

## **SUPPORTING INFORMATION**

**XeOF<sub>2</sub>, F<sub>2</sub>OXeN≡CCH<sub>3</sub>, and XeOF<sub>2</sub>·nHF;**

**Rare Examples of Xe(IV) Oxide Fluorides**

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**Table S1.** Experimental Raman frequencies for  $\text{XeOF}_2$ ,  $\text{F}_2\text{OXeN}\equiv\text{CCH}_3$ ,  $\text{F}_2\text{OXeN}\equiv\text{CCH}_3/\text{CH}_3\text{CN}/\text{CH}_3\text{CN}\cdot m\text{HF}$  mixtures and  $\text{XeOF}_2/\text{F}_2\text{OXeN}\equiv\text{CCH}_3$  mixtures <sup>a</sup>

$\text{F}_2\text{OXeN}\equiv\text{CCH}_3$ $\text{CH}_3\text{CN}\cdot m\text{HF}$ $\text{CH}_3\text{CN}$	$\text{F}_2\text{OXeN}\equiv\text{CCH}_3$	$\text{F}_2\text{OXeN}\equiv\text{CCH}_3$ $\text{XeOF}_2$	$\text{XeOF}_2$	assgnts <sup>b</sup>
3018.1(3)				$\nu_{\text{as}}(\text{CH}_3)$
2949.0(9)				$\nu_{\text{s}}(\text{CH}_3)$
2309.6(2)				$\nu(\text{CN})$
2282.1(6)				$\text{CH}_3$ def. as
1451.9(2)				$\text{CH}_3$ def. s
1361.7(3)				$\nu(\text{CC})$
932.5(2)				$\nu(\text{CN})$
2247.4(2)				$\text{CH}_3$ def. as
1457.0sh				$\text{CH}_3$ def. s
1375.8(1)				
3009.1(8)	3009.0(7)	3008.9(7)		$\nu_{\text{as}}(\text{CH}_3)$
2998.8(8)	2999.3(7)	2999.1(7)		
2937.5(44)	2937.6(40)	2937.7(43)		
2726.2(1)	2726.2(2)	2726.1(1)		$\nu_{\text{s}}(\text{CH}_3)$
2297.1(2)	2297.1(2)	2296.6(2)		$\nu(\text{CN})$
2286.1(5)	2286.9(5)	2286.9(6)		
2254.3(39)	2254.2(39)	2254.2(42)		$\nu(\text{CN})$
1438.0(1)	1438.8(2)	1438.3(1)		
1407.3(1)	1409.4(2)	1407.0(1)		$\text{CH}_3$ def. as
1370.6(5)	1370.3(5)	1370.3(5)		
1356.9(6)	1356.9(5)	1357.0(5)		$\text{CH}_3$ def. s
1034.6(2)	1034.4(2)	1034.1(1)		$\rho_{\text{rock}}(\text{CH}_3)$
926.6sh	926.6(sh)	926.2(sh)		
923.9(8)	923.7(8)	923.7(8)		$\nu(\text{CC})$
767.0(4)	767.0(4)	767.0(5)		
762.3(46)	762.3(45)	762.3(47)		$\nu(\text{XeO})$
754.4(41)	754.4(41)	754.5(45)		
525.2(2)	525.2(3)	525.3(2)		$\nu_{\text{as}}(\text{XeF}_2)$
498.8(12)	498.8(12)	498.8(12)		
494.5(21)	494.6(20)	494.5(20)		
487.6(100)	487.6(100)	487.8(100)		$\nu_{\text{s}}(\text{XeF}_2)$
481.8(44)	481.8(49)	481.8(52)		
397.4(5)	397.4(4)	397.4(4)		
392.8(3)	392.8(3)	392.6(2)		$\delta(\text{CCN})$
390.2(4)	390.2(4)	390.0(4)		

