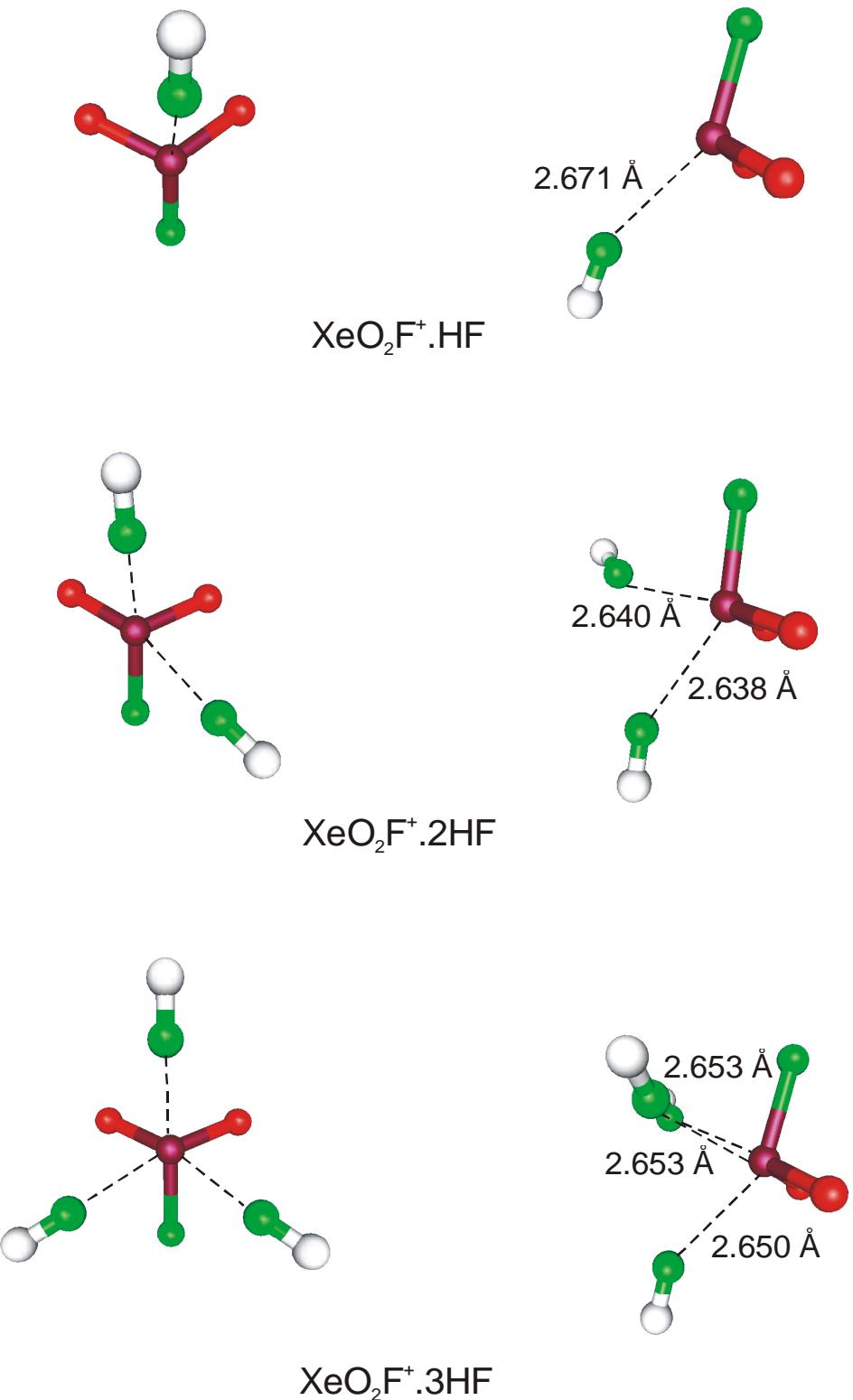


Figure S2 (continued ...).

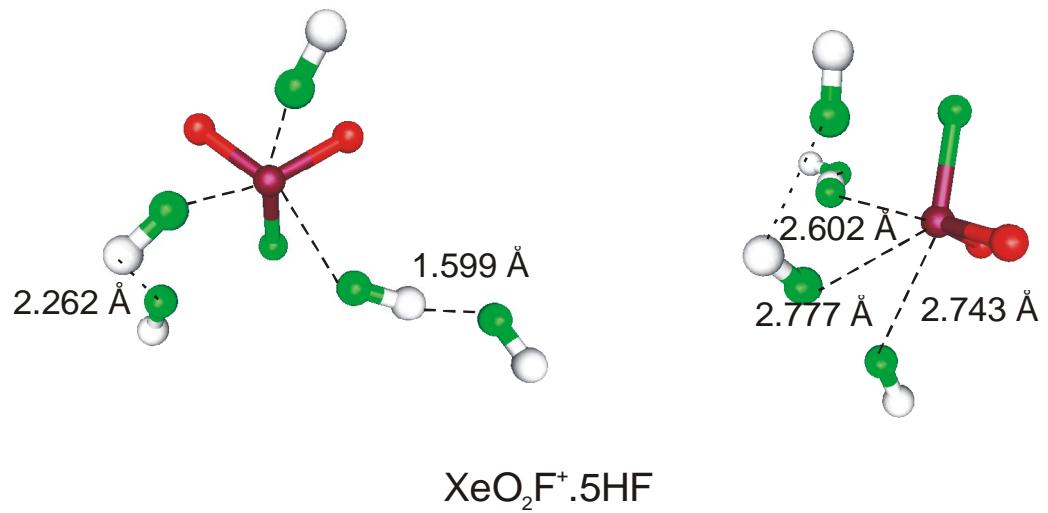
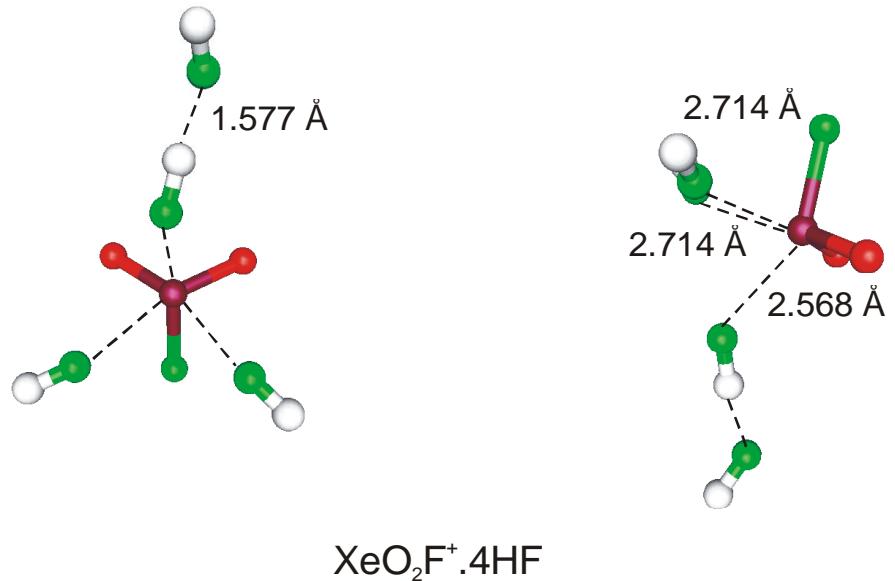


Table S1. A Comparison of the Bond Lengths and Bond Angles for XeO_2F^+ , IO_2F , ClO_2F , and TeO_2F^-

Species	Bond Length (\AA) ^e		Bond Angle (deg) ^e	
	<u>E-O</u>	<u>E-F</u>	<u>O-E-O</u>	<u>F-E-O</u>
XeO_2F^+ ^a	1.740(3)	1.849(2)	105.0(2)	95.7(1)
	1.727(3)			98.2(1)
IO_2F ^b	1.805(6) (b)	1.903(5)	99.2(3) (t,b)	94.6(2) (b)
	1.773(6) (t)			90.7(2) (t)
ClO_2F ^c	1.418(2)	1.697(3)	115.23(5)	101.72(3)
TeO_2F^- ^d	1.807(4) (t)	2.095(8)	99.7(1.3) (t,b)	87.4(8) (t)
	1.904(10) (b)		91.4(1.9) (t,b)	85.0(1.7) (b)
	2.080(6) (b)		89.5(9) (b,b)	173.2(1.7) (b)

^a This work; ^b ref 21; ^c ref 23; ^d ref 22. The symbols t and b denote terminal and bridging oxygens, respectively; ^e Averages of esd's (σ) were calculated using the following, $\langle L \rangle = \sum L_M / M$ and $\sigma \langle L \rangle = [\sum (L_M - \langle L \rangle)^2 / M(M-1)]^{1/2}$, where $\langle L \rangle$ is the average geometric parameter and M is the number of parameters.

Table S2. Electronic Energies and Gibb's Free Energies for the Calculated Species at the MP2 Level

species	Stutt RLC ECP		DZVP	
	E ^a	Gibbs E ^b	E ^a	Gibbs E ^b
XeO ₂ F ⁺	-70.817351	-70.846353	-7480.260235	-7480.289510
XeO ₂ F ₂	-95.364501	-95.394412	-7580.225240	-7580.255416
FO ₂ XeFXeO ₂ F ⁺ (C _s)	-166.219034	-166.260929	-15060.531013	-15060.573213
FO ₂ XeFXeO ₂ F ⁺ (C ₁)	-166.219054	-166.263721	-15060.531025	-15060.576541
AsF ₅	-127.216080	-127.245569	-2731.958221	-2731.987794
AsF ₆ ⁻	-151.588404	-151.617103	-2831.751835	-2831.780735
SbF ₅	-126.453911	-126.485176	-6810.962328	-6810.993937
SbF ₆ ⁻	-150.848721	-150.879151	-6910.783227	-6910.814291
XeF ⁺	-39.132568	-39.155926	-7330.482438	-7330.505863
XeF ₂	-63.684660	-63.709374	-7430.456565	-7430.481349
O ₂	-31.814858	-31.834877	-149.951391	-149.971431
F ⁻	-24.2004530	-24.214612	-99.6065733	-99.620732
F ₂	-48.210190	-48.229853	-199.063471	-199.083136
Sb ₂ F ₁₀	-252.957003	-252.998761	-13621.968199	-13622.011418
Sb ₂ F ₁₁ ⁻	-277.365898	-277.414688	-13721.807122	-13721.859362
Xe	-15.433714	-15.450617	-7231.366016	-7231.382919

^a Calculated electronic energies in a.u. (1 a.u. = 2625.499748 kJmol⁻¹). ^b Sum of electronic energies and thermal free energies in a.u.

Table S3. Standard Entropies for Equations A-I in Table 3

$$\Delta S^{\circ}(A,B) = S^{\circ}([XeO_2F][MF_6](s)) - S^{\circ}(MF_5(g/l)) - S^{\circ}(XeO_2F_2(s)) = -562.17 \text{ (As); } -328.53 \text{ (Sb)}$$

$$\Delta S^{\circ}(C) = S^{\circ}([XeO_2F][Sb_2F_{11}](s)) - 2S^{\circ}(SbF_5(g)) - S^{\circ}(XeO_2F_2(s)) = -453.23$$

$$\Delta S^{\circ}(D,E) = S^{\circ}([FO_2XeFXeO_2F][MF_6](s)) - S^{\circ}(MF_5(g/l)) - 2S^{\circ}(XeO_2F_2(s)) = -765.97 \text{ (As); } -529.97 \text{ (Sb)}$$

$$\Delta S^{\circ}(F) = S^{\circ}([FO_2XeFXeO_2F][AsF_6](s)) + S^{\circ}(AsF_5(g)) - 2S^{\circ}([XeO_2F][AsF_6](s)) = 358.37$$

$$\Delta S^{\circ}(G,H) = S^{\circ}([XeF][MF_6](s)) + S^{\circ}(O_2(g)) - S^{\circ}([XeO_2F][MF_6](s)) = 179.41 \text{ (As); } 181.76 \text{ (Sb)}$$

$$\Delta S^{\circ}(I) = S^{\circ}([XeF][Sb_2F_{11}](s)) + S^{\circ}(O_2(g)) - S^{\circ}([XeO_2F][Sb_2F_{11}](s)) = 181.78$$

Table S4. Experimental and Calculated Vibrational Frequencies,^a Calculated Raman and Infrared Intensities, Assignments and Mode Descriptions for XeO_2F_2

XeO_2F_2		Stuttgart RLC ECP ^b						DZVP ^b		assgnts (C_{2v}) ^c			
exptl ^d		HF		SVWN		MP2		HF		SVWN		MP2	
902, w	[882, s]	926	(48)[12]	875	(80)[10]	1021	(153)[5]	715	(10)[9]	843	(79)[9]	1026	(209)[4]
845, vs	[850, vs]	837	(5)[36]	824	(11)[38]	1015	(35)[24]	604	(2)[47]	779	(13)[30]	1006	(56)[19]
578, w		666	(407)[0]	588	(258)[1]	591	(306)[1]	657	(354)[0]	586	(207)[0]	574	(230)[1]
490, s	[537, vs]	632	(3)[26]	512	(7)[30]	508	(6)[35]	574	(1)[23]	500	(4)[26]	473	(5)[29]
333, ms	[350, ms]	393	(20)[2]	283	(7)[3]	332	(7)[2]	335	(18)[3]	274	(10)[3]	318	(12)[3]
(317, ms)		372	(52)[3]	292	(22)[4]	341	(30)[4]	308	(55)[4]	266	(28)[5]	315	(42)[5]
313, ms	[315, vs]	360	(0)[3]	253	(0)[5]	295	(0)[4]	313	(0)[6]	243	(0)[6]	274	(0)[4]
223, vw	[224, w]	256	(23)[0]	170	(13)[0]	190	(17)[0]	255	(24)[0]	175	(13)[1]	180	(18)[1]
198, w	[205, ms]	221	(4)[1]	152	(6)[1]	172	(9)[1]	191	(0)[3]	143	(3)[1]	157	(7)[1]

^a Frequencies are in cm^{-1} . ^b Values in parentheses are calculated infrared intensities (km mol^{-1}) and values in brackets are calculated Raman intensities ($\text{\AA}^4 \text{ amu}^{-1}$). ^c Elongation of a bond(s) and angle opening(s) are denoted by plus (+) signs and bond contraction(s) and angle closing(s) are denoted by negative (-) signs. The abbreviations denote stretch (v), bending (δ), twisting (ρ_t), wagging (ρ_w) and rocking (ρ_r). The modes are relative to the OxeO plane. ^d Raman frequencies are from ref 20. Unless indicated, values are from a liquid. Values in square brackets are from a solid while that in parentheses is an infrared frequency. The symbols vw, w, ms, s, and vs denote very weak, weak, medium strong, strong and very strong.

Table S5.Experimental Raman and Calculated Vibrational Frequencies and Raman and Infrared ,^{a,b} Assignments and Mode Descriptions for α -XeO₂F⁺, IO₂F and TeO₂F

		Stuttgart RLC ECP				DZVP					
expt ^c	expt ^d	HF	SVWN	MP2	HF	HF	SVWN	MP2	assgnts		
α -XeO ₂ F ⁺ (C _s)											
931(23)	923(38)	979(25)[10]	892(23)[10]	1119(86)[9]	771(6)[8]	857(10)[25]	1160(140)[16]	A'', v _{as} (XeO ₂)			
873(100)	867(100)	882(10)[30]	835(6)[29]	1106(10)[24]	679(30)[62]	790(26)[7]	1132(17)[31]	A', v _s (XeO ₂)			
576(20)											
588(10)	580(58)	744(75)[23]	592(54)[16]	567(103)[13]	635(31)[1]	559(14)[46]	498(112)[6]	A', v(XeF)			
594(54)											
321(26)		349(34)[3]	273(11)[4]	325(16)[3]	276(5)[32]	245(5)[13]	307(22)[3]	A', δ (O ₁ XeO ₂) + δ (FXeO ₁ + FXeO ₂) _{small}			
281(35)	334(23)	294(12)[4]	210(6)[3]	255(7)[3]	223(6)[8]	185(4)[5]	230(7)[3]	A', ρ _{r(O₁XeO₂) + δ(FXeO₁ + FXeO₂)}			
249(24)		276(10)[3]	188(4)[4]	228(7)[4]	213(6)[12]	160(5)[4]	195(11)[4]	A'', δ (FXeO ₁ - FXeO ₂)			
IO₂F (C_s)											
970(104)[17]		864(91)[14]	991(186)[7]	933(102)[12]	863(86)[11]	1002(196)[6]	A'', v _{as} (IO ₂)				
920(21)[45]		831(17)[41]	988(10)[25]	878(29)[33]	826(20)[28]	993(45)[15]	A', v _s (IO ₂)				
685(141)[12]		541(96)[13]	515(132)[19]	642(136)[13]	545(86)[10]	500(120)[15]	A', v(IF)				
347(58)[3]		272(24)[4]	309(32)[4]	329(62)[4]	270(27)[5]	302(37)[4]	A', δ (O ₁ IO ₂) + small δ (FIO ₁ + FIO ₂)				
283(20)[3]		207(11)[3]	234(11)[3]	263(20)[4]	204(11)[4]	224(12)[4]	A', ρ _{r(O₁IO₂) + δ(FIO₁ + FIO₂)}				
261(12)[3]		185(5)[4]	210(9)[4]	241(13)[3]	179(6)[4]	195(9)[4]	A'', δ (FIO ₁ - FIO ₂)				
TeO₂F (C_s)											
911(242)[27]		801(202)[25]	851(65)[35]	884(199)[15]	798(147)[12]	849(62)[14]	A'', v _{as} (TeO ₂)				
901(62)[48]		797(42)[50]	839(284)[13]	868(64)[29]	785(40)[25]	848(221)[6]	A', v _s (TeO ₂)				
588(185)[5]		464(138)[9]	459(171)[10]	536(171)[4]	475(111)[6]	446(144)[8]	A', v(TeF)				
346(81)[3]		272(35)[5]	295(44)[5]	331(85)[4]	270(37)[5]	290(50)[5]	A', δ (O ₁ TeO ₂) + small δ (FTeO ₁ + FTeO ₂)				
278(28)[2]		206(13)[4]	226(13)[3]	259(27)[2]	202(15)[3]	216(15)[3]	A', ρ _{r(O₁TeO₂) + δ(FTeO₁ + FTeO₂)}				
254(11)[2]		187(5)[4]	207(8)[3]	233(12)[2]	179(5)[3]	191(9)[3]	A'', δ (FTeO ₁ - FTeO ₂)				

^a Frequencies are in cm⁻¹. ^b Values in parentheses are calculated infrared intensities (km mol⁻¹) and values in brackets are calculated Raman intensities (Å⁴ amu⁻¹). ^c Ref 8. ^d Ref 4.

Table S6. Experimental Raman and Calculated (C_1) Vibrational Frequencies,^a Assignments and Mode Descriptions for the $\text{FO}_2\text{XeF}\text{XeO}_2\text{F}^+$ Cation

expt ^d	$\text{FO}_2\text{XeF}\text{XeO}_2\text{F}^+$		Stuttgart RLC ECP ^b				DZVP ^b				Assigns (C_1) ^c		
	HF	SVWN	MP2		HF(C_1)	SVWN (C_1)	MP2 (C_1)		HF(C_1)	SVWN (C_1)	Assigns (C_1) ^c		
			HF	SVWN			HF	SVWN			HF	SVWN	
911(16)	947 (47)[5]	893 (17)	1079 (47)	735 (9)[3]	859 (16)	1102 (81)	A'', v(Xe ₁ O ₁ - Xe ₁ O ₂) + v(Xe ₂ O ₃ - Xe ₂ O ₄)						
863(86)	946 (13)[13]	892 (4)	1075 (2)	735 (5)[10]	859 (8)	1099 (11)	A'', v(Xe ₁ O ₁ - Xe ₁ O ₂) - v(Xe ₂ O ₃ - Xe ₂ O ₄)						
598(100)	851 (1)[61]	837 (1)	1072 (10)	689 (0)[116]	792 (1)	1084 (16)	A', v(Xe ₁ O ₁ + Xe ₁ O ₂) + v(Xe ₂ O ₃ + Xe ₂ O ₄)						
592sh	850 (14)[2]	837 (2)	1070 (2)	680 (250)[11]	791 (2)	1082 (1)	A', v(Xe ₁ O ₁ + Xe ₁ O ₂) - v(Xe ₂ O ₃ + Xe ₂ O ₄)						
412(3)	735 (1)[71]	598 (0)	583 (0)	589 (19)[3]	572 (0)	525 (1)	A', v(Xe ₁ F ₁) + v(Xe ₂ F ₂)						
370 (45)[2]	725 (285)[1]	588 (73)	572 (81)	588 (0)[54]	565 (76)	517 (100)	A', v(Xe ₁ F ₁) - v(Xe ₂ F ₂)						
341(32)	357 (55)[2]	357 (100)	349 (29)	354 (389)[0]	380 (100)	348 (81)	A', v(Xe ₁ F ₃) - v(Xe ₂ F ₃)						
296(13)	288 (7)	340 (9)	310 (14)[3]	262 (6)	316 (13)	A', $\delta(\text{O}_1\text{Xe}_1\text{O}_2) + \delta(\text{O}_3\text{Xe}_2\text{O}_4)$							
270(18)	352 (16)[1]	280 (8)	302 (0)	296 (42)[2]	253 (12)	293 (60)	A', v(Xe ₁ F ₃) - v(Xe ₂ F ₃) + $\delta(\text{O}_1\text{Xe}_1\text{O}_2) - \delta(\text{O}_3\text{Xe}_2\text{O}_4)$						
235(3)	335 (14)[1]	261 (0)	295 (100)	287 (29)[1]	242 (1)	281 (0)	A', $\rho_w(\text{O}_1\text{Xe}_1\text{O}_2 - \text{O}_3\text{Xe}_2\text{O}_4) + \delta(\text{O}_1\text{Xe}_1\text{O}_2 - \text{O}_3\text{Xe}_2\text{O}_4)_{\text{small}} + \delta(\text{Xe}_1\text{F}_3\text{Xe}_2\text{O}_4)_{\text{small}}$						
196(4)	320 (25)[4]	245 (7)	286 (0)	275 (364)[6]	228 (8)	266 (8)	A', $\rho_w(\text{O}_1\text{Xe}_1\text{O}_2 + \text{O}_3\text{Xe}_2\text{O}_4) + \delta(\text{O}_1\text{Xe}_1\text{O}_2 - \text{O}_3\text{Xe}_2\text{O}_4)_{\text{small}}$						
130(9)	318 (3)[5]	230 (1)	259 (1)	268 (13)[8]	208 (0)	231 (1)	A'', $\rho(\text{O}_1\text{Xe}_1\text{O}_1 - \text{O}_3\text{Xe}_2\text{O}_4) + \rho(\text{F}_1\text{Xe}_1\text{F}_3 - \text{F}_3\text{Xe}_2\text{F}_2)$						
	285 (652)[2]	224 (1)	254 (0)	262 (31)[5]	206 (0)	223 (0)	A'', $\rho(\text{O}_1\text{Xe}_1\text{O}_2 + \text{O}_3\text{Xe}_2\text{O}_4) + \delta(\text{F}_1\text{Xe}_1 - \text{F}_2\text{Xe}_2)$						
	250 (13)[1]	212 (2)	224 (4)	222 (14)[3]	183 (2)	178 (4)	A', $\delta(\text{Xe}_1\text{F}_3\text{Xe}_2)$						
	235 (26)[0]	157 (3)	176 (5)	221 (1)[1]	152 (3)	166 (7)	A'', $\rho(\text{F}_1\text{Xe}_1\text{F}_3 + \text{F}_3\text{Xe}_2\text{F}_2)$						
	154 (0)[0]	117 (1)	123 (0)	146 (0)[1]	116 (0)	117 (1)	A', $\delta(\text{F}_1\text{Xe}_1) + \delta(\text{F}_2\text{Xe}_2)$						
	128 (0)[0]	89 (0)	95 (0)	125 (0)[0]	91 (0)	90 (0)	A'', $\rho(\text{F}_1\text{Xe}_1\text{O}_1\text{O}_2 + \text{F}_3\text{Xe}_2\text{O}_3\text{O}_4)$						
	117 (9)[1]	84 (0)	87 (0)	119 (3)[1]	86 (0)	85 (0)	A', $\rho(\text{F}_1\text{Xe}_1\text{O}_1 - \text{F}_2\text{Xe}_2\text{O}_4)$						
	40 (1)[0]	21 (0)	26 (0)	39 (0)[0]	24 (0)	32 (0)	A', $\delta(\text{Xe}_1\text{F}_3\text{Xe}_2) + \rho(\text{F}_1\text{Xe}_1\text{O}_1 - \text{F}_2\text{Xe}_2\text{O}_4)$						
	32 (1)[0]	19 (0)	23 (0)	34 (1)[0]	22 (0)	30 (0)	A'', $\rho(\text{F}_1\text{Xe}_1\text{F}_3 - \text{F}_3\text{Xe}_2\text{F}_2) + \rho(\text{O}_1\text{Xe}_1\text{O}_2 - \text{O}_3\text{Xe}_2\text{O}_4)$						
	21 (1)[1]	14 (0)	12 (0)	16 (2)[1]	11 (0)	6 (0)	A'', $\rho(\text{O}_1\text{Xe}_1\text{O}_2 - \text{O}_3\text{Xe}_2\text{O}_4)$						

^a Frequencies are in cm^{-1} . ^b Values in parentheses are calculated infrared intensities (km mol^{-1}) and values in brackets are calculated Raman intensities ($\text{\AA}^4 \text{amu}^{-1}$). ^c The abbreviations denote stretch (v), bending (δ), twisting (ρ_l), wagging (ρ_w), rocking (ρ_r), in-plane bending (i.p.) and out-of-plane bending (o.o.p.) modes. The plane of the molecule is defined as perpendicular to the $\text{F}_1\text{Xe}_1\text{F}_3\text{Xe}_2\text{F}_2$ backbone and bisecting F_3 in Figure 5. ^d Spectrum recorded at RT in a $1/4''$ FEP tube. Bands at 693(15), 573(7), 549(7), 385(10), 379(10) and 374(sh) cm^{-1} were assigned to AsF₆ by comparison with previous assignments given in ref. 8.

Table S7. Experimental and Calculated Geometrical Parameters (\AA and degrees) in XeO_2F_2 (C_{2v}), XeO_2F^+ (C_s), IO_2F (C_s), TeO_2F^- (C_s), $\text{FO}_2\text{XeF}\text{XeO}_2\text{F}^+$ (C_1) $\text{XeO}_2(\text{OTeF}_5)_2$ (C_1) and $\text{XeO}_2(\text{OTeF}_5)^+$ (C_I)

XeO₂F₂		DZVP		
	exptl ^a	HF	SVWN	MP2
Xe-O	1.714(4)	1.807	1.811	1.765
Xe-F	1.899(3)	1.937	2.018	2.039
O-Xe-O	105.7(3)	113.5	113.3	112.6
O-Xe-F	91.6(1)	90.8	92.6	92.8
F-Xe-F	174.7(4)	177.3	170.5	169.7

XeO₂F⁺		DZVP		
	exptl ^b	HF	SVWN	MP2
Xe-O(1)	1.740(3)	1.780	1.808	1.752
Xe-O(2)	1.726(3)	1.780	1.808	1.752
Xe-F(1)	1.849(2)	1.877	1.977	2.014
O(1)-Xe-O(2)	105.0(2)	112.0	114.3	114.7
O(1)-Xe-F(1)	95.7(1)	101.6	102.0	100.2
O(2)-Xe-F(1)	98.2(1)	101.6	102.0	100.2

IO₂F		DZVP		
	exptl ^c	HF	SVWN	MP2
I-O (b)	1.805(6)	1.766	1.811	1.793
I-O (t)	1.773(6)			
I-F	1.903(5)	1.910	1.992	2.027
O-I-O (t,b)	99.2(3)	110.8	111.3	112.1
O-I-F (b)	94.6(2)	99.8	100.5	100.2
O-I-F (t)	90.7(2)			

TeO₂F		DZVP		
	exptl ^d	HF	SVWN	MP2
Te-O (t)	1.807(4)	1.811	1.849	1.850
Te-O (b)	1.904(10), 2.080(6)			
Te-F	2.095(8)	1.987	2.048	2.083
O-Te-O (t,b)	91.4(1.9), 99.7(1.3)	110.4	110.2	111.2
O-Te-O (b,b)	89.5(9)			
O-Te-F (b)	85.0(1.7), 173.2 (1.7)	99.3	100.0	100.2
O-Te-F (t)	87.4(8)			

Table S7. (continued ...)

FO₂XeFXeO₂F⁺	exptl ^b	DZVP		
		HF	SVWN	MP2
Xe(1)-F(1)	1.872(3)	1.884	1.980	2.013
Xe(1)-F(3)	2.230(3)	2.222	2.260	2.314
Xe(1)-O(1)	1.715(4)	1.792	1.805	1.754
Xe(1)-O(2)	1.721(4)	1.792	1.805	1.754
Xe(2)-F(2)	1.870(4)	1.884	1.980	2.013
Xe(2)-F(3)	2.161(3)	2.223	2.260	2.314
Xe(2)-O(3)	1.719(4)	1.792	1.805	1.754
Xe(2)-O(4)	1.719(4)	1.792	1.805	1.754
O(1)-Xe(1)-F(1)	96.0(2)	95.8	97.1	97.5
O(1)-Xe(1)-F(3)	89.9(2)	87.5	89.8	91.2
O(1)-Xe(1)-O(2)	105.8(2)	112.7	113.9	113.0
O(2)-Xe(1)-F(3)	89.8(2)	87.2	89.3	91.1
F(1)-Xe(1)-O(2)	95.4(2)	95.7	97.2	97.6
F(1)-Xe(1)-F(3)	170.8(2)	174.4	167.6	164.1
Xe(1)-F(3)-Xe(2)	166.4(2)	158.2	156.5	159.8
F(2)-Xe(2)-O(3)	95.2(2)	95.7	97.2	97.6
F(2)-Xe(2)-O(4)	95.6(2)	95.8	97.1	97.5
F(2)-Xe(2)-F(3)	169.7(2)	174.4	167.6	164.1
O(3)-Xe(2)-O(4)	105.8(2)	112.7	113.9	113.0
O(3)-Xe(2)-F(3)	91.1(2)	87.2	89.3	91.2
O(4)-Xe(2)-F(3)	90.6(2)	87.5	89.8	91.2

Table S7 (continued ...)

$\text{XeO}_2(\text{OTeF}_5)_2$	$\text{XeO}_2(\text{OTeF}_5)^+$				Stuttgart RLC ECP			
	expt ^e				HF		SVWN	
					HF	MP2	HF	SVWN
Xe-O(1), Xe-O(2)	1.720(5), 1.738(5)	1.726	1.786	1.743	Xe-O(1), Xe-O(2)	1.718	1.734	1.785
Xe-O(3), Xe-O(4)	2.024(5), 2.020(4)	1.956	2.080	2.071	Xe-O(3)	1.823	1.935	1.967
Te(1)-O(3), Te(2)-O(4)	1.854(5), 1.865(4)	1.864	1.928	1.919	Te-O(3)	2.003	2.028	2.043
Te(1)-F(1), Te(2)-F(6)	1.814(5), 1.824(5)	1.815	1.876	1.863	Te-F(1)	1.799	1.848	1.860
Te(1)-F(2), Te(2)-F(7)	1.834(5), 1.819(5)	1.815	1.876	1.863	Te-F(2)	1.799	1.848	1.860
Te(1)-F(3), Te(2)-F(8)	1.850(5), 1.833(5)	1.813	1.880	1.865	Te-F(3)	1.805	1.863	1.882
Te(1)-F(4), Te(2)-F(9)	1.821(5), 1.847(5)	1.807	1.867	1.852	Te-F(4)	1.783	1.828	1.843
Te(1)-F(5), Te(2)-F(10)	1.817(5), 1.816(5)	1.813	1.873	1.859	Te-F(5),	1.794	1.840	1.854
O(1)-Xe-O(2)	106.5(2)	108.9	108.7	108.2	O(1)-Xe-O(2)	108.5	109.2	108.6
O(1)-Xe-O(3), O(1)-Xe-O(4)	95.3(2), 94.4(2)	93.3	96.5	97.0	O(1)-Xe-O(3), O(1)-Xe-O(4)	104.0	105.6	106.8
O(2)-Xe-O(3), O(2)-Xe-O(4)	94.3(2), 95.3(2)							
O(3)-Xe-O(4)	163.7(2)	168.6	157.5	156.0				
Xe-O(3)-Te(1), Xe-O(4)-Te(2)	130.7(2), 132.5(2)	136.0	124.2	127.2	Xe-O(3)-Te	132.3	125.5	121.8
O(3)-Te(1)-F(1), O(4)-Te(2)-F(6)	91.6(2), 92.3(2)	91.4	91.6	91.6	O(3)-Te-F(1)	86.8	87.7	87.7
O(3)-Te(1)-F(2), O(4)-Te(2)-F(7)	92.3(2), 93.0(2)	91.4	91.6	91.6	O(3)-Te-F(2)	86.8	87.7	87.7
O(3)-Te(1)-F(3), O(4)-Te(2)-F(8)	92.6(2), 93.6(2)	92.6	91.5	92.4	O(3)-Te-F(3)	85.8	86.1	84.4
O(3)-Te(1)-F(4), O(4)-Te(2)-F(9)	179.0(2), 178.5(2)	178.2	178.7	180.0	O(3)-Te-F(4)	179.6	180.0	180.0
O(3)-Te(1)-F(5), O(4)-Te(2)-F(10)	90.1(2), 90.8(2)	89.0	88.8	88.6	O(3)-Te-F(5)	84.3	84.8	84.4
F(1)-Te(1)-F(2), F(6)-Te(2)-F(7)	175.0(2), 174.7(2)	177.2	176.7	176.8	F(1)-Te-F(2)	173.4	175.0	175.7
F(1)-Te(1)-F(3), F(6)-Te(2)-F(8)	89.6(2), 89.6(2)	90.1	89.8	89.8	F(1)-Te-F(3)	89.1	88.8	88.6
F(1)-Te(1)-F(4), F(6)-Te(2)-F(9)	88.2(2), 87.5(2)	88.6	88.4	88.4	F(1)-Te-F(4)	93.2	92.3	92.3
F(1)-Te(1)-F(5), F(6)-Te(2)-F(10)	91.8(2), 89.8(2)	89.9	90.2	90.2	F(1)-Te-F(5)	90.3	90.8	90.9
F(2)-Te(1)-F(3), F(7)-Te(2)-F(8)	87.2(2), 89.6(2)	90.1	89.8	89.4	F(2)-Te-F(3)	89.1	88.8	88.7
F(2)-Te(1)-F(4), F(7)-Te(2)-F(9)	87.9(2), 87.2(2)	88.6	88.4	88.4	F(2)-Te-F(4)	93.2	92.3	92.3
F(2)-Te(1)-F(5), F(7)-Te(2)-F(10)	91.3(2), 90.6(2)	89.9	90.1	90.2	F(2)-Te-F(5)	90.3	90.8	90.9
F(3)-Te(1)-F(4), F(8)-Te(2)-F(9)	88.3(2), 87.8(2)	89.3	89.8	89.4	F(3)-Te-F(4)	94.5	93.9	94.8
F(3)-Te(1)-F(5), F(8)-Te(2)-F(10)	176.9(2), 175.5(2)	178.5	179.7	179.0	F(3)-Te-F(5)	170.1	170.9	168.9
F(4)-Te(1)-F(5), F(9)-Te(2)-F(10)	89.0(2), 87.7(2)	89.2	89.9	89.6	F(4)-Te-F(5)	95.3	95.2	96.2

^a Ref 17. ^b This work. ^c Ref 21. ^d Ref 22. ^e Ref 28.

Table S8. Three Best Natural Lewis Structures Derived from Natural Bond Orbital Analyses for
 (a) XeO_2F_2 (C_{2v}), (b) XeO_2F^+ (C_s), (c) IO_2F (C_s), (d) TeO_2F^- (C_s), (e) $\text{FO}_2\text{XeF}\text{XeO}_2\text{F}^+$ (C_s and
 C_1), (f) $\text{O}_2\text{XeOTeF}_5^+$ (C_1), and (g) $\text{O}_2\text{Xe}(\text{OTeF}_5)_2$ (C_1) at MP2/Stutt RLC ECP level

a) XeO_2F_2 (C_{2v})

O1	0.	1.40803	-0.87727
F2	-1.95644	0.	0.35804
Xe3	0.	0.	0.14059
F4	1.95644	0.	0.35804
O5	0.	-1.40803	-0.87727

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list: 4BP-13LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure				Low	High	
		Occ.	-----	CR	BD	3C	LP	(L)	(NL)	Dev
1(1)	1.90	85.37322	2.62678	0	4	0	13	6	4	0.21
<hr/>										
Effective Core										
Valence Lewis										
Total Lewis										
Valence non-Lewis										
Rydberg non-Lewis										
Total non-Lewis										
<hr/>										
(Occupancy) Bond orbital/ Coefficients/ Hybrids										
1.	(1.96030)	BD (1) O	1-Xe 3							
		(88.39%)	0.9402* O 1 s(0.09%)p99.99(99.34%)d 6.40(0.57%)							
		(11.61%)	0.3407*Xe 3 s(10.47%)p 7.26(76.01%)d 1.12(11.74%)f 0.17(1.78%)							
2.	(1.85686)	BD (1) F	2-Xe 3							
		(86.20%)	0.9284* F 2 s(5.71%)p16.48(94.12%)d 0.03(0.17%)							
		(13.80%)	0.3715*Xe 3 s(14.44%)p 3.96(57.20%)d 1.92(27.68%)f 0.05(0.68%)							
3.	(1.85686)	BD (1)Xe	3- F 4							
		(13.80%)	0.3715*Xe 3 s(14.44%)p 3.96(57.20%)d 1.92(27.68%)f 0.05(0.68%)							
4.	(1.96030)	BD (1)Xe	3- O 5							
		(11.61%)	0.3407*Xe 3 s(10.47%)p 7.26(76.01%)d 1.12(11.74%)f 0.17(1.78%)							
		(88.39%)	0.9402* O 5 s(0.09%)p99.99(99.34%)d 6.40(0.57%)							
5.	(1.97217)	LP (1) O	1							
			s(91.38%)p 0.09(8.62%)d 0.00(0.00%)							
6.	(1.77060)	LP (2) O	1							
			s(0.00%)p 1.00(99.43%)d 0.01(0.57%)							
7.	(1.27136)	LP (3) O	1							
			s(8.45%)p10.73(90.63%)d 0.11(0.93%)							
8.	(1.98476)	LP (1) F	2							
			s(93.62%)p 0.07(6.38%)d 0.00(0.00%)							
9.	(1.94735)	LP (2) F	2							
			s(0.65%)p99.99(99.27%)d 0.14(0.09%)							
10.	(1.93715)	LP (3) F	2							
			s(0.00%)p 1.00(99.91%)d 0.00(0.09%)							
11.	(1.97213)	LP (1)Xe	3							
			s(72.49%)p 0.38(27.22%)d 0.00(0.26%)f 0.00(0.03%)							
12.	(1.98476)	LP (1) F	4							
			s(93.62%)p 0.07(6.38%)d 0.00(0.00%)							
13.	(1.94735)	LP (2) F	4							
			s(0.65%)p99.99(99.27%)d 0.14(0.09%)							
14.	(1.93715)	LP (3) F	4							
			s(0.00%)p 1.00(99.91%)d 0.00(0.09%)							
15.	(1.97217)	LP (1) O	5							
			s(91.38%)p 0.09(8.62%)d 0.00(0.00%)							
16.	(1.77060)	LP (2) O	5							
			s(0.00%)p 1.00(99.43%)d 0.01(0.57%)							
17.	(1.27136)	LP (3) O	5							
			s(8.45%)p10.73(90.63%)d 0.11(0.93%)							

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list: 3BP-14LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure				Low	High	
		Occ.	-----	CR	BD	3C	LP	(L)	(NL)	Dev
1(1)	1.90	85.27705	2.72295	0	3	0	14	5	4	0.40
<hr/>										
Effective Core										
Valence Lewis										
Total Lewis										
<hr/>										

Table S8. (continued...)