**Table S1.** (continued ...)

283.0(11)	283.0(11)	283.1(11)	$\rho_{\text{rock}}(\text{XeOF}_2)$ ip	F <sub>2</sub> O $\text{XeN}\equiv\text{CCH}_3$
277.2(8)	277.2(9)	277.4(8)	$\nu(\text{XeN}) + \delta(\text{XeF}_2)$ ip	
164.7(5)	164.7(4)	164(4)	$\nu(\text{XeN}) - \delta(\text{XeF}_2)$ ip	
148.9(9)	148.9(7)	148.6(8)	$\nu(\text{XeN}) - \delta(\text{XeF}_2)$ ip	
133.8(9)	133.8(7)	133.8(6)	$\nu(\text{XeN}) - \delta(\text{XeF}_2)$ ip	
	116.4(3)		lattice modes	
71.5(6)	71.5(5)			
		750.2(42)	$\nu(\text{XeO})$	XeOF <sub>2</sub>
		468.0(57)	$\nu_s(\text{XeF}_2)$	
		297.8(8)	$\rho_{\text{rock}}(\text{XeOF}_2)$ ip	
			$\delta(\text{XeF}_2)$ oop	
		253.2(1)	$\delta(\text{XeF}_2)$ oop	
		174.6(1)	$\delta(\text{XeF}_2)$ ip	
			$\delta(\text{XeF}_2)$ ip	
		108.1(15)	lattice modes	

<sup>a</sup> Frequencies are given in cm<sup>-1</sup>. The abbreviation denotes broad (br) and shoulder (sh). <sup>b</sup> The original sample was a mixture consisting of F<sub>2</sub>O $\text{XeN}\equiv\text{CCH}_3$ , CH<sub>3</sub>CN and CH<sub>3</sub>CN·mHF (column 1). Slow removal of uncoordinated CH<sub>3</sub>CN and CH<sub>3</sub>CN·mHF under dynamic vacuum gave F<sub>2</sub>O $\text{XeN}\equiv\text{CCH}_3$  (column 2). Gradual pumping of F<sub>2</sub>O $\text{XeN}\equiv\text{CCH}_3$  first gave a mixture of F<sub>2</sub>O $\text{XeN}\equiv\text{CCH}_3$  and XeOF<sub>2</sub> (column 3) while prolonged pumping resulted in unsolvated XeOF<sub>2</sub> (column 4). <sup>b</sup> The abbreviations denote symmetric (s), asymmetric (as), stretch (ν), bend (δ), rock ( $\rho_{\text{rock}}$ ), in-plane bend (ip), and out-of-plane bend (oop). The in-plane and out-of-plane mode descriptions are relative to the XeOF<sub>2</sub> plane.

**Table S2.** Experimental and Calculated ( $C_{3v}$ ) Vibrational Frequencies for  $\text{CH}_3\text{C}\equiv\text{N}$ 

expt <sup>b,c</sup>	calc		assgnts ( $C_{3v}$ ) symmetry
	SVWN <sup>d,e</sup>	MP2 <sup>d,f</sup>	
2999.0(54)	3062(65)[<1]	3193.6(55)[<1]	$\nu_5(\text{E})$ , $\nu_{\text{as}}(\text{CH}_3)$
2937.9(97)	2981(186)[<1]	3100.1(159)[2]	$\nu_1(\text{A}_1)$ , $\nu_{\text{s}}(\text{CH}_3)$
2911.7(1)			
2885.7(2)			$2\nu_6$
2849.8(1)			
2736.3(6)			$2\nu_3$
2295.1(2)			$\nu_3 + \nu_4$
2248.4(100)	2332(71)[14]	2218.0(38)[~0]	$\nu_2(\text{A}_1)$ , $\nu(\text{CN})$
1457.3(11)			
1454.3(7)	1391(8)[14]	1495.8(7)[10]	$\nu_6(\text{E})$ , $\text{CH}_3$ def. as
1425.2(3)			
1420.8(4)			
1375.6(15)	1335(9)[10]	1417.8(4)[2]	$\nu_3(\text{A}_1)$ , $\text{CH}_3$ def. s
1370.8(3)			
1042.3(1)	999(<<1)[5]	1065.8(<<1)[2]	$\nu_7(\text{E})$ , $\rho_{\text{r}}(\text{CH}_3)$
921.5(20)	959(4)[<1]	934.7(5)[1]	$\nu_4(\text{A}_1)$ , $\nu(\text{CC})$
399.9(3)			
395.0(12)	377(2)[<<1]	361.0(2)[<1]	$\nu_8(\text{E})$ , $\delta(\text{CCN})$
392.0(9)			
386.8(5)			
116.4(18)			
107.6(13)			
102.3(15)			
95.5(32)			lattice modes