Valence non-Lewis	1.93622	(2.200% of 88)
Rydberg non-Lewis	0.78673	(0.894% of 88)
<hr/>		
Total non-Lewis	2.72295	(3.094% of 88)
<hr/>		
(Occupancy) Bond orbital/ Coefficients/ Hybrids		
<hr/>		
1. (1.96631) BD (1) O 1-Xe 3		
(87.40%) 0.9349* O 1 s(0.09%)p99.99(99.34%)d 6.40(0.57%)		
(12.60%) 0.3550*Xe 3 s(11.54%)p 6.97(80.37%)d 0.55(6.36%)f 0.15(1.73%)		
2. (1.95090) BD (1) F 2-Xe 3		
(77.98%) 0.8830* F 2 s(5.71%)p16.48(94.12%)d 0.03(0.17%)		
(22.02%) 0.4693*Xe 3 s(1.73%)p55.26(95.76%)d 1.21(2.09%)f 0.24(0.42%)		
3. (1.96631) BD (1)Xe 3- O 5		
(12.60%) 0.3550*Xe 3 s(11.54%)p 6.97(80.37%)d 0.55(6.36%)f 0.15(1.73%)		
(87.40%) 0.9349* O 5 s(0.09%)p99.99(99.34%)d 6.40(0.57%)		
4. (1.97217) LP (1) O 1	s(91.38%)p 0.09(8.62%)d 0.00(0.00%)	
5. (1.77060) LP (2) O 1	s(0.00%)p 1.00(99.43%)d 0.01(0.57%)	
6. (1.27136) LP (3) O 1	s(8.45%)p10.73(90.63%)d 0.11(0.93%)	
7. (1.98476) LP (1) F 2	s(93.62%)p 0.07(6.38%)d 0.00(0.00%)	
8. (1.94735) LP (2) F 2	s(0.65%)p99.99(99.27%)d 0.14(0.09%)	
9. (1.93715) LP (3) F 2	s(0.00%)p 1.00(99.91%)d 0.00(0.09%)	
10. (1.97223) LP (1)Xe 3	s(72.72%)p 0.37(27.05%)d 0.00(0.20%)f 0.00(0.02%)	
11. (1.98476) LP (1) F 4	s(93.71%)p 0.07(6.28%)d 0.00(0.00%)	
12. (1.94735) LP (2) F 4	s(0.65%)p99.99(99.26%)d 0.14(0.09%)	
13. (1.93715) LP (3) F 4	s(0.00%)p 1.00(99.91%)d 0.00(0.09%)	
14. (1.65453) LP (4) F 4	s(5.62%)p16.76(94.20%)d 0.03(0.18%)	
15. (1.97217) LP (1) O 5	s(91.38%)p 0.09(8.62%)d 0.00(0.00%)	
16. (1.77060) LP (2) O 5	s(0.00%)p 1.00(99.43%)d 0.01(0.57%)	
17. (1.27136) LP (3) O 5	s(8.45%)p10.73(90.63%)d 0.11(0.93%)	

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list: 2BP-15LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure			Low	High		
		Thresh.	Lewis	Non-Lewis	CR	BD	3C	LCC	occ	
<hr/>										
1(1)	1.90	84.98286	3.01714	0	2	0	15	6	4	0.40
<hr/>										
Effective Core										
54.00000										
Valence Lewis										
30.98286 (91.126% of 34)										
<hr/>										
Total Lewis										
84.98286 (96.571% of 88)										
<hr/>										
Valence non-Lewis										
2.27016 (2.580% of 88)										
Rydberg non-Lewis										
0.74699 (0.849% of 88)										
<hr/>										
Total non-Lewis										
3.01714 (3.429% of 88)										
<hr/>										

1. (1.96739) BD (1) O 1-Xe 3		
(87.29%) 0.9343* O 1 s(0.09%)p99.99(99.34%)d 6.40(0.57%)		
(12.71%) 0.3566*Xe 3 s(11.86%)p 6.78(80.40%)d 0.51(6.02%)f 0.15(1.72%)		
<hr/>		
2. (1.96739) BD (1)Xe 3- O 5		
(12.71%) 0.3566*Xe 3 s(11.86%)p 6.78(80.40%)d 0.51(6.02%)f 0.15(1.72%)		
(87.29%) 0.9343* O 5 s(0.09%)p99.99(99.34%)d 6.40(0.57%)		
3. (1.97217) LP (1) O 1	s(91.38%)p 0.09(8.62%)d 0.00(0.00%)	
4. (1.77060) LP (2) O 1	s(0.00%)p 1.00(99.43%)d 0.01(0.57%)	
5. (1.27136) LP (3) O 1	s(8.45%)p10.73(90.63%)d 0.11(0.93%)	
6. (1.98476) LP (1) F 2	s(93.71%)p 0.07(6.28%)d 0.00(0.00%)	
7. (1.94735) LP (2) F 2	s(0.65%)p99.99(99.26%)d 0.14(0.09%)	
8. (1.93715) LP (3) F 2	s(0.00%)p 1.00(99.91%)d 0.00(0.09%)	
9. (1.65453) LP (4) F 2	s(5.62%)p16.76(94.20%)d 0.03(0.18%)	
10. (1.97225) LP (1)Xe 3	s(72.76%)p 0.37(27.02%)d 0.00(0.20%)f 0.00(0.02%)	
11. (1.98476) LP (1) F 4	s(93.71%)p 0.07(6.28%)d 0.00(0.00%)	
12. (1.94735) LP (2) F 4	s(0.65%)p99.99(99.26%)d 0.14(0.09%)	
13. (1.93715) LP (3) F 4	s(0.00%)p 1.00(99.91%)d 0.00(0.09%)	
14. (1.65453) LP (4) F 4	s(5.62%)p16.76(94.20%)d 0.03(0.18%)	

Table S8. (continued...)

15. (1.97217) LP (1) O 5	s(91.38%)p 0.09(8.62%)d 0.00(0.00%)
16. (1.77060) LP (2) O 5	s(0.00%)p 1.00(99.43%)d 0.01(0.57%)
17. (1.27136) LP (3) O 5	s(8.45%)p10.73(90.63%)d 0.11(0.93%)

NATURAL BOND ORBITAL ANALYSIS:
Reading \$CHOOSE input list: 6BP-11LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure				Low	High	Dev
		Lewis	Non-Lewis	CR	BD	3C	LP	(L)	(NL)	
1(1)	1.90	81.94698	6.05302	0	6	0	11	5	8	0.21
<hr/>										
Effective Core										
Valence Lewis										
Total Lewis										
<hr/>										
Valence non-Lewis										
Rydberg non-Lewis										
<hr/>										
Total non-Lewis										
<hr/>										
(Occupancy) Bond orbital/ Coefficients/ Hybrids										
<hr/>										
1. (1.96182) BD (1) O 1-Xe 3										
(87.53%)		0.9356*	O 1 s(0.29%)p99.99(99.15%)d 1.97(0.57%)							
(12.47%)		0.3531*Xe 3 s(12.92%)p 6.08(78.60%)d 0.45(5.77%)f 0.21(2.71%)								
2. (1.39780) BD (2) O 1-Xe 3										
(82.11%)		0.9062*	O 1 s(9.71%)p 9.07(88.11%)d 0.22(2.17%)							
(17.89%)		0.4229*Xe 3 s(6.27%)p 8.81(55.24%)d 3.88(24.36%)f 2.25(14.13%)								
3. (0.15478) BD (1) F 2-Xe 3										
(100.00%)		1.0000* F 2 s(3.40%)p27.65(94.00%)d 0.76(2.60%)								
(0.00%)		0.0000*Xe 3 s(0.00%)								
4. (0.15478) BD (1)Xe 3- F 4										
(0.00%)		0.0000*Xe 3 s(0.00%)								
(100.00%)		1.0000* F 4 s(3.40%)p27.65(94.00%)d 0.76(2.60%)								
5. (1.90748) BD (1)Xe 3- O 5										
(6.98%)		0.2642*Xe 3 s(8.15%)p 6.20(50.49%)d 2.94(23.95%)f 2.14(17.41%)								
(93.02%)		0.9645* O 5 s(0.09%)p99.99(99.34%)d 6.40(0.57%)								
6. (1.96454) BD (2)Xe 3- O 5										
(15.26%)		0.3906*Xe 3 s(0.00%)p 1.00(94.54%)d 0.04(4.11%)f 0.01(1.35%)								
(84.74%)		0.9206* O 5 s(0.00%)p 1.00(99.44%)d 0.01(0.56%)								
7. (1.93907) LP (1) O 1										
		s(98.53%)p 0.01(1.39%)d 0.00(0.08%)								
8. (1.77060) LP (2) O 1										
		s(0.00%)p 1.00(99.43%)d 0.01(0.57%)								
9. (1.91426) LP (1) F 2										
		s(90.80%)p 0.10(9.10%)d 0.00(0.10%)								
10. (1.91806) LP (2) F 2										
		s(0.50%)p99.99(99.29%)d 0.42(0.21%)								
11. (1.90871) LP (3) F 2										
		s(0.01%)p99.99(99.81%)d12.04(0.17%)								
12. (1.97051) LP (1)Xe 3										
		s(73.58%)p 0.36(26.30%)d 0.00(0.09%)f 0.00(0.03%)								
13. (1.91426) LP (1) F 4										
		s(90.80%)p 0.10(9.10%)d 0.00(0.10%)								
14. (1.91806) LP (2) F 4										
		s(0.50%)p99.99(99.29%)d 0.42(0.21%)								
15. (1.90871) LP (3) F 4										
		s(0.01%)p99.99(99.81%)d12.04(0.17%)								
16. (1.97217) LP (1) O 5										
		s(91.38%)p 0.09(8.62%)d 0.00(0.00%)								
17. (1.27136) LP (2) O 5										
		s(8.45%)p10.73(90.63%)d 0.11(0.93%)								

b) XeO₂F⁺ (C_s)

Xe1	-0.23477	0.06961	0.
O2	0.5071	0.7215	1.41962
O3	0.5071	0.7215	-1.41962
F4	0.5071	-1.70032	0.

NATURAL BOND ORBITAL ANALYSIS:
Reading \$CHOOSE input list: 5BP-8LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure				Low	High	Dev
		Lewis	Non-Lewis	CR	BD	3C	LP	(L)	(NL)	
1(1)	1.90	75.83492	2.16508	0	5	0	8	6	5	0.31
<hr/>										

Table S8. (continued...)

Effective Core	52.00000			
Valence Lewis	23.83492 (91.673% of 26)			
Total Lewis	75.83492 (97.224% of 78)			
Valence non-Lewis	1.72468 (2.211% of 78)			
Rydberg non-Lewis	0.44040 (0.565% of 78)			
Total non-Lewis	2.16508 (2.776% of 78)			
(Occupancy) Bond orbital/ Coefficients/ Hybrids				
1. (1.82632) BD (1)Xe	1- O 2 (14.13%) 0.3759*Xe 1 s(7.22%)p 6.53(47.13%)d 5.25(37.92%)f 1.07(7.73%) (85.87%) 0.9267* O 2 s(0.54%)p99.99(98.76%)d 1.30(0.70%)			
2. (1.88845) BD (2)Xe	1- O 2 (9.00%) 0.3000*Xe 1 s(4.93%)p 9.73(47.95%)d 7.55(37.21%)f 2.01(9.91%) (91.00%) 0.9539* O 2 s(0.31%)p99.99(99.01%)d 2.19(0.68%)			
3. (1.94571) BD (1)Xe	1- O 3 (14.43%) 0.3798*Xe 1 s(6.84%)p11.76(80.44%)d 1.48(10.09%)f 0.39(2.64%) (85.57%) 0.9251* O 3 s(0.30%)p99.99(99.02%)d 2.25(0.68%)			
4. (1.75119) BD (2)Xe	1- O 3 (28.90%) 0.5376*Xe 1 s(16.65%)p 3.32(55.21%)d 1.32(22.03%)f 0.37(6.11%) (71.10%) 0.8432* O 3 s(8.11%)p11.21(90.92%)d 0.12(0.97%)			
5. (1.75644) BD (1)Xe	1- F 4 (13.60%) 0.3688*Xe 1 s(9.15%)p 5.51(50.45%)d 3.37(30.83%)f 1.05(9.58%) (86.40%) 0.9295* F 4 s(3.68%)p26.07(96.07%)d 0.07(0.24%)			
6. (1.97648) LP (1)Xe	1 s(74.33%)p 0.34(25.55%)d 0.00(0.10%)f 0.00(0.02%)			
7. (1.97145) LP (1) O	2 s(91.34%)p 0.09(8.65%)d 0.00(0.00%)			
8. (1.28630) LP (2) O	2 s(7.73%)p11.81(91.27%)d 0.13(1.00%)			
9. (1.97143) LP (1) O	3 s(91.06%)p 0.10(8.93%)d 0.00(0.00%)			
10. (1.61621) LP (2) O	3 s(0.45%)p99.99(98.85%)d 1.57(0.70%)			
11. (1.98453) LP (1) F	4 s(96.12%)p 0.04(3.88%)d 0.00(0.00%)			
12. (1.93348) LP (2) F	4 s(0.17%)p99.99(99.68%)d 0.91(0.15%)			
13. (1.92694) LP (3) F	4 s(0.00%)p 1.00(99.85%)d 0.00(0.15%)			
NATURAL BOND ORBITAL ANALYSIS:				
Reading \$CHOOSE input list: 4BP-9LP Lewis Structure				
Occ.	Occupancies	Lewis Structure	Low	High
Cycle	Thresh.	Lewis Non-Lewis	CR BD 3C LP	occ occ
1(1)	1.90	75.76291	2.23709 0 4 0 9	(L) (NL) Dev
Effective Core	52.00000			
Valence Lewis	23.76291 (91.396% of 26)			
Total Lewis	75.76291 (97.132% of 78)			
Valence non-Lewis	1.72908 (2.217% of 78)			
Rydberg non-Lewis	0.50801 (0.651% of 78)			
Total non-Lewis	2.23709 (2.868% of 78)			
(Occupancy) Bond orbital/ Coefficients/ Hybrids				
1. (1.90765) BD (1)Xe	1- O 2 (22.25%) 0.4717*Xe 1 s(6.31%)p12.06(76.16%)d 2.43(15.37%)f 0.34(2.16%) (77.75%) 0.8818* O 2 s(0.54%)p99.99(98.76%)d 1.30(0.70%)			
2. (1.89887) BD (2)Xe	1- O 2 (9.97%) 0.3158*Xe 1 s(6.27%)p 8.77(55.00%)d 5.05(31.64%)f 1.13(7.09%) (90.03%) 0.9488* O 2 s(0.31%)p99.99(99.01%)d 2.19(0.68%)			
3. (1.95272) BD (1)Xe	1- O 3 (15.22%) 0.3901*Xe 1 s(7.45%)p11.22(83.61%)d 1.01(7.52%)f 0.19(1.41%) (84.78%) 0.9208* O 3 s(0.30%)p99.99(99.02%)d 2.25(0.68%)			
4. (1.76819) BD (2)Xe	1- O 3 (30.22%) 0.5497*Xe 1 s(21.10%)p 2.59(54.57%)d 0.93(19.54%)f 0.23(4.79%) (69.78%) 0.8354* O 3 s(8.11%)p11.21(90.92%)d 0.12(0.97%)			
5. (1.97652) LP (1)Xe	1 s(74.48%)p 0.34(25.41%)d 0.00(0.10%)f 0.00(0.02%)			

Table S8. (continued...)

6.	(1.97145)	LP	(1)	O	2	s(91.34%)p 0.09(8.65%)d 0.00(0.00%)
7.	(1.28630)	LP	(2)	O	2	s(7.73%)p11.81(91.27%)d 0.13(1.00%)
8.	(1.97143)	LP	(1)	O	3	s(91.06%)p 0.10(8.93%)d 0.00(0.00%)
9.	(1.61621)	LP	(2)	O	3	s(0.45%)p99.99(98.85%)d 1.57(0.70%)
10.	(1.98453)	LP	(1)	F	4	s(96.20%)p 0.04(3.80%)d 0.00(0.00%)
11.	(1.93348)	LP	(2)	F	4	s(0.16%)p99.99(99.68%)d 0.92(0.15%)
12.	(1.92694)	LP	(3)	F	4	s(0.00%)p 1.00(99.85%)d 0.00(0.15%)
13.	(1.56862)	LP	(4)	F	4	s(3.63%)p26.48(96.11%)d 0.07(0.26%)

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list: 4BP-9LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure				Low	High			
		Occ.	Thresh.	Lewis	Non-Lewis	CR	BD	3C	LP	(L)	(NL)	Dev
1(1)	1.90	75.45970		2.54030		0	4	0	9	5	5	0.31
Effective Core		52.00000										
Valence Lewis		23.45970	(90.230% of	26)								
Total Lewis		75.45970	(96.743% of	78)								
Valence non-Lewis		1.99631	(2.559% of	78)								
Rydberg non-Lewis		0.54399	(0.697% of	78)								
Total non-Lewis		2.54030	(3.257% of	78)								
(Occupancy) Bond orbital/ Coefficients/ Hybrids												
1.	(1.94608)	BD	(1)	Xe	1- O 2							
			(14.39%)		0.3793*Xe 1 s(6.80%)p11.79(80.12%)d 1.57(10.70%)f 0.35(2.39%)							
			(85.61%)		0.9253* O 2 s(0.32%)p99.99(99.00%)d 2.10(0.68%)							
2.	(1.83085)	BD	(1)	Xe	1- O 3							
			(14.52%)		0.3811*Xe 1 s(6.75%)p 7.21(48.66%)d 5.46(36.80%)f 1.16(7.80%)							
			(85.48%)		0.9245* O 3 s(0.54%)p99.99(98.76%)d 1.30(0.70%)							
3.	(1.95936)	BD	(2)	Xe	1- O 3							
			(16.06%)		0.4008*Xe 1 s(5.92%)p14.80(87.61%)d 0.86(5.06%)f 0.24(1.41%)							
			(83.94%)		0.9162* O 3 s(0.31%)p99.99(99.01%)d 2.19(0.68%)							
4.	(1.77103)	BD	(1)	Xe	1- F 4							
			(15.28%)		0.3909*Xe 1 s(17.04%)p 2.93(49.99%)d 1.51(25.68%)f 0.43(7.29%)							
			(84.72%)		0.9204* F 4 s(3.68%)p26.12(96.08%)d 0.07(0.24%)							
5.	(1.97649)	LP	(1)	Xe	1							
6.	(1.97145)	LP	(1)	O	2	s(74.27%)p 0.34(25.60%)d 0.00(0.11%)f 0.00(0.02%)						
7.	(1.61694)	LP	(2)	O	2	s(91.35%)p 0.09(8.65%)d 0.00(0.00%)						
8.	(1.28481)	LP	(3)	O	2	s(0.29%)p99.99(99.01%)d 2.45(0.70%)						
9.	(1.97145)	LP	(1)	O	3	s(7.96%)p11.43(91.03%)d 0.13(1.00%)						
10.	(1.28630)	LP	(2)	O	3	s(91.34%)p 0.09(8.65%)d 0.00(0.00%)						
11.	(1.98453)	LP	(1)	F	4	s(7.73%)p11.81(91.27%)d 0.13(1.00%)						
12.	(1.93347)	LP	(2)	F	4	s(96.12%)p 0.04(3.87%)d 0.00(0.00%)						
13.	(1.92694)	LP	(3)	F	4	s(0.17%)p99.99(99.68%)d 0.89(0.15%)						
						s(0.00%)p 1.00(99.85%)d 0.00(0.15%)						

c) IO₂F (C_s)

I1	-0.24304	0.07498	0.
O2	0.51525	0.73906	1.4746
O3	0.51525	0.73906	-1.4746
F4	0.51525	-1.75545	0.

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list: 5BP-8LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure				Low	High			
		Occ.	Thresh.	Lewis	Non-Lewis	CR	BD	3C	LP	(L)	(NL)	Dev
1(1)	1.90	75.94401		2.05599		0	5	0	8	7	5	0.20
Effective Core		52.00000										
Valence Lewis		23.94401	(92.092% of	26)								

Table S8. (continued...)

Total Lewis	75.94401	(97.364% of 78)
Valence non-Lewis	1.64087	(2.104% of 78)
Rydberg non-Lewis	0.41512	(0.532% of 78)
Total non-Lewis	2.05599	(2.636% of 78)
<hr/>		
(Occupancy) Bond orbital/ Coefficients/ Hybrids		
1. (1.88328) BD (1) I 1- O 2		
(8.33%) 0.2886* I 1 s(7.51%)p 6.60(49.53%)d 5.72(42.96%)		
(91.67%) 0.9574* O 2 s(2.20%)p44.29(97.33%)d 0.21(0.47%)		
2. (1.89142) BD (2) I 1- O 2		
(9.85%) 0.3138* I 1 s(4.06%)p16.21(65.83%)d 7.41(30.10%)		
(90.15%) 0.9495* O 2 s(0.16%)p99.99(99.38%)d 2.97(0.46%)		
3. (1.88328) BD (1) I 1- O 3		
(8.33%) 0.2886* I 1 s(7.51%)p 6.60(49.53%)d 5.72(42.96%)		
(91.67%) 0.9574* O 3 s(2.20%)p44.29(97.33%)d 0.21(0.47%)		
4. (1.89142) BD (2) I 1- O 3		
(9.85%) 0.3138* I 1 s(4.06%)p16.21(65.83%)d 7.41(30.10%)		
(90.15%) 0.9495* O 3 s(0.16%)p99.99(99.38%)d 2.97(0.46%)		
5. (1.79406) BD (1) I 1- F 4		
(9.02%) 0.3004* I 1 s(26.81%)p 1.60(42.98%)d 1.13(30.21%)		
(90.98%) 0.9538* F 4 s(6.84%)p13.60(92.97%)d 0.03(0.19%)		
6. (1.97932) LP (1) I 1	s(75.63%)p 0.32(24.22%)d 0.00(0.14%)	
7. (1.97154) LP (1) O 2	s(87.71%)p 0.14(12.28%)d 0.00(0.01%)	
8. (1.40171) LP (2) O 2	s(9.86%)p 9.07(89.43%)d 0.07(0.70%)	
9. (1.97154) LP (1) O 3	s(87.71%)p 0.14(12.28%)d 0.00(0.01%)	
10. (1.40171) LP (2) O 3	s(9.86%)p 9.07(89.43%)d 0.07(0.70%)	
11. (1.98444) LP (1) F 4	s(92.61%)p 0.08(7.39%)d 0.00(0.00%)	
12. (1.94710) LP (2) F 4	s(0.53%)p99.99(99.38%)d 0.17(0.09%)	
13. (1.94316) LP (3) F 4	s(0.00%)p 1.00(99.91%)d 0.00(0.09%)	
<hr/>		
NATURAL BOND ORBITAL ANALYSIS:		
Reading \$CHOOSE input list: 4BP-9LP Lewis Structure		
Occupancies	Lewis Structure	Low High
Occ.		occ occ
Cycle	Thresh.	Lewis Non-Lewis CR BD 3C LP (L) (NL) Dev
<hr/>		
1(1)	1.90	75.86499 2.13501 0 4 0 9 5 5 0.40
<hr/>		
Effective Core	52.00000	
Valence Lewis	23.86499 (91.788% of 26)	
Total Lewis	75.86499 (97.263% of 78)	
<hr/>		
Valence non-Lewis	1.58418 (2.031% of 78)	
Rydberg non-Lewis	0.55082 (0.706% of 78)	
Total non-Lewis	2.13501 (2.737% of 78)	
<hr/>		
(Occupancy) Bond orbital/ Coefficients/ Hybrids		
1. (1.90626) BD (1) I 1- O 2		
(10.55%) 0.3248* I 1 s(6.29%)p10.28(64.65%)d 4.62(29.06%)		
(89.45%) 0.9458* O 2 s(2.20%)p44.29(97.33%)d 0.21(0.47%)		
2. (1.89348) BD (2) I 1- O 2		
(10.01%) 0.3163* I 1 s(3.87%)p17.19(66.56%)d 7.63(29.56%)		
(89.99%) 0.9487* O 2 s(0.16%)p99.99(99.38%)d 2.97(0.46%)		
3. (1.90626) BD (1) I 1- O 3		
(10.55%) 0.3248* I 1 s(6.29%)p10.28(64.65%)d 4.62(29.06%)		
(89.45%) 0.9458* O 3 s(2.20%)p44.29(97.33%)d 0.21(0.47%)		
4. (1.89348) BD (2) I 1- O 3		
(10.01%) 0.3163* I 1 s(3.87%)p17.19(66.56%)d 7.63(29.56%)		
(89.99%) 0.9487* O 3 s(0.16%)p99.99(99.38%)d 2.97(0.46%)		
5. (1.97940) LP (1) I 1	s(75.94%)p 0.32(23.94%)d 0.00(0.12%)	
6. (1.97154) LP (1) O 2	s(87.71%)p 0.14(12.28%)d 0.00(0.01%)	
7. (1.40171) LP (2) O 2	s(9.86%)p 9.07(89.43%)d 0.07(0.70%)	
8. (1.97154) LP (1) O 3	s(87.71%)p 0.14(12.28%)d 0.00(0.01%)	
9. (1.40171) LP (2) O 3	s(9.86%)p 9.07(89.43%)d 0.07(0.70%)	

Table S8. (continued...)

10. (1.98445) LP (1) F 4	s(92.67%)p 0.08(7.33%)d 0.00(0.00%)
11. (1.94710) LP (2) F 4	s(0.52%)p99.99(99.39%)d 0.17(0.09%)
12. (1.94316) LP (3) F 4	s(0.00%)p 1.00(99.91%)d 0.00(0.09%)
13. (1.66489) LP (4) F 4	s(6.79%)p13.70(93.02%)d 0.03(0.19%)

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list: 3BP-10LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure				Low	High	
		Lewis	Non-Lewis	CR	BD	3C	LP	OCC (L)	OCC (NL)	Dev
1(1)	1.90	75.80307	2.19693	0	3	0	10	4	4	0.40
<hr/>										
Effective Core										
Valence Lewis										
Total Lewis										
Valence non-Lewis										
Rydberg non-Lewis										
Total non-Lewis										
<hr/>										
(Occupancy) Bond orbital/ Coefficients/ Hybrids										
1. (1.91941)	BD (1) I	1- O 2								
	(11.96%)	0.3458*	I 1 s(8.73%)p 8.89(77.58%)d 1.57(13.69%)							
	(88.04%)	0.9383*	O 2 s(2.21%)p44.06(97.32%)d 0.21(0.47%)							
2. (1.95166)	BD (1) I	1- O 3								
	(14.19%)	0.3767*	I 1 s(2.56%)p35.94(91.99%)d 2.13(5.45%)							
	(85.81%)	0.9264*	O 3 s(2.20%)p44.29(97.33%)d 0.21(0.47%)							
3. (1.92547)	BD (2) I	1- O 3								
	(12.95%)	0.3598*	I 1 s(7.75%)p10.49(81.29%)d 1.42(10.96%)							
	(87.05%)	0.9330*	O 3 s(0.16%)p99.99(99.38%)d 2.97(0.46%)							
4. (1.97940)	LP (1) I	1								
			s(75.97%)p 0.31(23.91%)d 0.00(0.12%)							
5. (1.97154)	LP (1) O	2								
			s(87.71%)p 0.14(12.28%)d 0.00(0.01%)							
6. (1.74101)	LP (2) O	2								
			s(0.14%)p99.99(99.41%)d 3.30(0.45%)							
7. (1.40171)	LP (3) O	2								
			s(9.87%)p 9.06(89.43%)d 0.07(0.70%)							
8. (1.97154)	LP (1) O	3								
			s(87.71%)p 0.14(12.28%)d 0.00(0.01%)							
9. (1.40171)	LP (2) O	3								
			s(9.86%)p 9.07(89.43%)d 0.07(0.70%)							
10. (1.98445)	LP (1) F	4								
			s(92.67%)p 0.08(7.33%)d 0.00(0.00%)							
11. (1.94710)	LP (2) F	4								
			s(0.52%)p99.99(99.39%)d 0.17(0.09%)							
12. (1.94316)	LP (3) F	4								
			s(0.00%)p 1.00(99.91%)d 0.00(0.09%)							
13. (1.66489)	LP (4) F	4								
			s(6.79%)p13.70(93.02%)d 0.03(0.19%)							

d) TeO₂F⁻ (C_s)

Te1	-0.22248	0.0721	0.
O2	0.48056	0.75564	1.51967
O3	0.48056	0.75564	-1.51967
F4	0.48056	-1.77596	0.

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list: 4BP-9LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure				Low	High	
		Lewis	Non-Lewis	CR	BD	3C	LP	OCC (L)	OCC (NL)	Dev
1(1)	1.90	76.57012	1.42988	0	4	0	9	4	4	0.35
<hr/>										
Effective Core										
Valence Lewis										
Total Lewis										
Valence non-Lewis										
Rydberg non-Lewis										
Total non-Lewis										
<hr/>										

Table S8. (continued...)

Total non-Lewis	1.42988	(1.833% of 78)															

(Occupancy) Bond orbital/ Coefficients/ Hybrids																	
1. (1.93797) BD (1)Te	1- O 2																
(6.95%)	0.2636*Te	1 s(15.85%)p 4.40(69.84%)d 0.90(14.31%)															
(93.05%)	0.9646* O	2 s(6.65%)p14.00(93.04%)d 0.05(0.32%)															
2. (1.89989) BD (2)Te	1- O 2																
(21.98%)	0.4688*Te	1 s(33.59%)p 1.89(63.64%)d 0.08(2.77%)															
(78.02%)	0.8833* O	2 s(10.38%)p 8.59(89.18%)d 0.04(0.44%)															
3. (1.92772) BD (1)Te	1- O 3																
(6.15%)	0.2479*Te	1 s(25.68%)p 2.12(54.54%)d 0.77(19.77%)															
(93.85%)	0.9688* O	3 s(6.69%)p13.90(92.99%)d 0.05(0.32%)															
4. (1.93413) BD (2)Te	1- O 3																
(10.27%)	0.3205*Te	1 s(4.38%)p20.21(88.62%)d 1.60(7.00%)															
(89.73%)	0.9472* O	3 s(0.99%)p99.99(98.68%)d 0.34(0.33%)															
5. (1.97671) LP (1)Te	1	s(74.59%)p 0.34(25.11%)d 0.00(0.30%)															
6. (1.96742) LP (1) O	2	s(81.91%)p 0.22(18.08%)d 0.00(0.01%)															
7. (1.76964) LP (2) O	2	s(0.98%)p99.99(98.69%)d 0.34(0.33%)															
8. (1.96743) LP (1) O	3	s(82.11%)p 0.22(17.88%)d 0.00(0.01%)															
9. (1.54631) LP (2) O	3	s(10.12%)p 8.83(89.44%)d 0.04(0.43%)															
10. (1.98241) LP (1) F	4	s(85.55%)p 0.17(14.45%)d 0.00(0.00%)															
11. (1.95358) LP (2) F	4	s(0.81%)p99.99(99.13%)d 0.08(0.06%)															
12. (1.95065) LP (3) F	4	s(0.00%)p 1.00(99.94%)d 0.00(0.06%)															
13. (1.75626) LP (4) F	4	s(13.62%)p 6.33(86.23%)d 0.01(0.15%)															
NATURAL BOND ORBITAL ANALYSIS:																	
Reading \$CHOOSE input list: 4BP-9LP Lewis Structure																	

Cycle	Occ.	Occupancies	Lewis Structure	Low	High												
	Occ.	Lewis	Non-Lewis	CR	BD	3C	LP	occ	occ								
				(L)	(NL)												
1(1)	1.90	76.38278	1.61722	0	4	0	9	3	4	0.11							
=====			=====														
Effective Core			52.00000														
Valence Lewis			24.38278 (93.780% of 26)														
=====			=====														
Total Lewis			76.38278 (97.927% of 78)														
-----			-----														
Valence non-Lewis			1.22135 (1.566% of 78)														
Rydberg non-Lewis			0.39586 (0.508% of 78)														
=====			=====														
Total non-Lewis			1.61722 (2.073% of 78)														
-----			-----														
(Occupancy) Bond orbital/ Coefficients/ Hybrids																	
1. (1.93268) BD (1)Te	1- O 2																
(6.49%)	0.2548*Te	1 s(21.01%)p 2.92(61.30%)d 0.84(17.69%)															
(93.51%)	0.9670* O	2 s(6.69%)p13.90(92.99%)d 0.05(0.32%)															
2. (1.93382) BD (1)Te	1- O 3																
(6.57%)	0.2562*Te	1 s(20.97%)p 2.95(61.86%)d 0.82(17.17%)															
(93.43%)	0.9666* O	3 s(6.69%)p13.90(92.99%)d 0.05(0.32%)															
3. (1.93195) BD (2)Te	1- O 3																
(10.71%)	0.3273*Te	1 s(9.29%)p 9.29(86.31%)d 0.47(4.41%)															
(89.29%)	0.9449* O	3 s(0.99%)p99.99(98.68%)d 0.34(0.33%)															
4. (1.92389) BD (1)Te	1- F 4																
(10.99%)	0.3315*Te	1 s(29.51%)p 2.19(64.60%)d 0.20(5.89%)															
(89.01%)	0.9435* F	4 s(13.77%)p 6.25(86.07%)d 0.01(0.16%)															
5. (1.97666) LP (1)Te	1	s(74.47%)p 0.34(25.21%)d 0.00(0.32%)															
6. (1.96743) LP (1) O	2	s(82.13%)p 0.22(17.86%)d 0.00(0.01%)															
7. (1.78143) LP (2) O	2	s(0.07%)p99.99(99.60%)d 4.50(0.32%)															
8. (1.53456) LP (3) O	2	s(11.02%)p 8.03(88.54%)d 0.04(0.43%)															
9. (1.96743) LP (1) O	3	s(82.11%)p 0.22(17.88%)d 0.00(0.01%)															
10. (1.54631) LP (2) O	3	s(10.12%)p 8.83(89.44%)d 0.04(0.43%)															
11. (1.98240) LP (1) F	4	s(85.39%)p 0.17(14.61%)d 0.00(0.00%)															
12. (1.95358) LP (2) F	4	s(0.81%)p99.99(99.13%)d 0.08(0.06%)															
13. (1.95065) LP (3) F	4	s(0.00%)p 1.00(99.94%)d 0.00(0.06%)															

Table S8. (continued...)

NATURAL BOND ORBITAL ANALYSIS:
Reading \$CHOOSE input list: 3BP-10LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure				Low	High		
		Thresh.	Lewis	Non-Lewis	CR	BD	3C	LP	OCC (L)	OCC (NL)	Dev
1(1)	1.90	76.24543	1.75457		0	3	0	10	4	4	0.11
<hr/>											
Effective Core		52.00000									
Valence Lewis		24.24543	(93.252% of 26)								
Total Lewis		76.24543	(97.751% of 78)								
Valence non-Lewis		0.76484	(0.981% of 78)								
Rydberg non-Lewis		0.98972	(1.269% of 78)								
Total non-Lewis		1.75457	(2.249% of 78)								
<hr/>											
(Occupancy) Bond orbital/ Coefficients/ Hybrids											
1. (1.93783) BD (1)Te	1-	O 2									
(6.81%)	0.2611*	Te 1 s (21.02%)p 2.98(62.73%)d 0.77(16.25%)									
(93.19%)	0.9653*	O 2 s (6.69%)p13.90(92.99%)d 0.05(0.32%)									
2. (1.93783) BD (1)Te	1-	O 3									
(6.81%)	0.2611*	Te 1 s (21.02%)p 2.98(62.73%)d 0.77(16.25%)									
(93.19%)	0.9653*	O 3 s (6.69%)p13.90(92.99%)d 0.05(0.32%)									
3. (1.93963) BD (1)Te	1-	F 4									
(11.46%)	0.3385*	Te 1 s (22.00%)p 3.27(71.91%)d 0.28(6.09%)									
(88.54%)	0.9410*	F 4 s (13.77%)p 6.25(86.07%)d 0.01(0.16%)									
4. (1.97666) LP (1)Te	1		s(74.65%)p 0.34(25.03%)d 0.00(0.32%)								
5. (1.96743) LP (1)O	2		s(82.13%)p 0.22(17.86%)d 0.00(0.01%)								
6. (1.78143) LP (2)O	2		s(0.07%)p99.99(99.60%)d 4.50(0.32%)								
7. (1.53456) LP (3)O	2		s(11.02%)p 8.03(88.54%)d 0.04(0.43%)								
8. (1.96743) LP (1)O	3		s(82.13%)p 0.22(17.86%)d 0.00(0.01%)								
9. (1.78143) LP (2)O	3		s(0.07%)p99.99(99.60%)d 4.50(0.32%)								
10. (1.53456) LP (3)O	3		s(11.02%)p 8.03(88.54%)d 0.04(0.43%)								
11. (1.98240) LP (1)F	4		s(85.39%)p 0.17(14.61%)d 0.00(0.00%)								
12. (1.95358) LP (2)F	4		s(0.81%)p99.99(99.13%)d 0.08(0.06%)								
13. (1.95065) LP (3)F	4		s(0.00%)p 1.00(99.94%)d 0.00(0.06%)								

e) $\text{FO}_2\text{XeFXeO}_2\text{F}^+ (C_s)$

O1	0.82656	-1.91002	1.40457
F2	-0.13683	-4.08322	0.
Xe3	-0.15202	-2.15878	0.
O4	0.82656	1.90984	1.40456
F5	-0.84193	0.00014	0.
O6	0.82656	-1.91002	-1.40457
Xe7	-0.15195	2.15881	0.
F8	-0.13634	4.08325	0.
O9	0.82656	1.90984	-1.40456

NATURAL BOND ORBITAL ANALYSIS:
Reading \$CHOOSE input list: 6BP-24LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure				Low	High		
		Thresh.	Lewis	Non-Lewis	CR	BD	3C	LP	OCC (L)	OCC (NL)	Dev
1(1)	1.90	160.67334	5.32666		0	6	0	24	9	8	0.25
<hr/>											
Effective Core		106.00000									
Valence Lewis		54.67334	(91.122% of 60)								
Total Lewis		160.67334	(96.791% of 166)								
Valence non-Lewis		3.80932	(2.295% of 166)								
Rydberg non-Lewis		1.51734	(0.914% of 166)								
<hr/>											

Table S8. (continued...)