<sup>a</sup> Frequencies are given in  $\text{cm}^{-1}$ . <sup>b</sup> Present work. <sup>c</sup> The Raman spectrum of  $\text{CH}_3\text{CN}$  was recorded in a 5-mm glass tube at  $-150$   $^{\circ}\text{C}$  using 1064-nm excitation. Values in parentheses denote Raman intensities. <sup>d</sup> SDB-cc-pVTZ. Values in parentheses denote Raman intensities ( $\text{\AA}^4 \text{ amu}^{-1}$ ). Values in square brackets denote infrared intensities ( $\text{km mol}^{-1}$ ). <sup>e</sup> Calculated bond lengths ( $\text{\AA}$ ): N–C, 1.155; C–C, 1.433. <sup>f</sup> Calculated bond lengths ( $\text{\AA}$ ): N–C, 1.169; C–C, 1.457.

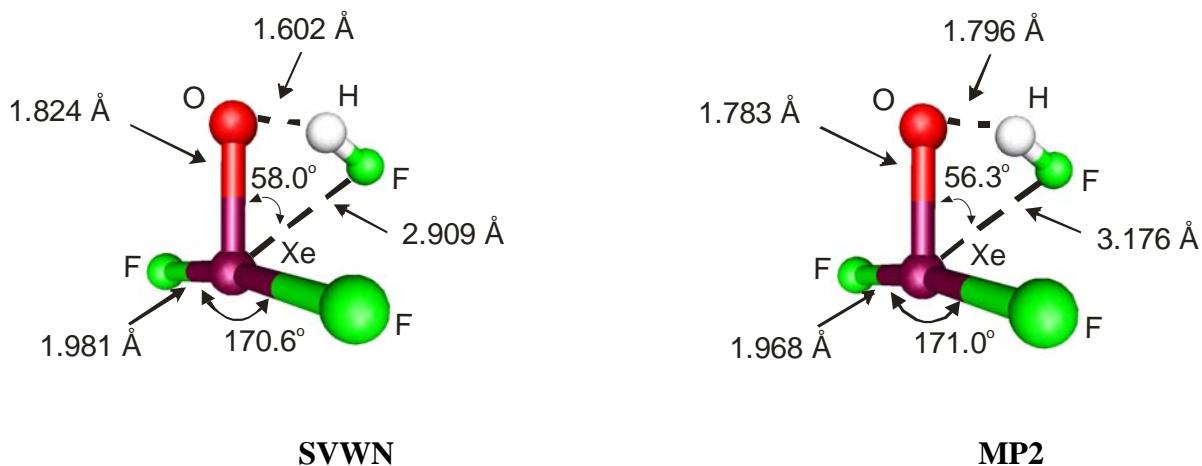
**Table S3.** Experimental Vibrational Frequencies<sup>a</sup> for CH<sub>3</sub>CN·*m*HF

expt <sup>b,c</sup>	assgnts <sup>d</sup>
3016.9(40)	$\nu_{\text{as}}(\text{CH}_3)$
2950.2(80)	$\nu_{\text{s}}(\text{CH}_3)$
2724.8(3)	overtone (2 x 1367.5)
2313.2(48)	combination mode (1367.5 + 935.9)
2286.0(100)	$\nu(\text{CN})$
1449.6(14)	
1414.3(31)	CH <sub>3</sub> def. as
1367.5(68)	CH <sub>3</sub> def. s
935.9(40)	$\nu(\text{CC})$
392.4(57)	$\delta(\text{CCN})$
131.3(22)	
113.2(17)	lattice modes
70.8(14)	
59.9(17)	

<sup>a</sup> Frequencies are given in cm<sup>-1</sup>. <sup>b</sup> Present work. The sample was prepared from a 2:1 molar ratio of HF and CH<sub>3</sub>CN. <sup>c</sup> The Raman spectrum of CH<sub>3</sub>CN·*m*HF was recorded in a ¼ -in FEP tube at −150 °C using 1064-nm excitation. Values in parentheses denote Raman intensities. <sup>d</sup> Because the structure of CH<sub>3</sub>CN·*m*HF is unknown, the vibrational mode descriptions are based on those of CH<sub>3</sub>CN and do not take into account possible coupling with associated HF. The modes corresponding to associated HF were not observed.