Total non-Lewis	5.32666	(3.209% of 166)
(Occupancy) Bond orbital/ Coefficients/ Hybrids		
1. (1.96183) BD (1) O 1-Xe 3 (87.20%) 0.9338* O 1 s(0.20%)p99.99(99.16%)d 3.28(0.64%) (12.80%) 0.3578*Xe 3 s(10.74%)p 7.46(80.06%)d 0.69(7.41%)f 0.17(1.79%)		
2. (1.91921) BD (1) F 2-Xe 3 (74.48%) 0.8630* F 2 s(4.87%)p19.49(94.90%)d 0.05(0.23%) (25.52%) 0.5051*Xe 3 s(1.42%)p67.21(95.18%)d 1.97(2.79%)f 0.44(0.62%)		
3. (1.96183) BD (1)Xe 3- O 6 (12.80%) 0.3578*Xe 3 s(10.74%)p 7.46(80.06%)d 0.69(7.41%)f 0.17(1.79%) (87.20%) 0.9338* O 6 s(0.20%)p99.99(99.16%)d 3.28(0.64%)		
4. (1.96183) BD (1) O 4-Xe 7 (87.20%) 0.9338* O 4 s(0.20%)p99.99(99.16%)d 3.28(0.64%) (12.80%) 0.3578*Xe 7 s(10.74%)p 7.46(80.06%)d 0.69(7.41%)f 0.17(1.79%)		
5. (1.91921) BD (1)Xe 7- F 8 (25.51%) 0.5051*Xe 7 s(1.42%)p67.21(95.18%)d 1.97(2.79%)f 0.44(0.62%) (74.49%) 0.8630* F 8 s(4.87%)p19.49(94.90%)d 0.05(0.23%)		
6. (1.96183) BD (1)Xe 7- O 9 (12.80%) 0.3578*Xe 7 s(10.74%)p 7.46(80.06%)d 0.69(7.41%)f 0.17(1.79%) (87.20%) 0.9338* O 9 s(0.20%)p99.99(99.16%)d 3.28(0.64%)		
7. (1.97162) LP (1) O 1 8. (1.67893) LP (2) O 1 9. (1.27704) LP (3) O 1 10. (1.98445) LP (1) F 2 11. (1.93925) LP (2) F 2 12. (1.92920) LP (3) F 2 13. (1.97086) LP (1)Xe 3 14. (1.97162) LP (1) O 4 15. (1.67899) LP (2) O 4 16. (1.27704) LP (3) O 4 17. (1.97972) LP (1) F 5 18. (1.95518) LP (2) F 5 19. (1.92455) LP (3) F 5 20. (1.77011) LP (4) F 5 21. (1.97162) LP (1) O 6 22. (1.67893) LP (2) O 6 23. (1.27704) LP (3) O 6 24. (1.97085) LP (1)Xe 7 25. (1.98445) LP (1) F 8 26. (1.93925) LP (2) F 8 27. (1.92920) LP (3) F 8 28. (1.97162) LP (1) O 9 29. (1.67899) LP (2) O 9 30. (1.27704) LP (3) O 9	s(91.37%)p 0.09(8.63%)d 0.00(0.00%) s(0.01%)p99.99(99.34%)d62.72(0.65%) s(8.34%)p10.87(90.68%)d 0.12(0.98%) s(94.73%)p 0.06(5.27%)d 0.00(0.00%) s(0.38%)p99.99(99.49%)d 0.35(0.13%) s(0.00%)p 1.00(99.87%)d 0.00(0.13%) s(74.71%)p 0.34(25.15%)d 0.00(0.12%)f 0.00(0.02%) s(91.37%)p 0.09(8.63%)d 0.00(0.00%) s(0.01%)p99.99(99.34%)d62.87(0.65%) s(8.34%)p10.87(90.68%)d 0.12(0.98%) s(86.87%)p 0.15(13.12%)d 0.00(0.01%) s(0.00%)p 1.00(99.99%)d 0.00(0.01%) s(13.12%)p 6.62(86.87%)d 0.00(0.01%) s(0.00%)p 1.00(99.98%)d 0.00(0.02%) s(91.37%)p 0.09(8.63%)d 0.00(0.00%) s(0.01%)p99.99(99.34%)d62.72(0.65%) s(8.34%)p10.87(90.68%)d 0.12(0.98%) s(74.71%)p 0.34(25.15%)d 0.00(0.12%)f 0.00(0.02%) s(94.73%)p 0.06(5.27%)d 0.00(0.00%) s(0.38%)p99.99(99.49%)d 0.35(0.13%) s(0.00%)p 1.00(99.87%)d 0.00(0.13%) s(91.37%)p 0.09(8.63%)d 0.00(0.00%) s(0.01%)p99.99(99.34%)d62.87(0.65%) s(8.34%)p10.87(90.68%)d 0.12(0.98%)	

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list: 7BP-23LP Lewis Structure

Cycle	Occ.	Occupancies			Lewis Structure			Low	High		
		Occ.	Thresh.	Lewis	Non-Lewis	CR	BD	3C	LP	(L)	(NL)
1(1)	1.90	160.61323	5.38677	0	7	0	23	10	8	0.25	
<hr/>											
Effective Core		106.00000									
Valence Lewis		54.61323	(91.022% of 60)								
<hr/>											
Total Lewis		160.61323	(96.755% of 166)								
<hr/>											
Valence non-Lewis		4.01316	(2.418% of 166)								
Rydberg non-Lewis		1.37361	(0.827% of 166)								
<hr/>											
Total non-Lewis		5.38677	(3.245% of 166)								
<hr/>											

(Occupancy) Bond orbital/ Coefficients/ Hybrids		
1. (1.95765) BD (1) O 1-Xe 3 (87.94%) 0.9378* O 1 s(0.20%)p99.99(99.16%)d 3.28(0.64%) (12.06%) 0.3472*Xe 3 s(10.12%)p 7.57(76.56%)d 1.13(11.41%)f 0.19(1.92%)		

Table S8. (continued...)

2.	(1.80787)	BD (1) F	2-Xe 3					
		(84.72%)	0.9204* F	2 s(4.87%)p19.49(94.90%)d 0.05(0.23%)				
		(15.28%)	0.3909*Xe	3 s(14.79%)p 3.76(55.63%)d 1.87(27.67%)f 0.13(1.91%)				
3.	(1.83099)	BD (1)Xe	3- F 5					
		(4.77%)	0.2184*Xe	3 s(14.80%)p 3.96(58.68%)d 1.72(25.42%)f 0.07(1.10%)				
		(95.23%)	0.9759* F	5 s(0.00%)p 1.00(99.98%)d 0.00(0.02%)				
4.	(1.95765)	BD (1)Xe	3- O 6					
		(12.06%)	0.3472*Xe	3 s(10.12%)p 7.57(76.56%)d 1.13(11.41%)f 0.19(1.92%)				
		(87.94%)	0.9378* O	6 s(0.20%)p99.99(99.16%)d 3.28(0.64%)				
5.	(1.96183)	BD (1) O	4-Xe 7					
		(87.20%)	0.9338* O	4 s(0.20%)p99.99(99.16%)d 3.28(0.64%)				
		(12.80%)	0.3578*Xe	7 s(10.74%)p 7.46(80.06%)d 0.69(7.41%)f 0.17(1.79%)				
6.	(1.91921)	BD (1)Xe	7- F 8					
		(25.51%)	0.5051*Xe	7 s(1.42%)p67.21(95.18%)d 1.97(2.79%)f 0.44(0.62%)				
		(74.49%)	0.8630* F	8 s(4.87%)p19.49(94.90%)d 0.05(0.23%)				
7.	(1.96183)	BD (1)Xe	7- O 9					
		(12.80%)	0.3578*Xe	7 s(10.74%)p 7.46(80.06%)d 0.69(7.41%)f 0.17(1.79%)				
		(87.20%)	0.9338* O	9 s(0.20%)p99.99(99.16%)d 3.28(0.64%)				
8.	(1.97162)	LP (1) O	1	s(91.37%)p 0.09(8.63%)d 0.00(0.00%)				
9.	(1.67893)	LP (2) O	1	s(0.01%)p99.99(99.34%)d62.72(0.65%)				
10.	(1.27704)	LP (3) O	1	s(8.34%)p10.87(90.68%)d 0.12(0.98%)				
11.	(1.98445)	LP (1) F	2	s(94.73%)p 0.06(5.27%)d 0.00(0.00%)				
12.	(1.93925)	LP (2) F	2	s(0.38%)p99.99(99.49%)d 0.35(0.13%)				
13.	(1.92920)	LP (3) F	2	s(0.00%)p 1.00(99.87%)d 0.00(0.13%)				
14.	(1.96959)	LP (1)Xe	3	s(73.84%)p 0.35(25.87%)d 0.00(0.26%)f 0.00(0.03%)				
15.	(1.97162)	LP (1) O	4	s(91.37%)p 0.09(8.63%)d 0.00(0.00%)				
16.	(1.67899)	LP (2) O	4	s(0.01%)p99.99(99.34%)d62.87(0.65%)				
17.	(1.27704)	LP (3) O	4	s(8.34%)p10.87(90.68%)d 0.12(0.98%)				
18.	(1.97972)	LP (1) F	5	s(86.87%)p 0.15(13.12%)d 0.00(0.01%)				
19.	(1.95518)	LP (2) F	5	s(0.00%)p 1.00(99.99%)d 0.00(0.01%)				
20.	(1.92454)	LP (3) F	5	s(13.12%)p 6.62(86.87%)d 0.00(0.01%)				
21.	(1.97162)	LP (1) O	6	s(91.37%)p 0.09(8.63%)d 0.00(0.00%)				
22.	(1.67893)	LP (2) O	6	s(0.01%)p99.99(99.34%)d62.72(0.65%)				
23.	(1.27704)	LP (3) O	6	s(8.34%)p10.87(90.68%)d 0.12(0.98%)				
24.	(1.97085)	LP (1)Xe	7	s(74.71%)p 0.34(25.15%)d 0.00(0.12%)f 0.00(0.02%)				
25.	(1.98445)	LP (1) F	8	s(94.73%)p 0.06(5.27%)d 0.00(0.00%)				
26.	(1.93925)	LP (2) F	8	s(0.38%)p99.99(99.49%)d 0.35(0.13%)				
27.	(1.92920)	LP (3) F	8	s(0.00%)p 1.00(99.87%)d 0.00(0.13%)				
28.	(1.97162)	LP (1) O	9	s(91.37%)p 0.09(8.63%)d 0.00(0.00%)				
29.	(1.67899)	LP (2) O	9	s(0.01%)p99.99(99.34%)d62.87(0.65%)				
30.	(1.27704)	LP (3) O	9	s(8.34%)p10.87(90.68%)d 0.12(0.98%)				

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list. 8BP-22LP Lewis Structure

Cycle	Occ.	Occupancies			Lewis Structure			Low	High	
		Thresh.	Lewis	Non-Lewis	CR	BD	3C	LP	occ	occ
=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	
1(1)	1.90	160.54837	5.45163	0	8	0	22	10	8	0.25
=====	=====	=====	=====	=====	=====	=====	=====	=====	=====	

Structure accepted: NBOs selected via the \$CHOOSE keylist

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Effective Core	106.00000			
Valence Lewis	54.54837 (90.914% of 60)			
=====	=====	=====	=====	=====
Total Lewis	160.54837 (96.716% of 166)			
-----	-----	-----	-----	-----
Valence non-Lewis	4.25540 (2.563% of 166)			
Rydberg non-Lewis	1.19624 (0.721% of 166)			
=====	=====	=====	=====	=====
Total non-Lewis	5.45163 (3.284% of 166)			
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(b) Occupancy Bond orbital/ Coefficients/ Hybrids

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1.	(1.95717)	BD (1) O	1-Xe 3	
		(88.02%)	0.9382* O	1 s(0.20%)p99.99(99.16%)d 3.28(0.64%)
		(11.98%)	0.3461*Xe	3 s(9.57%)p 7.91(75.75%)d 1.33(12.78%)f 0.20(1.90%)
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Table S8. (continued...)

2.	(1.79903)	BD (1) F	2-Xe 3					
		(85.50%)	0.9247* F	2 s(4.87%)p19.49(94.90%)d 0.05(0.23%)				
		(14.50%)	0.3807*Xe	3 s(11.47%)p 4.60(52.77%)d 3.04(34.85%)f 0.08(0.92%)				
3.	(1.91446)	BD (1)Xe	3- F 5					
		(5.15%)	0.2268*Xe	3 s(8.31%)p 7.73(64.25%)d 3.27(27.19%)f 0.03(0.26%)				
		(94.85%)	0.9739* F	5 s(6.64%)p14.07(93.35%)d 0.00(0.02%)				
4.	(1.95717)	BD (1)Xe	3- O 6					
		(11.98%)	0.3461*Xe	3 s(9.57%)p 7.91(75.75%)d 1.33(12.78%)f 0.20(1.90%)				
		(88.02%)	0.9382* O	6 s(0.20%)p99.99(99.16%)d 3.28(0.64%)				
5.	(1.95717)	BD (1) O	4-Xe 7					
		(88.02%)	0.9382* O	4 s(0.20%)p99.99(99.16%)d 3.28(0.64%)				
		(11.98%)	0.3461*Xe	7 s(9.57%)p 7.91(75.75%)d 1.33(12.78%)f 0.20(1.90%)				
6.	(1.91446)	BD (1) F	5-Xe 7					
		(94.85%)	0.9739* F	5 s(6.64%)p14.06(93.34%)d 0.00(0.02%)				
		(5.15%)	0.2269*Xe	7 s(8.31%)p 7.73(64.25%)d 3.27(27.18%)f 0.03(0.26%)				
7.	(1.79905)	BD (1)Xe	7- F 8					
		(14.50%)	0.3808*Xe	7 s(11.47%)p 4.60(52.77%)d 3.04(34.84%)f 0.08(0.92%)				
		(85.50%)	0.9247* F	8 s(4.87%)p19.49(94.90%)d 0.05(0.23%)				
8.	(1.95717)	BD (1)Xe	7- O 9					
		(11.98%)	0.3461*Xe	7 s(9.57%)p 7.91(75.75%)d 1.33(12.78%)f 0.20(1.90%)				
		(88.02%)	0.9382* O	9 s(0.20%)p99.99(99.16%)d 3.28(0.64%)				
9.	(1.97162)	LP (1) O	1	s(91.37%)p 0.09(8.63%)d 0.00(0.00%)				
10.	(1.67893)	LP (2) O	1	s(0.01%)p99.99(99.34%)d62.72(0.65%)				
11.	(1.27704)	LP (3) O	1	s(8.34%)p10.87(90.68%)d 0.12(0.98%)				
12.	(1.98445)	LP (1) F	2	s(94.73%)p 0.06(5.27%)d 0.00(0.00%)				
13.	(1.93925)	LP (2) F	2	s(0.38%)p99.99(99.49%)d 0.35(0.13%)				
14.	(1.92920)	LP (3) F	2	s(0.00%)p 1.00(99.87%)d 0.00(0.13%)				
15.	(1.97074)	LP (1)Xe	3	s(74.42%)p 0.34(25.40%)d 0.00(0.16%)f 0.00(0.02%)				
16.	(1.97162)	LP (1) O	4	s(91.37%)p 0.09(8.63%)d 0.00(0.00%)				
17.	(1.67899)	LP (2) O	4	s(0.01%)p99.99(99.34%)d62.87(0.65%)				
18.	(1.27704)	LP (3) O	4	s(8.34%)p10.87(90.68%)d 0.12(0.98%)				
19.	(1.97972)	LP (1) F	5	s(86.71%)p 0.15(13.28%)d 0.00(0.01%)				
20.	(1.95518)	LP (2) F	5	s(0.00%)p 1.00(99.99%)d 0.00(0.01%)				
21.	(1.97162)	LP (1) O	6	s(91.37%)p 0.09(8.63%)d 0.00(0.00%)				
22.	(1.67893)	LP (2) O	6	s(0.01%)p99.99(99.34%)d62.72(0.65%)				
23.	(1.27704)	LP (3) O	6	s(8.34%)p10.87(90.68%)d 0.12(0.98%)				
24.	(1.97074)	LP (1)Xe	7	s(74.42%)p 0.34(25.40%)d 0.00(0.16%)f 0.00(0.02%)				
25.	(1.98445)	LP (1) F	8	s(94.73%)p 0.06(5.27%)d 0.00(0.00%)				
26.	(1.93925)	LP (2) F	8	s(0.38%)p99.99(99.49%)d 0.35(0.13%)				
27.	(1.92920)	LP (3) F	8	s(0.00%)p 1.00(99.87%)d 0.00(0.13%)				
28.	(1.97162)	LP (1) O	9	s(91.37%)p 0.09(8.63%)d 0.00(0.00%)				
29.	(1.67899)	LP (2) O	9	s(0.01%)p99.99(99.34%)d62.87(0.65%)				
30.	(1.27704)	LP (3) O	9	s(8.34%)p10.87(90.68%)d 0.12(0.98%)				

FO₂XeFXeO₂F⁺ (C₁) MP2/Stutt RLC ECP

O1	-2.06606	1.61818	0.37601
F2	-4.05733	-0.24292	-0.06471
Xe3	-2.14719	-0.02814	-0.148
O4	1.73678	1.05292	1.1842
F5	0.00001	0.00083	-0.86784
O6	-1.73606	-1.05282	1.18402
Xe7	2.14721	0.0282	-0.14801
F8	4.05751	0.24163	-0.0647
O9	2.06498	-1.61816	0.37572

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list: 6BP-24LP Lewis Structure

Cycle	Occ.	Occupancies			Lewis Structure			Low	High		
		Thresh.	Lewis	Non-Lewis	CR	BD	3C	LP	(L)	(NL)	Dev
1(1)	1.90	160.68213	5.31787		0	6	0	24	9	8	0.25
<hr/>											<hr/>
Effective Core											106.00000
Valence Lewis											54.68213 (91.137% of 60)
<hr/>											<hr/>
Total Lewis											160.68213 (96.796% of 166)
<hr/>											<hr/>
Valence non-Lewis											3.81066 (2.296% of 166)

Table S8. (continued...)