**Table S4.** Calculated Vibrational Frequencies<sup>a</sup> and Geometries for Xe<sup>16/18</sup>OF<sub>2</sub>·HF (O---H Coordinated)

calc <sup>b</sup>				assgnts	
SVWN <sup>c</sup>		MP2 <sup>d</sup>		$(C_1)$ symmetry	
Xe <sup>16</sup> OF <sub>2</sub> ·HF	Xe <sup>18</sup> OF <sub>2</sub> ·HF	Xe <sup>16</sup> OF <sub>2</sub> ·HF	Xe <sup>18</sup> OF <sub>2</sub> ·HF	$v_1$	$v(HF) + \text{minor } v(O\text{---H---F})$
3268.8(92)[644]	3260.8(92)[650]	3826.4(51)[468]	3831.0(51)[468]	$v_2$	$\delta(O\text{---H---F})$
962.6(5)[367]	968.5(5)[366]	738.1(6)[318]	733.7(6)[326]	$v_3$	$v(XeO)$
762.6(16)[26]	724.4(14)[25]	897.1(8)[49]	852.7(9)[39]	$v_4$	HF oop wag
747.3(<1)[101]	750.0(<1)[100]	623.8(1)[270]	620.8(1)[289]	$v_5$	$v_{as}(XeF_2) + \text{minor HF oop wag}$
584.3(<1)[179]	585.9(<1)[180]	584.3(<1)[67]	584.0(<1)[49]	$v_6$	$v_s(XeF_2)$
518.6(25)[8]	518.6(25)[8]	521.3(36)[10]	521.3(36)[10]	$v_7$	$\delta(F_HXeO)$
347.6(2)[46]	336.6(1)[41]	286.9(4)[1]	276.1(4)[<1]	$v_8$	$\rho_{rock}(XeOF_2) \text{ ip} + \text{minor HF oop wag}$
248.8(4)[1]	239.5(4)[1]	245.8(1)[62]	239.4(1)[59]	$v_9$	$\delta(XeF_2) \text{ oop}$
204.2(<<1)[21]	204.8(<<1)[21]	214.0(<1)[6]	213.5(<1)[4]	$v_{10}$	$\delta(XeF_2) \text{ ip}$
162.9(<1)[20]	162.7(<1)[20]	182.8(<1)[29]	182.7(<1)[29]	$v_{11}$	$\rho_{rock}(XeOF_2) \text{ oop} + v(HF\text{---Xe})$
119.7(<1)[9]	118.9(<1)[9]	85.6(<1)[11]	84.4(<1)[11]	$v_{12}$	XeF <sub>2</sub> torsion about XeO bond
43.9(2)[<1]	44.3(2)[1]	41.1(<1)[<<1]	40.6(1)[<1]		



<sup>a</sup> Frequencies are given in cm<sup>-1</sup>. <sup>b</sup> Values in parentheses denote Raman intensities (Å<sup>4</sup> amu<sup>-1</sup>). Values in square brackets denote infrared intensities (km mol<sup>-1</sup>). <sup>c</sup> SVWN/SDB-cc-pVTZ. <sup>d</sup> MP2/SDB-cc-pVTZ.

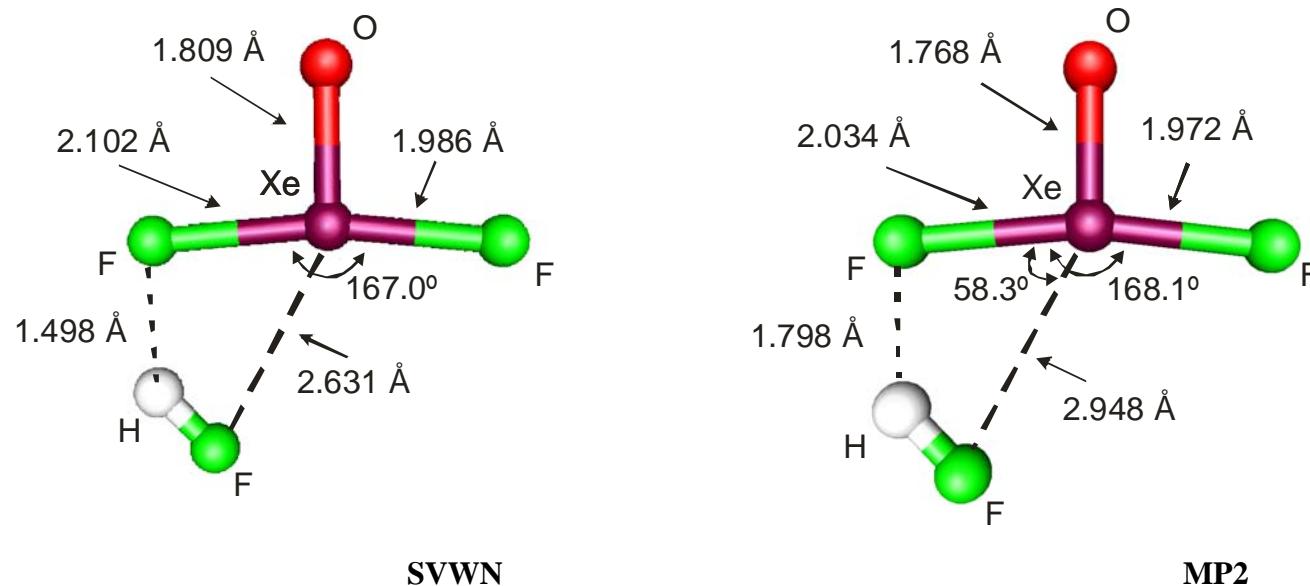
**Table S5.** Calculated Vibrational Frequencies<sup>a</sup> for Xe<sup>16/18</sup>OF<sub>2</sub>·DF (O---D Coordinated)

calc <sup>b</sup>				assgnts (C <sub>1</sub> ) symmetry	
SVWN <sup>c</sup>		MP2 <sup>d</sup>			
Xe <sup>16</sup> OF <sub>2</sub> ·DF	Xe <sup>18</sup> OF <sub>2</sub> ·DF	Xe <sup>16</sup> OF <sub>2</sub> ·DF	Xe <sup>18</sup> OF <sub>2</sub> ·DF	v <sub>1</sub>	v(DF) + minor v(O---D-F)
2368.4(48)[338]	2368.3(48)[338]	2776.0(27)[243]	2780.2(27)[243]	v <sub>3</sub>	v(XeO)
763.2(15)[36]	724.6(14)[37]	897.6(9)[62]	851.7(9)[56]	v <sub>2</sub>	$\delta$ (O---D-F)
694.2(3)[160]	693.6(3)[159]	540.0(11)[88]	537.0(14)[78]	v <sub>5</sub>	v <sub>as</sub> (XeF <sub>2</sub> ) + minor DF oop wag
591.9(<<1)[243]	591.6(<<1)[242]	598.1(<1)[264]	598.0(<1)[263]	v <sub>4</sub>	DF oop wag
537.1(<<1)[5]	536.0(<<1)[6]	443.3(<1)[33]	438.3(<1)[34]	v <sub>6</sub>	v <sub>s</sub> (XeF <sub>2</sub> )
518.4(25)[9]	518.3(25)[10]	516.7(27)[56]	515.2(25)[70]	v <sub>7</sub>	$\delta$ (F <sub>D</sub> XeO)
342.1(2)[51]	330.5(2)[45]	240.6(1)[67]	235.0(1)[62]	v <sub>8</sub>	$\rho_{\text{rock}}$ (XeOF <sub>2</sub> ) + minor DF oop wag
246.7(4)[<1]	237.8(4)[<<1]	283.8(4)[<1]	273.5(4)[<1]	v <sub>9</sub>	$\delta$ (XeF <sub>2</sub> ) oop
204.7(~0)[20]	204.7(~0)[20]	213.5(<1)[4]	212.1(<1)[2]	v <sub>10</sub>	$\delta$ (XeF <sub>2</sub> ) ip
163.0(<1)[21]	162.7(<1)[20]	182.8(<1)[31]	182.5(<1)[31]	v <sub>11</sub>	$\rho_{\text{rock}}$ (XeOF <sub>2</sub> ) oop + v(DF---Xe)
119.4(<<1)[8]	118.6(<1)[8]	85.5(<1)[10]	84.1(<1)[11]	v <sub>12</sub>	XeF <sub>2</sub> torsion about XeO bond
44.3(2)[<<1]	44.2(2)[<1]	41.0(1)[<1]	40.4(1)[<1]		