Rydberg non-Lewis	1.50722	(0.908% of 166)
Total non-Lewis	5.31787	(3.204% of 166)
<hr/>		
(Occupancy) Bond orbital/ Coefficients/ Hybrids		
1. (1.96191) BD (1) O 1-Xe 3		
(87.21%) 0.9339* O 1 s(0.20%)p99.99(99.15%)d 3.14(0.64%)		
(12.79%) 0.3576*Xe 3 s(10.70%)p 7.49(80.09%)d 0.69(7.42%)f 0.17(1.79%)		
2. (1.92160) BD (1) F 2-Xe 3		
(74.34%) 0.8622* F 2 s(4.88%)p19.44(94.89%)d 0.05(0.23%)		
(25.66%) 0.5066*Xe 3 s(1.46%)p65.13(95.33%)d 1.79(2.62%)f 0.40(0.59%)		
3. (1.96311) BD (1)Xe 3- O 6		
(12.83%) 0.3582*Xe 3 s(10.79%)p 7.44(80.24%)d 0.67(7.23%)f 0.16(1.75%)		
(87.17%) 0.9336* O 6 s(0.19%)p99.99(99.16%)d 3.30(0.64%)		
4. (1.96311) BD (1) O 4-Xe 7		
(87.17%) 0.9336* O 4 s(0.19%)p99.99(99.16%)d 3.30(0.64%)		
(12.83%) 0.3582*Xe 7 s(10.79%)p 7.44(80.24%)d 0.67(7.23%)f 0.16(1.75%)		
5. (1.92159) BD (1)Xe 7- F 8		
(25.66%) 0.5066*Xe 7 s(1.46%)p65.14(95.33%)d 1.79(2.62%)f 0.40(0.59%)		
(74.34%) 0.8622* F 8 s(4.88%)p19.44(94.89%)d 0.05(0.23%)		
6. (1.96191) BD (1)Xe 7- O 9		
(12.79%) 0.3576*Xe 7 s(10.70%)p 7.49(80.09%)d 0.69(7.42%)f 0.17(1.79%)		
(87.21%) 0.9339* O 9 s(0.20%)p99.99(99.15%)d 3.15(0.64%)		
7. (1.97163) LP (1) O 1	s(91.35%)p 0.09(8.65%)d 0.00(0.00%)	
8. (1.67712) LP (2) O 1	s(0.01%)p99.99(99.33%)d58.80(0.65%)	
9. (1.27725) LP (3) O 1	s(8.35%)p10.86(90.67%)d 0.12(0.98%)	
10. (1.98445) LP (1) F 2	s(94.72%)p 0.06(5.28%)d 0.00(0.00%)	
11. (1.93924) LP (2) F 2	s(0.37%)p99.99(99.50%)d 0.35(0.13%)	
12. (1.92924) LP (3) F 2	s(0.00%)p 1.00(99.87%)d 0.00(0.13%)	
13. (1.97094) LP (1)Xe 3	s(74.67%)p 0.34(25.19%)d 0.00(0.12%)f 0.00(0.02%)	
14. (1.97167) LP (1) O 4	s(91.38%)p 0.09(8.62%)d 0.00(0.00%)	
15. (1.68259) LP (2) O 4	s(0.01%)p 1.00(99.34%)d 0.01(0.65%)	
16. (1.27655) LP (3) O 4	s(8.33%)p10.88(90.69%)d 0.12(0.98%)	
17. (1.97993) LP (1) F 5	s(86.99%)p 0.15(12.99%)d 0.00(0.01%)	
18. (1.95541) LP (2) F 5	s(0.00%)p 1.00(99.99%)d 0.00(0.01%)	
19. (1.92230) LP (3) F 5	s(13.00%)p 6.69(86.99%)d 0.00(0.01%)	
20. (1.76985) LP (4) F 5	s(0.00%)p 1.00(99.98%)d 0.00(0.02%)	
21. (1.97167) LP (1) O 6	s(91.38%)p 0.09(8.62%)d 0.00(0.00%)	
22. (1.68260) LP (2) O 6	s(0.01%)p 1.00(99.34%)d 0.01(0.65%)	
23. (1.27656) LP (3) O 6	s(8.33%)p10.88(90.69%)d 0.12(0.98%)	
24. (1.97094) LP (1)Xe 7	s(74.67%)p 0.34(25.19%)d 0.00(0.12%)f 0.00(0.02%)	
25. (1.98445) LP (1) F 8	s(94.72%)p 0.06(5.28%)d 0.00(0.00%)	
26. (1.93924) LP (2) F 8	s(0.37%)p99.99(99.50%)d 0.35(0.13%)	
27. (1.92924) LP (3) F 8	s(0.00%)p 1.00(99.87%)d 0.00(0.13%)	
28. (1.97163) LP (1) O 9	s(91.35%)p 0.09(8.65%)d 0.00(0.00%)	
29. (1.67714) LP (2) O 9	s(0.01%)p99.99(99.33%)d58.69(0.65%)	
30. (1.27726) LP (3) O 9	s(8.35%)p10.86(90.67%)d 0.12(0.98%)	

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list: 7BP-23LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure				Low occ	High occ	Dev	
		Thresh.	Lewis	Non-Lewis	CR	BD	3C	LP			
<hr/>											
1(1)	1.90	160.62146	5.37854		0	7	0	23	10	8	0.25
<hr/>											
Effective Core											
Valence Lewis											
Total Lewis											
<hr/>											
Valence non-Lewis											
Rydberg non-Lewis											
<hr/>											
Total non-Lewis											

Table S8. (continued...)

		(Occupancy)		Bond orbital/		Coefficients/		Hybrids	
1.	(1.95793)	BD	(1)	O	1-Xe	3			
		(87.93%)		0.9377*	O	1 s(0.20%)p99.99(99.15%)d 3.14(0.64%)			
		(12.07%)		0.3474*Xe	3 s(10.12%)p	7.57(76.61%)d 1.12(11.38%)f 0.19(1.89%)			
2.	(1.80982)	BD	(1)	F	2-Xe	3			
		(84.55%)		0.9195*	F	2 s(4.88%)p19.44(94.89%)d 0.05(0.23%)			
		(15.45%)		0.3931*Xe	3 s(14.67%)p	3.82(56.07%)d 1.87(27.44%)f 0.12(1.82%)			
3.	(1.83079)	BD	(1)	Xe	3- F	5			
		(4.76%)		0.2181*Xe	3 s(14.61%)p	3.99(58.34%)d 1.78(25.97%)f 0.07(1.09%)			
		(95.24%)		0.9759*	F	5 s(0.00%)p 1.00(99.98%)d 0.00(0.02%)			
4.	(1.95851)	BD	(1)	Xe	3- O	6			
		(12.04%)		0.3470*Xe	3 s(10.12%)p	7.57(76.59%)d 1.13(11.40%)f 0.19(1.89%)			
		(87.96%)		0.9379*	O	6 s(0.19%)p99.99(99.16%)d 3.30(0.64%)			
5.	(1.96311)	BD	(1)	O	4-Xe	7			
		(87.17%)		0.9336*	O	4 s(0.19%)p99.99(99.16%)d 3.30(0.64%)			
		(12.83%)		0.3582*Xe	7 s(10.79%)p	7.44(80.24%)d 0.67(7.23%)f 0.16(1.75%)			
6.	(1.92159)	BD	(1)	Xe	7- F	8			
		(25.66%)		0.5066*Xe	7 s(1.46%)p65.14(95.33%)d	1.79(2.62%)f 0.40(0.59%)			
		(74.34%)		0.8622*	F	8 s(4.88%)p19.44(94.89%)d 0.05(0.23%)			
7.	(1.96191)	BD	(1)	Xe	7- O	9			
		(12.79%)		0.3576*Xe	7 s(10.70%)p	7.49(80.09%)d 0.69(7.42%)f 0.17(1.79%)			
		(87.21%)		0.9339*	O	9 s(0.20%)p99.99(99.15%)d 3.15(0.64%)			
8.	(1.97163)	LP	(1)	O	1		s(91.35%)p 0.09(8.65%)d 0.00(0.00%)		
9.	(1.67712)	LP	(2)	O	1		s(0.01%)p99.99(99.33%)d58.80(0.65%)		
10.	(1.27725)	LP	(3)	O	1		s(8.35%)p10.86(90.67%)d 0.12(0.98%)		
11.	(1.98445)	LP	(1)	F	2		s(94.72%)p 0.06(5.28%)d 0.00(0.00%)		
12.	(1.93924)	LP	(2)	F	2		s(0.37%)p99.99(99.50%)d 0.35(0.13%)		
13.	(1.92924)	LP	(3)	F	2		s(0.00%)p 1.00(99.87%)d 0.00(0.13%)		
14.	(1.96971)	LP	(1)	Xe	3		s(73.84%)p 0.35(25.87%)d 0.00(0.26%)f 0.00(0.03%)		
15.	(1.97167)	LP	(1)	O	4		s(91.38%)p 0.09(8.62%)d 0.00(0.00%)		
16.	(1.68259)	LP	(2)	O	4		s(0.01%)p 1.00(99.34%)d 0.01(0.65%)		
17.	(1.27655)	LP	(3)	O	4		s(8.33%)p10.88(90.69%)d 0.12(0.98%)		
18.	(1.97993)	LP	(1)	F	5		s(86.99%)p 0.15(12.99%)d 0.00(0.01%)		
19.	(1.95541)	LP	(2)	F	5		s(0.00%)p 1.00(99.99%)d 0.00(0.01%)		
20.	(1.92229)	LP	(3)	F	5		s(13.00%)p 6.69(86.99%)d 0.00(0.01%)		
21.	(1.97167)	LP	(1)	O	6		s(91.38%)p 0.09(8.62%)d 0.00(0.00%)		
22.	(1.68260)	LP	(2)	O	6		s(0.01%)p 1.00(99.34%)d 0.01(0.65%)		
23.	(1.27656)	LP	(3)	O	6		s(8.33%)p10.88(90.69%)d 0.12(0.98%)		
24.	(1.97094)	LP	(1)	Xe	7		s(74.67%)p 0.34(25.19%)d 0.00(0.12%)f 0.00(0.02%)		
25.	(1.98445)	LP	(1)	F	8		s(94.72%)p 0.06(5.28%)d 0.00(0.00%)		
26.	(1.93924)	LP	(2)	F	8		s(0.37%)p99.99(99.50%)d 0.35(0.13%)		
27.	(1.92924)	LP	(3)	F	8		s(0.00%)p 1.00(99.87%)d 0.00(0.13%)		
28.	(1.97163)	LP	(1)	O	9		s(91.35%)p 0.09(8.65%)d 0.00(0.00%)		
29.	(1.67714)	LP	(2)	O	9		s(0.01%)p99.99(99.33%)d58.69(0.65%)		
30.	(1.27726)	LP	(3)	O	9		s(8.35%)p10.88(90.67%)d 0.12(0.98%)		

NATURAL BOND ORBITAL ANALYSIS:

Reading \$CHOOSE input list: 8BP-22LP Lewis Structure

Cycle	Occ.	Occupancies		Lewis Structure			Low	High	Dev		
		Thresh.	Lewis	Non-Lewis	CR	BD	3C	LP			
1(1)	1.90	160.55648	5.44352		0	8	0	22	10	8	0.25
<hr/>											
Effective Core											
Valence Lewis											
Total Lewis											
<hr/>											
Valence non-Lewis											
Rydberg non-Lewis											

Table S8. (continued...)

Total non-Lewis	5.44352 (3.279% of 166)
(Occupancy) Bond orbital/ Coefficients/ Hybrids	

1. (1.95582) BD (1) O 1-Xe 3 (88.22%) 0.9392* O 1 s(0.20%)p99.99(99.15%)d 3.14(0.64%) (11.78%) 0.3432*Xe 3 s(9.49%)p 7.87(74.62%)d 1.46(13.84%)f 0.22(2.05%)	
2. (1.80032) BD (1) F 2-Xe 3 (85.37%) 0.9240* F 2 s(4.88%)p19.44(94.89%)d 0.05(0.23%) (14.63%) 0.3824*Xe 3 s(11.61%)p 4.58(53.12%)d 2.95(34.29%)f 0.08(0.97%)	
3. (1.91411) BD (1)Xe 3- F 5 (5.18%) 0.2277*Xe 3 s(8.28%)p 7.71(63.88%)d 3.32(27.49%)f 0.04(0.35%) (94.82%) 0.9737* F 5 s(6.58%)p14.21(93.41%)d 0.00(0.02%)	
4. (1.95973) BD (1)Xe 3- O 6 (12.19%) 0.3491*Xe 3 s(9.80%)p 7.86(77.01%)d 1.17(11.45%)f 0.18(1.74%) (87.81%) 0.9371* O 6 s(0.19%)p99.99(99.16%)d 3.30(0.64%)	
5. (1.95972) BD (1) O 4-Xe 7 (87.81%) 0.9371* O 4 s(0.19%)p99.99(99.16%)d 3.30(0.64%) (12.19%) 0.3491*Xe 7 s(9.80%)p 7.86(77.00%)d 1.17(11.46%)f 0.18(1.74%)	
6. (1.91410) BD (1) F 5-Xe 7 (94.82%) 0.9737* F 5 s(6.58%)p14.21(93.41%)d 0.00(0.02%) (5.18%) 0.2277*Xe 7 s(8.28%)p 7.71(63.88%)d 3.32(27.49%)f 0.04(0.34%)	
7. (1.80033) BD (1)Xe 7- F 8 (14.63%) 0.3824*Xe 7 s(11.61%)p 4.58(53.12%)d 2.95(34.29%)f 0.08(0.97%) (85.37%) 0.9240* F 8 s(4.88%)p19.44(94.89%)d 0.05(0.23%)	
8. (1.95583) BD (1)Xe 7- O 9 (11.78%) 0.3432*Xe 7 s(9.49%)p 7.87(74.63%)d 1.46(13.83%)f 0.22(2.05%) (88.22%) 0.9392* O 9 s(0.20%)p99.99(99.15%)d 3.15(0.64%)	
9. (1.97163) LP (1) O 1 10. (1.67712) LP (2) O 1 11. (1.27725) LP (3) O 1 12. (1.98445) LP (1) F 2 13. (1.93924) LP (2) F 2 14. (1.92924) LP (3) F 2 15. (1.97083) LP (1)Xe 3 16. (1.97167) LP (1) O 4 17. (1.68259) LP (2) O 4 18. (1.27655) LP (3) O 4 19. (1.97993) LP (1) F 5 20. (1.95541) LP (2) F 5 21. (1.97167) LP (1) O 6 22. (1.68260) LP (2) O 6 23. (1.27656) LP (3) O 6 24. (1.97083) LP (1)Xe 7 25. (1.98445) LP (1) F 8 26. (1.93924) LP (2) F 8 27. (1.92924) LP (3) F 8 28. (1.97163) LP (1) O 9 29. (1.67714) LP (2) O 9 30. (1.27726) LP (3) O 9	s(91.35%)p 0.09(8.65%)d 0.00(0.00%) s(0.01%)p99.99(99.33%)d58.80(0.65%) s(8.35%)p10.86(90.67%)d 0.12(0.98%) s(94.72%)p 0.06(5.28%)d 0.00(0.00%) s(0.37%)p99.99(99.50%)d 0.35(0.13%) s(0.00%)p 1.00(99.87%)d 0.00(0.13%) s(74.39%)p 0.34(25.42%)d 0.00(0.16%)f 0.00(0.02%) s(91.38%)p 0.09(8.62%)d 0.00(0.00%) s(0.01%)p 1.00(99.34%)d 0.01(0.65%) s(8.33%)p10.88(90.69%)d 0.12(0.98%) s(86.84%)p 0.15(13.15%)d 0.00(0.01%) s(0.00%)p 1.00(99.99%)d 0.00(0.01%) s(91.38%)p 0.09(8.62%)d 0.00(0.00%) s(0.01%)p 1.00(99.34%)d 0.01(0.65%) s(8.33%)p10.88(90.69%)d 0.12(0.98%) s(74.39%)p 0.34(25.42%)d 0.00(0.16%)f 0.00(0.02%) s(94.72%)p 0.06(5.28%)d 0.00(0.00%) s(0.37%)p99.99(99.50%)d 0.35(0.13%) s(0.00%)p 1.00(99.87%)d 0.00(0.13%) s(91.35%)p 0.09(8.65%)d 0.00(0.00%) s(0.01%)p99.99(99.33%)d58.69(0.65%) s(8.35%)p10.86(90.67%)d 0.12(0.98%)

**f) O₂Xe(OTeF₅)⁺ (C₁), MP2/Stutt RLC, 9 BP - 24 LP Lewis structure, 169.406 el.
Lewis type (97.4 %), 4.594 el. Non-Lewis type (2.6%)**

orbital	orb pop	% s	% p	% d	% f
1. σ [Xe - O(1)]	1.88[Xe (13%)] [O (87%)]	3.35 1.13	54.5 98.2	38.6 0.68	3.54
2. σ [Xe - O(2)]	1.88[Xe (13%)] [O (87%)]	3.34 1.13	54.5 98.2	38.6 0.68	3.54

Table S8. (continued...)

3.	σ [Xe - O(3)]	1.95[Xe (5%)] [O (95%)]	0.00 0.00	78.9 99.8	19.29 0.20	1.83
4.	σ [Te - O(3)]	1.83[Te (9%)] [O (91%)]	14.2 15.1	55.2 84.7	30.6 0.23	
5.	σ [Te - F(1)]	1.84[Te (12%)] [F (88%)]	17.3 12.1	51.2 87.6	31.5 0.33	
6.	σ [Te - F(2)]	1.84[Te (12%)] [F (88%)]	17.3 12.1	51.2 87.6	31.5 0.33	
7.	σ [Te - F(3)]	1.84[Te (11%)] [F (89%)]	16.1 12.3	50.9 87.4	33.0 0.31	
8.	σ [Te - F(4)]	1.85[Te (13%)] [F (87%)]	18.1 13.2	58.6 86.5	23.3 0.35	
9.	σ [Te - F(5)]	1.84[Te (13%)] [F (87%)]	18.0 12.3	53.1 87.4	28.9 0.34	
10.	LP [Xe]	1.97	71.7	28.1	0.10	0.01
11.	LP [O(1)]	1.97	91.1	8.85	0.01	
12.	LP [O(1)]	1.74	0.18	99.2	0.65	
13.	LP [O(1)]	1.28	7.47	91.6	0.97	
14.	LP [O(2)]	1.97	91.1	8.85	0.01	
15.	LP [O(2)]	1.74	0.18	99.2	0.65	
16.	LP [O(2)]	1.28	7.47	91.6	0.97	
17.	LP [O(3)]	1.95	79.0	20.9	0.13	
18.	LP [O(3)]	1.46	5.88	93.8	0.36	
19.	LP [F(1)]	1.97	87.7	12.3	0.00	
20.	LP [F(1)]	1.95	0.01	99.8	0.19	
21.	LP [F(1)]	1.94	0.14	99.7	0.19	
22.	LP [F(2)]	1.97	87.7	12.3	0.00	
23.	LP [F(2)]	1.95	0.01	99.8	0.19	
24.	LP [F(2)]	1.94	0.14	99.7	0.19	
25.	LP [F(3)]	1.97	87.6	12.4	0.00	
26.	LP [F(3)]	1.95	0.00	99.8	0.17	
27.	LP [F(3)]	1.94	0.05	99.8	0.17	
28.	LP [F(4)]	1.97	86.8	13.2	0.00	
29.	LP [F(4)]	1.94	0.00	99.8	0.21	
30.	LP [F(4)]	1.94	0.00	99.8	0.21	
31.	LP [F(5)]	1.97	87.5	12.5	0.00	
32.	LP [F(5)]	1.95	0.00	99.8	0.19	
33.	LP [F(5)]	1.94	0.21	99.6	0.20	

**(g) $O_2Xe(OTeF_5)_2 (C_1)$ in MP2/Stutt RLC, 16 BP - 41 LP Lewis structure, 274.820 el.
Lewis type (98.2 %), 5.180 el. Non-Lewis type (1.8%)**

orbital	orb pop	% s	% p	% d	% f
1. σ [Xe - O(1)]	1.90[Xe (38%)] [O (62%)]	10.6 8.55	84.8 90.5	4.05 0.94	0.54
2. σ [Xe - O(2)]	1.90[Xe (38%)] [O (62%)]	10.6 8.54	84.7 90.5	4.11 0.94	0.55
3. σ [Xe - O(3)]	1.80[Xe (14%)] [O (86%)]	10.7 9.13	60.1 90.7	28.6 0.19	0.60
4. σ [Xe - O(4)]	1.80[Xe (14%)] [O (86%)]	10.7 9.14	60.1 90.7	28.6 0.19	0.60
5. σ [Te(1) - O(3)]	1.80[Te (14%)] [O (86%)]	19.1 14.4	50.7 85.3	30.2 0.32	
6. σ [Te(2) - O(4)]	1.80[Te (14%)] [O (86%)]	19.1 14.4	50.7 85.3	30.2 0.32	
7. σ [Te(1) - F(1)]	1.85[Te (11%)] [F (89%)]	16.8 13.2	50.4 86.5	32.8 0.29	

Table S8. (continued...)