<sup>a</sup> Frequencies are given in cm<sup>-1</sup>. <sup>b</sup> Values in parentheses denote Raman intensities (Å<sup>4</sup> amu<sup>-1</sup>). Values in square brackets denote infrared intensities (km mol<sup>-1</sup>). <sup>c</sup> SVWN/SDB-cc-pVTZ. <sup>d</sup> MP2/SDB-cc-pVTZ.

**Table S6.** Calculated Vibrational Frequencies<sup>a</sup> and Geometries for Xe<sup>16/18</sup>OF<sub>2</sub>·HF (F---H Coordinated)

SVWN <sup>c</sup>	calc <sup>b</sup>				assgnts (C <sub>1</sub> ) symmetry
	Xe <sup>16</sup> OF <sub>2</sub> ·HF	Xe <sup>18</sup> OF <sub>2</sub> ·HF	MP2 <sup>d</sup>	Xe <sup>18</sup> OF <sub>2</sub> ·HF	
3121.8(68)[414]	3124.7(68)[413]	3894.1(27)[246]	3894.1(27)[246]	v(HF)	
1007.8(9)[404]	1006.6(9)[404]	664.6(5)[258]	664.8(5)[257]	$\delta(F\cdots H\cdots F)$	
802.1(30)[36]	762.6(27)[35]	954.7(11)[57]	907.5(10)[51]	v(XeO)	
781.8(1)[101]	780.5(1)[101]	575.5(1)[133]	575.5(8)[132]	HF oop wag	
549.2(6)[178]	550.1(6)[180]	550.5(8)[330]	551.5(8)[334]	v <sub>as</sub> (XeF <sub>2</sub> )	
477.7(18)[12]	477.6(18)[11]	477.9(32)[52]	478.0(32)[52]	v <sub>s</sub> (XeF <sub>2</sub> )	
306.0(6)[76]	305.6(6)[77]	279.2(2)[93]	278.0(1)[90]	$\delta(HF\cdots XeF) + \text{minor } \rho_{\text{rock}}(HF\cdots XeO)$	
228.9(3)[10]	220.4(2)[10]	240.8(5)[7]	233.0(4)[10]	$\rho_{\text{rock}}(XeOF_2) + \text{minor } \delta(HF\cdots XeO)$	
189.7(<<1)[14]	189.6(<<1)[14]	209.7(<<1)[14]	210.0(<<1)[14]	$\delta(XeF_2)$ oop	
185.6(<<1)[13]	185.3(<<1)[12]	145.9(<1)[6]	145.6(<<1)[6]	minor $\delta(XeF_2)$ ip + v(HF---Xe)	
102.5(<1)[2]	102.0(<1)[2]	81.4(<1)[8]	81.2(<1)[8]	$\delta(XeF_2)$ ip - minor v(HF---Xe)	
87.1(<1)[3]	84.9(<1)[3]	58.8(1)[5]	57.1(1)[4]	$\delta(HF\cdots XeF)$ oop - $\delta(FXeO)$ oop	



<sup>a</sup> Frequencies are given in cm<sup>-1</sup>. <sup>b</sup> Values in parentheses denote Raman intensities (Å<sup>4</sup> amu<sup>-1</sup>). Values in square brackets denote infrared intensities (km mol<sup>-1</sup>). <sup>c</sup> SVWN/SDB-cc-pVTZ. <sup>d</sup> MP2/SDB-cc-pVTZ.

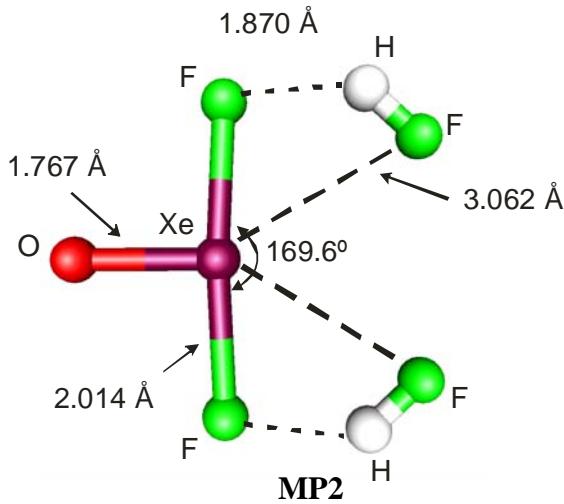
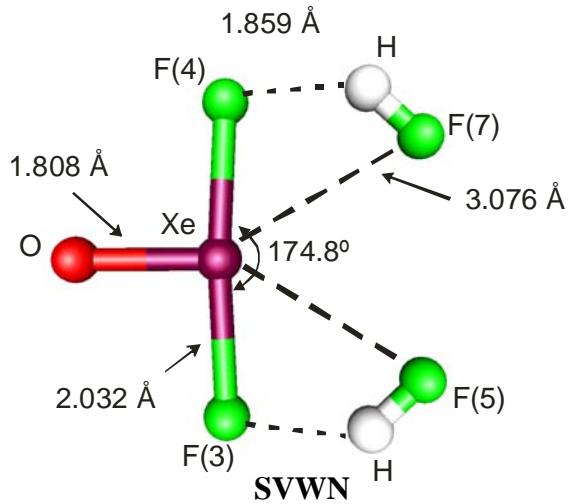
**Table S7.** Calculated Vibrational Frequencies<sup>a</sup> for Xe<sup>16/18</sup>OF<sub>2</sub>·DF (F---D Coordinated)

SVWN <sup>c</sup>		calc <sup>b</sup>		assgnts (C <sub>1</sub> ) symmetry
Xe <sup>16</sup> OF <sub>2</sub> ·DF	Xe <sup>18</sup> OF <sub>2</sub> ·DF	MP2 <sup>d</sup>	Xe <sup>18</sup> OF <sub>2</sub> ·DF	
2268.7(36)[217]	2268.7(36)[217]	2824.0(14)[129]	2824.0(14)[129]	v(DF)
803.2(31)[31]	762.7(28)[25]	955.6(11)[64]	907.2(10)[58]	v(XeO)
724.6(3)[3]	724.5(3)[194]	464.0(4)[254]	463.9(4)[255]	δ(F---D-F)
564.4(<1)[57]	564.4(<1)[57]	417.1(<1)[76]	417.1(<1)[76]	DF oop wag
549.0(6)[188]	548.9(6)[188]	573.0(3)[159]	572.9(3)[158]	v <sub>as</sub> (XeF <sub>2</sub> )
476.2(19)[10]	476.1(19)[10]	482.7(35)[6]	482.7(35)[6]	v <sub>s</sub> (XeF <sub>2</sub> )
302.8(6)[78]	302.5(6)[78]	272.9(2)[101]	271.6(2)[98]	δ(DF---XeF) + minor ρ <sub>rock</sub> (DF---XeO)
228.9(3)[11]	220.5(2)[10]	240.1(5)[7]	240.0(4)[10]	ρ <sub>rock</sub> (XeOF <sub>2</sub> ) + minor δ(DF---XeO)
189.4(<<1)[11]	188.5(<<1)[13]	208.9(<<1)[13]	208.5(<<1)[12]	δ(XeF <sub>2</sub> ) oop
183.7(<<1)[2]	183.1(<<1)[11]	144.1(<<1)[5]	143.4(<<1)[5]	minor δ(XeF <sub>2</sub> ) ip + v(DF---Xe)
102.3(<1)[2]	101.9(<1)[2]	81.2(<1)[8]	81.0(<1)[8]	δ(XeF <sub>2</sub> ) ip – minor v(DF---Xe)
87.0(<1)[3]	84.8(<1)[3]	58.8(1)[5]	57.0(1)[4]	δ(DF---XeF) oop – δ(FXeO) oop

<sup>a</sup> Frequencies are given in cm<sup>-1</sup>. <sup>b</sup> Values in parentheses denote Raman intensities (Å<sup>4</sup> amu<sup>-1</sup>). Values in square brackets denote infrared intensities (km mol<sup>-1</sup>). <sup>c</sup> SVWN/SDB-cc-pVTZ. <sup>d</sup> MP2/SDB-cc-pVTZ.