8.	σ [Te(1) - F(2)]	1.85[Te (11%)] [F (89%)]	16.8 13.2	50.4 86.5	32.9 0.29
9.	σ [Te(1) - F(3)]	1.84[Te (10%)] [F (90%)]	16.3 13.2	49.0 86.5	34.7 0.29
10.	σ [Te(1) - F(4)]	1.85[Te (11%)] [F (89%)]	16.8 13.7	53.0 86.0	30.2 0.31
11.	σ [Te(1) - F(5)]	1.85[Te (12%)] [F (88%)]	17.4 13.5	51.8 86.2	30.8 0.30
12.	σ [Te(2) - F(6)]	1.85[Te (11%)] [F (89%)]	16.8 13.2	50.4 86.5	32.8 0.29
13.	σ [Te(2) - F(7)]	1.85[Te (11%)] [F (89%)]	16.8 13.2	50.4 86.5	32.8 0.29
14.	σ [Te(2) - F(8)]	1.84[Te (10%)] [F (90%)]	16.3 13.2	49.0 86.5	34.7 0.29
15.	σ [Te(2) - F(9)]	1.85[Te (11%)] [F (89%)]	16.8 13.7	53.0 86.0	30.2 0.31
16.	σ [Te(2) - F(10)]	1.85[Te (12%)] [F (88%)]	17.4 13.5	51.8 86.2	30.8 0.30
17.	LP [Xe]	1.95	75.3	24.5	0.20
18.	LP [O(1)]	1.97	91.0	9.02	0.00
19.	LP [O(1)]	1.80	0.40	99.0	0.58
20.	LP [O(1)]	1.75	0.00	99.4	0.58
21.	LP [O(2)]	1.97	91.0	9.00	0.00
22.	LP [O(2)]	1.80	0.40	99.0	0.58
23.	LP [O(2)]	1.75	0.00	99.4	0.58
24.	LP [O(3)]	1.95	76.4	23.5	0.10
25.	LP [O(3)]	1.90	0.00	99.8	0.16
26.	LP [O(4)]	1.95	76.4	23.5	0.10
27.	LP [O(4)]	1.90	0.00	99.8	0.16
28.	LP [F(1)]	1.97	86.7	13.3	0.00
29.	LP [F(1)]	1.95	0.00	99.8	0.16
30.	LP [F(1)]	1.95	0.00	99.8	0.16
31.	LP [F(2)]	1.97	86.7	13.3	0.00
32.	LP [F(2)]	1.95	0.00	99.8	0.16
33.	LP [F(2)]	1.95	0.00	99.8	0.16
34.	LP [F(3)]	1.97	86.6	13.3	0.00
35.	LP [F(3)]	1.95	0.00	99.8	0.16
36.	LP [F(3)]	1.95	0.08	99.8	0.16
37.	LP [F(4)]	1.97	86.2	13.8	0.00
38.	LP [F(4)]	1.95	0.00	99.8	0.17
39.	LP [F(4)]	1.95	0.00	99.8	0.17
40.	LP [F(5)]	1.97	86.4	13.6	0.00
41.	LP [F(5)]	1.95	0.00	99.8	0.16
42.	LP [F(5)]	1.95	0.00	99.8	0.16
43.	LP [F(6)]	1.97	86.7	13.3	0.00
44.	LP [F(6)]	1.95	0.00	99.8	0.16
45.	LP [F(6)]	1.95	0.00	99.8	0.16
46.	LP [F(7)]	1.97	86.7	13.3	0.00
47.	LP [F(7)]	1.95	0.00	99.8	0.16
48.	LP [F(7)]	1.95	0.00	99.8	0.16
49.	LP [F(8)]	1.97	86.7	13.3	0.00
50.	LP [F(8)]	1.95	0.00	99.8	0.16
51.	LP [F(8)]	1.95	0.08	99.8	0.16
52.	LP [F(9)]	1.97	86.2	13.8	0.00
53.	LP [F(9)]	1.95	0.00	99.8	0.17
54.	LP [F(9)]	1.95	0.00	99.8	0.17
55.	LP [F(10)]	1.97	86.4	13.6	0.00
56.	LP [F(10)]	1.95	0.00	99.8	0.16
57.	LP [F(10)]	1.95	0.00	99.8	0.16

Table S9. Natural Atomic Charges, Mayer Natural Atomic Orbital Valencies, and Natural Atomic Orbital Overlap-weighted Bond Orders Between Atoms in XeO_2F_2 (C_{2v}), XeO_2F^+ (C_s), IO_2F (C_s), TeO_2F^- (C_s) and $\text{FO}_2\text{XeFXeO}_2\text{F}^+$ (C_s , and C_l), $\text{XeO}_2(\text{OTeF}_5)^+$ (C_l) and $\text{XeO}_2(\text{OTeF}_5)_2$ (C_l)

XeO_2F_2		charge						valency	
		DZVP		Stuttgart RLC ECP		DZVP		Stuttgart RLC ECP	
		SVWN	HF	SVWN	MP2	SVWN	HF	SVWN	MP2
Xe	2.699	3.331	2.768	3.000	2.080	2.465	2.295	2.389	
O(1), O(2)	-0.781, -0.781	-0.998, -0.998	-0.816, -0.816	-0.899, -0.899	0.664, 0.664	0.828, 0.828	0.752, 0.752	0.816, 0.816	
F(1), F(2)	-0.568, -0.568	-0.667, -0.667	-0.568, -0.568	-0.601, -0.601	0.256, 0.256	0.327, 0.327	0.290, 0.290	0.286, 0.286	
bond order									
$\text{Xe-O}(1), \text{Xe-O}(2)$	0.740, 0.740	0.880, 0.880	0.821, 0.821	0.878, 0.878					
$\text{Xe-F}(1), \text{Xe-F}(2)$	0.301, 0.301	0.353, 0.353	0.327, 0.327	0.317, 0.317					
XeO_2F^+		charge						valency	
		DZVP		Stuttgart RLC ECP		DZVP		Stuttgart RLC ECP	
		SVWN	HF	SVWN	MP2	SVWN	HF	SVWN	MP2
Xe	2.576	3.264	2.664	2.889	1.853	2.292	2.042	2.162	
O(1), O(2)	-0.581, -0.581	-0.873, -0.873	-0.622, -0.622	-0.699, -0.699	0.706, 0.706	0.886, 0.886	0.778, 0.778	0.854, 0.854	
F	-0.414	-0.518	-0.421	-0.490	0.300	0.425	0.358	0.323	
bond order									
$\text{Xe-O}(1), \text{Xe-O}(2)$	0.757, 0.757	0.921, 0.921	0.826, 0.826	0.899, 0.899					
Xe-F	0.338	0.450	0.390	0.363					
IO_2F		charge						valency	
		DZVP		Stuttgart RLC ECP		DZVP		Stuttgart RLC ECP	
		SVWN	HF	SVWN	MP2	SVWN	HF	SVWN	MP2
I	2.312	2.869	2.332	2.525	1.930	2.017	1.934	1.992	
O(1), O(2)	-0.872, -0.872	-1.107, -1.107	-0.882, -0.882	-0.952, -0.952	0.744, 0.744	0.803, 0.803	0.732, 0.732	0.801, 0.801	
F	-0.567	-0.656	-0.568	-0.622	0.307	0.331	0.299	0.279	
bond order									
$\text{I-O}(1), \text{I-O}(2)$	0.794, 0.794	0.830, 0.830	0.796, 0.796	0.838, 0.838					
I-F	0.342	0.357	0.341	0.316					

Table S9. (continued...)

TeO₂F⁻		charge		Stuttgart RLC ECP		DZVP		valency		Stuttgart RLC ECP	
		DZVP	HF	SVWN	MP2	SVWN	HF	SVWN	HF	SVWN	MP2
Te		1.895	2.399	1.946	2.095	1.875	1.774	1.843	1.843	1.837	
O(1), O(2)	-1.105, -1.105	-1.320, -1.320	-1.128, -1.128	-1.183, -1.183	-0.730	0.737, 0.737	0.682, 0.682	0.693, 0.693	0.693, 0.693	0.745, 0.745	
F	-0.685	-0.760	-0.690	-0.730	0.291	0.274	0.266	0.266	0.266	0.251	
Te-O(1), Te-O(2)	0.778, 0.778	0.733, 0.733	0.766, 0.766	0.775, 0.775							
Te-F	0.318	0.308	0.312	0.286							

FO₂XeFXeO₂F⁺		charge		valency		(C _s)		(C _i)		bond order	
atom		(C _s)	(C _i)			(C _s)	(C _i)	(C _s)	(C _i)	(C _s)	(C _i)
Xe(1), Xe(2)	2.668, 2.668	2.670, 2.670	1.988, 1.988	1.987, 1.987	Xe(1)-O(1), Xe(2)-O(4)	0.757, 0.757	0.757, 0.756				
O(1), O(4)	-0.681, -0.681	-0.683, -0.683	0.690, 0.690	0.690, 0.690	Xe(1)-O(2), Xe(2)-O(3)	0.757, 0.757	0.756, 0.757				
O(2), O(3)	-0.681, -0.681	-0.679, -0.679	0.690, 0.690	0.689, 0.689	Xe(1)-F(1), Xe(2)-F(2)	0.332, 0.332	0.332, 0.332				
F(1), F(2)	-0.472, -0.472	-0.472, -0.472	0.288, 0.288	0.288, 0.288	Xe(1)-F(3), Xe(2)-F(3)	0.139, 0.139	0.139, 0.139				
F(3)	-0.670	-0.670	0.229	0.229	HF, Stuttgart RLC ECP						
Xe(1), Xe(2)	3.330, 3.330	3.333, 3.333	2.371, 2.371	2.349, 2.349	Xe(1)-O(1), Xe(2)-O(4)	0.898, 0.898	0.897, 0.897				
O(1), O(4)	-0.934, -0.934	-0.937, -0.937	0.853, 0.853	0.851, 0.851	Xe(1)-O(2), Xe(2)-O(3)	0.898, 0.898	0.897, 0.897				
O(2), O(3)	-0.934, -0.934	-0.936, -0.936	0.853, 0.853	0.849, 0.849	Xe(1)-F(1), Xe(2)-F(2)	0.425, 0.424	0.425, 0.425				
F(1), F(2)	-0.568, -0.568	-0.567, -0.567	0.396, 0.396	0.400, 0.400	Xe(1)-F(3), Xe(2)-F(3)	0.153, 0.153	0.133, 0.133				
F(3)	-0.787	-0.784	0.279	0.240	SVWN, Stuttgart RLC ECP						
Xe(1), Xe(2)	2.949, 2.949	2.749, 2.749	2.434, 2.434	2.239, 2.239	Xe(1)-O(1), Xe(2)-O(4)	0.899, 0.899	0.840, 0.840				
O(1), O(4)	-0.806, -0.806	-0.720, -0.720	0.831, 0.831	0.779, 0.779	Xe(1)-O(2), Xe(2)-O(3)	0.898, 0.898	0.838, 0.838				
O(2), O(3)	-0.808, -0.808	-0.726, -0.726	0.823, 0.823	0.771, 0.771	Xe(1)-F(1), Xe(2)-F(2)	0.452, 0.452	0.386, 0.386				
F(1), F(2)	-0.499, -0.499	-0.475, -0.475	0.409, 0.409	0.350, 0.350	Xe(1)-F(3), Xe(2)-F(3)	0.186, 0.186	0.175, 0.175				
F(3)	-0.674	-0.654	0.329	0.314	MP2, Stuttgart RLC ECP						
Xe(1), Xe(2)	2.978, 2.978	2.982, 2.982	2.423, 2.423	2.425, 2.425	Xe(1)-O(1), Xe(2)-O(4)	0.941, 0.941	0.936, 0.936				
O(1), O(4)	-0.801, -0.801	-0.800, -0.800	0.887, 0.887	0.882, 0.882	Xe(1)-O(2), Xe(2)-O(3)	0.941, 0.941	0.935, 0.935				
O(2), O(3)	-0.801, -0.801	-0.806, -0.806	0.887, 0.887	0.881, 0.881	Xe(1)-F(1), Xe(2)-F(2)	0.396, 0.396	0.399, 0.399				
F(1), F(2)	-0.519, -0.519	-0.519, -0.519	0.361, 0.361	0.364, 0.364	Xe(1)-F(3), Xe(2)-F(3)	0.147, 0.147	0.147, 0.147				
F(3)	-0.715	-0.713	0.262	0.261							

Table S9. (continued...)**XeO₂(OTeF₅)₂ (MP2/ Stuttgart RLC ECP)**

atom	charge	valency	bond	bond order
Xe	2.908	2.393	Xe-O(1); Xe-O(2)	0.865; 0.865
Te(1); Te(2)	3.551; 3.551	2.744; 2.744	Xe-O(3); Xe-O(4)	0.330; 0.330
O(1); O(2)	-0.862; -0.862	0.808; 0.807	Te(1)-O(3); Te(2)-O(4)	0.529; 0.529
O(3); O(4)	-1.114; -1.114	0.752; 0.752	Te(1)-F(1); Te(2)-F(6)	0.441; 0.441
F(1); F(6)	-0.607; -0.606	0.375; 0.375	Te(1)-F(2); Te(2)-F(7)	0.441; 0.441
F(2); F(7)	-0.607; -0.606	0.375; 0.375	Te(1)-F(3); Te(2)-F(8)	0.439; 0.439
F(3); F(8)	-0.612; -0.612	0.372; 0.372	Te(1)-F(4); Te(2)-F(9)	0.450; 0.450
F(4); F(9)	-0.601; -0.601	0.383; 0.383	Te(1)-F(5); Te(2)-F(10)	0.443; 0.443
F(5); F(10)	-0.603; -0.603	0.378; 0.378		

XeO₂(OTeF₅)⁺ (MP2/ Stuttgart RLC ECP)

atom	charge	valency	bond	bond order
Xe	2.926	2.402	Xe-O(1); Xe-O(2)	0.929; 0.929
Te	3.542	2.681	Xe-O(3)	0.516
O(1); O(2)	-0.777; -0.777	0.886; 0.886	Te-O(3)	0.390
O(3)	-1.053	0.807	Te-F(1)	0.453
F(1)	-0.571	0.378	Te-F(2)	0.453
F(2)	-0.571	0.378	Te-F(3)	0.436
F(3)	-0.601	0.376	Te-F(4)	0.469
F(4)	-0.559	0.396	Te-F(5)	0.460
F(5)	-0.558	0.388		

Table S10. The Basin Volume V , Basin Population N_i , Relative Fluctuation λ and Contribution (%) of Other Basins to Variance $\sigma^2(N_i)$ at HF/DZVP level.

Basin	V	N_i	λ	Relative fluctuations (%) ^a
XeO₂F₂ (C_{2v})				
C(Xe)	9.50	45.24	0.04	41% V ₂ (Xe); 15% V(Xe,O1); 17% V(Xe,O2)
C(O1)	0.28	2.10	0.18	42% V ₁ (O1); 48% V ₂ (O1)
C(O2)	0.25	2.05	0.19	44% V ₁ (O2); 39% V ₂ (O2)
C(F1)	0.20	2.17	0.22	29% V ₁ (F1); 27% V ₂ (F1); 40% V ₃ (F1)
C(F2)	0.20	2.17	0.22	27% V ₁ (F2); 29% V ₂ (F2); 38% V ₃ (F2)
V ₁ (Xe)	3.43	0.16	0.96	26% C(Xe); 13% V(Xe,O1); 13% V(Xe,O2)
V ₂ (Xe)	89.31	3.06	0.53	46% C(Xe)
V ₁ (O1)	69.67	3.16	0.43	12% C(O1); 56% V ₂ (O1); 15% V(Xe,O1)
V ₂ (O1)	72.24	3.44	0.41	13% C(O1); 54% V ₁ (O1); 15% V(Xe,O1)
V ₁ (O2)	70.48	3.25	0.42	12% C(O2); 55% V ₂ (O2); 15% V(Xe,O2)
V ₂ (O2)	71.23	3.34	0.41	13% C(O2); 55% V ₁ (O2); 15% V(Xe,O2)
V ₁ (F1)	36.68	2.15	0.53	12% C(F1); 33% V ₂ (F1); 42% V ₃ (F1)
V ₂ (F1)	38.11	2.32	0.51	11% C(F1); 32% V ₁ (F1); 44% V ₃ (F1)
V ₃ (F1)	44.58	3.11	0.45	14% C(F1); 34% V ₂ (F1); 37% V ₂ (F1)
V ₁ (F2)	36.28	2.12	0.53	12% C(F2); 35% V ₂ (F2); 43% V ₃ (F2)
V ₂ (F2)	38.56	2.37	0.51	12% C(F2); 32% V ₁ (F2); 43% V ₁ (F2)
V ₃ (F2)	44.61	3.09	0.45	13% C(F2); 35% V ₁ (F2); 37% V ₂ (F2)
V(Xe,O1)	15.42	1.30	0.78	28% C(Xe); 20% V ₁ (O1); 21% V ₂ (O1)
V(Xe,O2)	16.15	1.37	0.77	28% C(Xe); 19% V ₁ (O2); 20% V ₂ (O2)
XeO₂F⁺ (C_s)				
C(Xe)	8.48	44.83	0.04	46% V(Xe); 11% V ₁ (O1); 14% V ₂ (O1); 12% V ₁ (O2); 13% V ₂ (O2)
C(O1)	0.25	2.04	0.20	39% V ₁ (O1); 54% V ₂ (O1)
C(O2)	0.25	2.04	0.20	39% V ₁ (O2); 54% V ₂ (O2)
C(F)	0.18	2.15	0.20	30% V ₁ (F); 30% V ₂ (F); 35% V ₃ (F)
V(Xe)	103.41	3.26	0.52	49% C(Xe); 11% V ₁ (O1); 11% V ₁ (O2)
V ₁ (O1)	81.58	3.83	0.44	12% C(Xe); 11% V(Xe); 58% V ₂ (O1)
V ₂ (O1)	84.30	4.23	0.44	13% C(Xe); 12% C(O1); 53% V ₁ (O1)
V ₁ (O2)	81.79	3.86	0.44	12% C(Xe); 11% V(Xe); 57% V ₂ (O2)
V ₂ (O1)	84.00	4.19	0.44	12% C(Xe); 12% C(O1); 53% V ₁ (O2)
V ₁ (F)	37.45	2.37	0.51	11% C(F); 35% V ₂ (F); 38% V ₃ (F)
V ₂ (F)	38.23	2.40	0.50	11% C(F); 35% V ₁ (F); 39% V ₃ (F)
V ₃ (F)	39.98	2.75	0.48	11% C(F); 35% V ₁ (F); 36% V ₂ (F)
IO₂F (C_s)				
C(I)	10.95	45.13	0.04	45% V(I); 11% V ₁ (O1); 12% V ₂ (O1); 12% V ₁ (O2); 10% V ₂ (O2)
C(O1)	0.19	1.92	0.19	38% V ₁ (O1); 58% V ₂ (O1)
C(O2)	0.23	1.99	0.19	48% V ₁ (O2); 50% V ₂ (O2)
C(F)	0.16	2.03	0.23	28% V ₁ (F); 36% V ₂ (F); 36% V ₃ (F)
V(I)	126.36	3.03	0.51	52% C(I); 10% V ₁ (O1); 10% V ₁ (O2)
V ₁ (O1)	89.43	3.78	0.42	10% V(I); 63% V ₂ (O1)
V ₂ (O1)	90.50	4.32	0.42	12% C(I); 12% C(O1); 57% V ₁ (O1)
V ₁ (O2)	89.87	3.94	0.43	11% C(I); 11% C(O2); 61% V ₂ (O2)

Table S10. (continued...)

$V_2(O2)$	87.73	4.06	0.42	11% C(I); 11% C(O2); 60% $V_1(O2)$
$V_1(F)$	39.70	2.29	0.52	11% C(F); 37% $V_2(F)$; 39% $V_3(F)$
$V_2(F)$	42.52	2.68	0.49	12% C(F); 34% $V_1(F)$; 41% $V_3(F)$
$V_3(F)$	41.75	2.81	0.48	12% C(F); 35% $V_1(F)$; 40% $V_2(F)$

TeO₂F⁻ (C_s)

C(Te)	13.82	45.21	0.03	63% V(Te); 10% $V_1(O1)$; 13% $V_2(O1)$; 10% $V_1(O2)$; 13% $V_2(O2)$
C(O1)	0.19	1.94	0.19	41% $V_1(O1)$; 54% $V_2(O1)$
C(O2)	0.19	1.94	0.19	41% $V_1(O2)$; 54% $V_2(O2)$
C(F)	0.19	2.17	0.20	28% $V_1(F)$; 30% $V_2(F)$; 39% $V_3(F)$
V(Te)	166.81	2.99	0.50	57% C(Te)
$V_1(O1)$	94.98	3.77	0.42	68% $V_2(O1)$
$V_2(O1)$	100.32	4.24	0.40	10% C(Te); 12% C(O1); 63% $V_1(O1)$
$V_1(O2)$	95.26	3.79	0.42	67% $V_2(O2)$
$V_2(O2)$	100.22	4.23	0.40	11% C(Te); 12% C(O2); 63% $V_1(O2)$
$V_1(F)$	38.95	2.14	0.53	11% C(F); 36% $V_2(F)$; 45% $V_3(F)$
$V_2(F)$	41.86	2.33	0.52	11% C(F); 34% $V_1(F)$; 46% $V_3(F)$
$V_3(F)$	51.69	3.23	0.43	12% C(F); 37% $V_1(F)$; 40% $V_2(F)$

FO₂XeFXeO₂F⁺ (C_s)

C(Xe1)	8.64	44.89	0.04	48% $V_2(Xe1)$; 13% $V_2(O1)$; 11% $V_1(O3)$; 13% $V_2(O3)$
C(Xe2)	8.68	44.91	0.04	47% $V_2(Xe2)$; 12% $V_2(O2)$; 11% $V_1(O4)$; 13% $V_2(O4)$
C(O1)	0.30	2.13	0.19	47% $V_1(O1)$; 47% $V_2(O1)$
C(O2)	0.18	1.95	0.18	46% $V_1(O2)$; 48% $V_2(O2)$
C(O3)	0.30	2.13	0.19	47% $V_1(O3)$; 47% $V_2(O3)$
C(O4)	0.18	1.95	0.18	46% $V_1(O4)$; 48% $V_2(O4)$
C(F1)	0.18	2.13	0.21	31% $V_1(F1)$; 31% $V_2(F1)$; 36% $V_3(F1)$
C(F2)	0.18	2.15	0.20	47% $V_1(F2)$; 51% $V_2(F2)$
C(F3)	0.18	2.12	0.21	31% $V_1(F3)$; 31% $V_2(F3)$; 36% $V_3(F3)$
$V_1(Xe1)$	3.97	0.17	0.95	25% C(Xe1); 25% $V_2(O1)$; 12% $V_1(O3)$; 25% $V_2(O3)$
$V_2(Xe1)$	87.60	3.30	0.53	49% C(Xe1)
$V_1(Xe2)$	4.16	0.20	0.95	32% C(Xe2); 21% $V_2(O2)$; 11% $V_1(O2)$; 21% $V_2(O4)$
$V_2(Xe2)$	88.11	3.28	0.53	48% C(Xe2)
$V_1(O1)$	72.48	3.66	0.43	10% C(Xe1); 12% C(O1); 10% $V_2(Xe1)$; 60% $V_2(O1)$
$V_2(O1)$	78.92	4.16	0.43	13% C(Xe1); 11% C(O1); 53% $V_1(O1)$
$V_1(O2)$	73.10	3.74	0.43	10% C(O2); 10% $V_2(Xe2)$; 61% $V_2(O2)$
$V_2(O2)$	78.87	4.24	0.42	12% C(Xe2); 10% C(O2); 55% $V_1(O2)$
$V_1(O3)$	72.82	3.77	0.44	12% C(Xe1); 10% $V_2(Xe1)$; 11% C(O3); 57% $V_2(O3)$
$V_2(O3)$	79.06	4.15	0.43	13% C(Xe1); 11% C(O3); 53% $V_1(O3)$
$V_1(O4)$	73.03	3.81	0.44	12% C(Xe2); 10% C(O4); 10% $V_2(Xe2)$; 59% $V_2(O4)$
$V_2(O4)$	79.57	4.29	0.42	13% C(Xe2); 55% $V_1(O4)$
$V_1(F1)$	36.74	2.27	0.53	12% C(F1); 35% $V_2(F1)$; 40% $V_3(F1)$
$V_2(F1)$	37.66	2.42	0.51	11% C(F1); 34% $V_1(F1)$; 40% $V_3(F1)$
$V_3(F1)$	41.17	2.91	0.47	12% C(F1); 35% $V_1(F1)$; 36% $V_2(F1)$
$V_1(F2)$	44.42	3.65	0.41	13% C(F2); 69% $V_2(F2)$
$V_2(F2)$	47.75	3.95	0.38	15% C(F2); 69% $V_1(F2)$

Table S10. (continued...)

$V_1(F3)$	36.78	2.28	0.52	12% $C(F3)$; 35% $V_2(F3)$; 40% $V_3(F3)$
$V_2(F3)$	37.64	2.43	0.50	12% $C(F3)$; 35% $V_1(F3)$; 41% $V_3(F3)$
$V_3(F3)$	36.78	2.92	0.48	11% $C(F3)$; 34% $V_1(F3)$; 36% $V_2(F3)$

FO₂XeFxO₂F⁺ (C_1)

C(Xe1)	8.51	44.83	0.04	49% $V_2(Xe1)$; 13% $V_2(O1)$; 17% $V_2(O2)$
C(Xe2)	8.68	44.91	0.04	47% $V_2(Xe2)$; 11% $V_1(O3)$; 16% $V_2(O4)$
C(O1)	0.30	2.12	0.19	47% $V_1(O1)$; 47% $V_2(O1)$
C(O2)	0.28	2.08	0.20	50% $V_1(O2)$; 46% $V_2(O2)$
C(O3)	0.28	2.07	0.19	46% $V_1(O3)$; 53% $V_2(O3)$
C(O4)	0.28	2.07	0.20	46% $V_1(O4)$; 48% $V_2(O4)$
C(F1)	0.19	2.18	0.19	24% $V_1(F1)$; 29% $V_2(F1)$; 34% $V_3(F1)$
C(F2)	0.14	1.94	0.24	28% $V_1(F2)$; 32% $V_2(F2)$; 37% $V_3(F2)$
C(F3)	0.19	2.12	0.22	94% $V(F3)$
$V_1(Xe1)$	4.51	0.21	0.95	25% $C(Xe1)$; 10% $V_1(O1)$; 25% $V_2(O1)$; 10% $V_1(O2)$; 25% $V_2(O2)$
$V_2(Xe1)$	88.14	3.33	0.53	49% $C(Xe1)$
$V_1(Xe2)$	1.05	0.07	0.98	29% $C(Xe2)$; 29% $V_1(O3)$; 15% $V_2(O3)$; 15% $V_1(O4)$; 29% $V_2(O4)$
$V_2(Xe2)$	87.75	3.28	0.53	49% $C(Xe2)$
$V_1(O1)$	74.03	3.69	0.44	12% $C(Xe1)$; 12% $C(O1)$; 59% $V_2(O1)$
$V_2(O1)$	77.17	4.15	0.43	13% $C(Xe1)$; 11% $C(O1)$; 54% $V_1(O1)$
$V_1(O2)$	76.07	3.97	0.42	13% $C(O2)$; 58% $V_2(O2)$
$V_2(O2)$	78.79	4.04	0.47	16% $C(Xe1)$; 10% $C(O2)$; 51% $V_1(O2)$
$V_1(O3)$	79.79	3.91	0.44	12% $C(Xe2)$; 10% $C(O3)$; 56% $V_2(O3)$
$V_2(O3)$	75.12	3.96	0.42	10% $C(Xe2)$; 13% $C(O3)$; 58% $V_1(O3)$; 10% $V_2(Xe2)$
$V_1(O4)$	74.00	3.72	0.44	10% $C(Xe2)$; 12% $C(O4)$; 59% $V_2(O4)$
$V_2(O4)$	80.31	4.31	0.43	15% $C(Xe2)$; 11% $C(O4)$; 52% $V_1(O4)$
$V_1(F1)$	37.06	2.36	0.50	11% $C(F1)$; 36% $V_2(F1)$; 40% $V_3(F1)$
$V_2(F1)$	37.57	2.38	0.50	10% $C(F1)$; 36% $V_1(F1)$; 40% $V_3(F1)$
$V_3(F1)$	41.18	2.79	0.48	10% $C(F1)$; 36% $V_1(F1)$; 31% $V_2(F1)$
$V_1(F2)$	37.22	2.38	0.51	11% $C(F2)$; 35% $V_2(F2)$; 40% $V_3(F2)$
$V_2(F2)$	37.71	2.53	0.51	12% $C(F2)$; 33% $V_1(F2)$; 40% $V_3(F2)$
$V_3(F2)$	41.25	2.91	0.49	12% $C(F2)$; 36% $V_1(F2)$; 34% $V_2(F2)$
$V(F3)$	89.70	7.62	0.49	44% $C(F3)$; 11% $V_2(Xe1)$; 11% $V_2(Xe1)$

XeO₂(OTeF₅)⁺ (C_1)

C(Xe)	8.26	44.73	0.04	47% $V_2(Xe)$; 12% $V(Xe,O1)$; 11% $V(Xe,O2)$
C(Te)	18.25	45.76	0.03	10% $V_2(F3)$
C(O1)	0.30	2.09	0.20	45% $V_1(O1)$; 48% $V_2(O1)$
C(O2)	0.30	2.09	0.20	45% $V_1(O2)$; 48% $V_2(O2)$
C(O3)	0.27	2.03	0.22	13% $V_1(O3)$; 36% $V_2(O3)$; 43% $V_3(O3)$
C(F1)	0.16	1.99	0.25	34% $V_1(F1)$; 62% $V_2(F1)$
C(F2)	0.16	1.98	0.26	39% $V_1(F2)$; 58% $V_2(F2)$
C(F3)	0.16	2.00	0.25	38% $V_1(F3)$; 58% $V_2(F3)$
C(F4)	0.14	1.89	0.26	43% $V_1(F4)$; 55% $V_2(F4)$
C(F5)	0.11	1.78	0.27	42% $V_1(F5)$; 56% $V_2(F5)$
$V_1(Xe)$	5.02	0.27	0.95	31% $C(Xe)$; 12% $V_1(O1)$; 12% $V_1(O2)$
$V_2(Xe)$	102.82	3.31	0.52	49% $C(Xe)$
$V_1(O1)$	66.31	3.41	0.43	13% $C(O1)$; 55% $V_2(O1)$; 10% $V(Xe,O1)$

Table S10. (continued...)

$V_2(O1)$	79.03	3.63	0.43	13%C(O1); 10%V ₂ (Xe); 51%V ₁ (O1)
$V_1(O2)$	66.20	3.42	0.43	13%C(O2); 10%C(F5); 54%V ₂ (O2)
$V_2(O2)$	79.19	3.63	0.43	13%C(O2); 10%V ₂ (Xe); 51%V ₁ (O2)
$V_1(O3)$	10.42	1.21	0.70	31%V ₂ (O3); 33%V ₃ (O3)
$V_2(O3)$	45.74	2.84	0.49	11%C(O3); 37%V ₃ (O3); 19%V ₁ (O3)
$V_3(O3)$	48.82	3.20	0.46	13%C(O3); 35%V ₂ (O3); 19%V ₃ (O3)
$V_1(F1)$	46.66	3.14	0.46	12%C(F1); 73%V ₂ (F1)
$V_2(F1)$	57.05	4.88	0.35	18%C(F1); 62%V ₁ (F1)
$V_1(F2)$	57.24	3.52	0.44	13%C(F2); 71%V ₂ (F2)
$V_2(F2)$	61.29	4.49	0.37	18%C(F2); 66%V ₁ (F2)
$V_1(F3)$	53.76	3.37	0.45	13%C(F3); 71%V ₂ (F3)
$V_2(F3)$	61.21	4.68	0.36	17%C(F3); 63%V ₁ (F3)
$V_1(F4)$	55.48	3.85	0.43	13%C(F4); 69%V ₂ (F4)
$V_2(F4)$	59.62	4.36	0.39	16%C(F4); 68%V ₁ (F4)
$V_1(F5)$	55.57	3.87	0.43	12%C(F5); 70%V ₂ (F5)
$V_2(F5)$	59.53	4.45	0.39	16%C(F5); 67%V ₁ (F5)
$V(Xe,O1)$	10.85	0.85	0.83	30%C(Xe); 21%V ₁ (O1); 20%V ₂ (O1)
$V(Xe,O2)$	10.18	0.84	0.83	29%C(Xe); 22%V ₁ (O2); 20%V ₂ (O2)
$V(Xe,O3)$	3.24	0.43	0.88	18%C(Xe); 24%V ₂ (O3); 26%V ₃ (O3)

XeO₂(OTeF₅)₂ (C_1)

$C(Xe)$	8.59	44.83	0.04	51%V ₂ (Xe); 14%V(Xe,O1); 15%V(Xe,O2)
$C(Te1)$	18.47	45.80	0.03	10%V ₂ (F6); 15%V ₁ (Asyn)
$C(Te2)$	18.04	45.72	0.03	20%V ₂ (Asyn)
$C(O1)$	0.27	2.06	0.20	39%V ₁ (O1); 53%V ₂ (O1)
$C(O2)$	0.27	2.06	0.20	41%V ₁ (O2); 49%V ₂ (O2)
$C(O3)$	0.24	1.98	0.22	37%V ₁ (O3); 41%V ₂ (O3)
$C(O4)$	0.24	1.98	0.22	37%V ₁ (O4); 41%V ₂ (O4)
$C(F1)$	0.16	1.97	0.26	20%V ₁ (F1); 25%V ₂ (F1); 31%V ₃ (F1); 23%V ₁ (Asyn)
$C(F2)$	0.16	1.97	0.26	20%V ₁ (F2); 33%V ₂ (F2); 31%V ₃ (F2); 16%V ₂ (Asyn)
$C(F3)$	0.16	1.98	0.25	30%V ₁ (F3); 53%V ₂ (F3); 16%V ₂ (Asyn)
$C(F4)$	0.16	1.94	0.27	29%V ₁ (F4); 32%V ₂ (F4); 38%V ₂ (Asyn)
$C(F5)$	0.14	1.89	0.26	45%V ₁ (F5); 39%V ₂ (F5); 12%V ₁ (Asyn)
$C(F6)$	0.19	2.01	0.28	25%V ₁ (F6); 73%V ₂ (F6)
$C(F7)$	0.14	1.89	0.26	39%V ₁ (F7); 45%V(Te2,F7); 14%V ₂ (Asyn)
$C(F8)$	0.14	1.90	0.26	28%V ₁ (F8); 14%V ₁ (Asyn)
$C(F9)$	0.14	1.89	0.22	45%V ₁ (F9); 39%V ₂ (F9); 12%V ₁ (Asyn)
$C(F10)$	0.14	1.89	0.26	45%V ₁ (F10); 39%V ₂ (F10); 12%V ₂ (Asyn)
$V_1(Xe)$	4.70	0.30	0.94	39%C(Xe); 14%V(Xe,O1); 14%V(Xe,O2)
$V_2(Xe)$	84.02	3.37	0.54	50%C(Xe)
$V_1(O1)$	54.22	2.78	0.45	13%C(O1); 57%V ₂ (O1); 14%V(Xe,O1)
$V_2(O1)$	65.56	3.69	0.39	15%C(O1); 49%V ₁ (O1); 16%V(Xe,O1)
$V_1(O2)$	62.05	3.21	0.42	13%C(O2); 56%V ₂ (O2); 16%V(Xe,O2)
$V_2(O2)$	57.64	3.26	0.42	15%C(O2); 55%V ₁ (O2); 15%V(Xe,O2)
$V_1(O3)$	50.03	3.12	0.48	11%C(O3); 10%V(Xe,O3); 39%V ₂ (O3); 10%V(Te1,O3)
$V_2(O3)$	52.54	3.47	0.46	11%C(O3); 11%V(Xe,O3); 37%V ₁ (O3); 10%V(Te1,O3)
$V_1(O4)$	50.25	3.13	0.49	10%C(O4); 10%V(Xe,O4); 38%V ₂ (O4)
$V_2(O4)$	52.62	3.48	0.46	11%C(O4); 11%V(Xe,O4); 37%V ₁ (O4); 10%V(Te2,O4)

Table S10. (Continued.)

$V_1(F1)$	26.24	1.26	0.79	10%C(F1); 17%V ₂ (F1); 24%V ₃ (F1); 41%V ₁ (Asyn)
$V_2(F1)$	32.48	1.70	0.69	11%C(F1); 14%V ₁ (F1); 26%V ₃ (F1); 40%V ₁ (Asyn)
$V_3(F1)$	28.97	2.56	0.54	12%C(F1); 17%V ₁ (F1); 22%V ₂ (F1); 38%V ₁ (Asyn)
$V_1(F2)$	27.54	1.32	0.77	10%C(F2); 22%V ₂ (F2); 24%V ₃ (F2); 36%V ₂ (Asyn)
$V_2(F2)$	30.64	2.00	0.68	12%C(F2); 16%V ₁ (F2); 24%V ₃ (F2); 37%V ₂ (Asyn)
$V_3(F2)$	28.38	2.51	0.55	12%C(F2); 17%V ₁ (F2); 24%V ₂ (F2); 35%V ₂ (Asyn)
$V_1(F3)$	48.20	2.47	0.55	11%C(F3); 35%V ₂ (F3); 43%V ₂ (Asyn)
$V_2(F3)$	51.27	3.22	0.53	15%C(F3); 28%V ₁ (F3); 45%V ₂ (Asyn)
$V_1(F4)$	27.19	1.65	0.76	12%C(F4); 37%V ₂ (F4); 42%V ₂ (Asyn)
$V_2(F4)$	51.79	3.15	0.49	11%C(F4); 30%V ₁ (F4); 49%V ₂ (Asyn)
$V_1(F5)$	49.41	3.02	0.53	14%C(F5); 37%V ₂ (F5); 39%V ₁ (Asyn)
$V_2(F5)$	46.36	3.10	0.53	12%C(F5); 36%V ₁ (F5); 39%V ₁ (Asyn)
$V_1(F6)$	41.07	1.80	0.64	12%C(F6); 80%V ₂ (F6)
$V_2(F6)$	74.82	6.13	0.28	24%C(F6); 54%V ₁ (F6)
$V_1(F7)$	46.41	2.93	0.55	12%C(F7); 35%V ₂ (F7); 40%V ₂ (Asyn)
$V_2(F7)$	49.65	3.10	0.53	13%C(F7); 35%V ₁ (F7); 40%V ₂ (Asyn)
$V_1(F8)$	48.52	2.48	0.55	10%C(F8); 37%V ₂ (F8); 40%V ₁ (Asyn)
$V_2(F8)$	53.62	3.44	0.53	15%C(F8); 28%V ₁ (F8); 42%V ₁ (Asyn)
$V_1(F9)$	46.25	3.06	0.53	14%C(F9); 36%V ₂ (F9); 39%V ₁ (Asyn)
$V_2(F9)$	49.25	3.06	0.53	12%C(F9); 36%V ₁ (F9); 39%V ₁ (Asyn)
$V_1(F10)$	49.11	3.06	0.53	14%C(F10); 37%V ₂ (F10); 38%V ₂ (Asyn)
$V_2(F10)$	47.09	3.12	0.53	11%C(F10); 36%V ₁ (F10); 39%V ₂ (Asyn)
$V(Xe,O1)$	15.66	1.35	0.76	25%C(Xe); 11%V ₂ (Xe); 17%V ₁ (O1)
$V(Xe,O2)$	15.69	1.37	0.75	26%C(Xe); 10%V ₂ (Xe); 20%V ₁ (O2); 19%V ₂ (O2)
$V(Xe,O3)$	5.00	0.70	0.83	10%C(Xe); 26%V ₁ (O3); 29%V ₂ (O3)
$V(Xe,O4)$	5.00	0.70	0.83	10%C(Xe); 26%V ₁ (O4); 29%V ₂ (O4)
$V(Te1,O3)$	4.00	0.53	0.87	33%V ₁ (O3); 35%V ₂ (O3)
$V(Te2,O4)$	3.75	0.52	0.87	31%V ₁ (O4); 35%V ₂ (O4)
$V_1(\text{Asyn})$	74.41	8.96	0.67	10%C(F7); 10%V ₁ (F5); 11%V ₂ (F5); 13%V ₂ (F8); 11%V ₂ (F9)
$V_2(\text{Asyn})$	114.26	12.10	0.63	10%V ₂ (F4); 10%V ₂ (F3)

^a Contributions less than 10% are not listed.