**Table S8.** Calculated Vibrational Frequencies<sup>a</sup> and Geometries for Xe<sup>16/18</sup>OF<sub>2</sub>·2HF

SVWN <sup>c</sup>		calc <sup>b</sup>		assgnts (C <sub>1</sub> ) symmetry
Xe <sup>16</sup> OF <sub>2</sub> ·2HF	Xe <sup>18</sup> OF <sub>2</sub> ·2HF	Xe <sup>16</sup> OF <sub>2</sub> ·2HF	Xe <sup>18</sup> OF <sub>2</sub> ·2HF	
3348.9(123)[564]	3348.9(123)[564]	3988.6(42)[297]	3988.6(42)[297]	v <sub>s</sub> (HF)
3331.2(19)[51]	3331.19(51)	3983.4(7)[92]	3983.4(7)[92]	v <sub>as</sub> (HF)
914.3(19)[524]	914.3(19)[524]	570.4(12)[351]	570.3(12)[352]	$\delta(F3---H-F5) + \delta(F4---H-F7)$
870.9(<<1)[228]	871.1(<<1)[227]	595.5(1)[26]	596.5(1)[25]	$\delta(F3---H-F5) - \delta(F4---H-F7)$
801.9(41)[41]	762.3(38)[33]	960.0(12)[56]	912.6(11)[50]	v(XeO)
705.0(<<1)[208]	705.0(<<1)[208]	498.1(<1)[243]	498.1(<1)[243]	H-F5---Xe---F7-H oop wag
697.2(2)[~0]	697.2(2)[~0]	491.6(2)[38]	491.6(2)[38]	H-F5---Xe---F7-H oop twist
500.3(<<1)[196]	501.0(<<1)[198]	469.2(1)[548]	469.5(1)[549]	v <sub>as</sub> (XeF <sub>2</sub> )
459.3(23)[1]	459.3(23)[1]	467.6(38)[22]	467.6(38)[22]	v <sub>s</sub> (XeF <sub>2</sub> )
326.5(10)[63]	326.5(10)[63]	231.1(2)[89]	231.1(2)[89]	$\delta(H-F5---XeF3) + \delta(H-F7---XeF4)$
325.1(3)[74]	323.6(3)[77]	286.0(5)[13]	276.8(5)[16]	$\rho_{\text{rock}}(\text{XeOF}_2)$
223.7(<<1)[25]	215.2(<<1)[21]	153.9(<1)[35]	152.8(<1)[34]	$\rho_{\text{rock}}(\text{XeOF}_{2\text{H}})$
175.0(<<1)[8]	174.6(<<1)[7]	207.6(<<1)[39]	207.3(<<1)[36]	$\delta(\text{XeF}_2)$ oop
165.0(<<1)[19]	165.1(<<1)[19]	127.8(<1)[6]	127.9(<1)[6]	v <sub>s</sub> (HF---Xe) + minor $\delta(\text{XeF}_2)$ ip
138.7(<<1)[9]	138.8(<<1)[9]	83.2(1)[4]	82.1(1)[14]	v <sub>as</sub> (HF---Xe)
126.8(<<1)[<<1]	126.9(<<1)[<<1]	63.5(1)[4]	63.5(<1)[4]	$\delta(\text{XeF}_{2\text{H}})$ ip
86.2(1)[3]	83.7(1)[3]	-26.8(1)[16]	-26.1(<1)[15]	$\delta(\text{HF---XeF})$ oop - $\delta(\text{HF---XeO})$ oop
20.6(<<1)[0]	20.6(<<1)[0]	28.2(<1)[<<1]	28.2(<1)[<<1]	XeF <sub>2</sub> & XeF <sub>2H</sub> torsions about XeO bond



<sup>a</sup> Frequencies are given in cm<sup>-1</sup>. <sup>b</sup> Values in parentheses denote Raman intensities (Å<sup>4</sup> amu<sup>-1</sup>). Values in square brackets denote infrared intensities (km mol<sup>-1</sup>). <sup>c</sup> SVWN/SDB-cc-pVTZ. <sup>d</sup> MP2/SDB-cc-pVTZ.

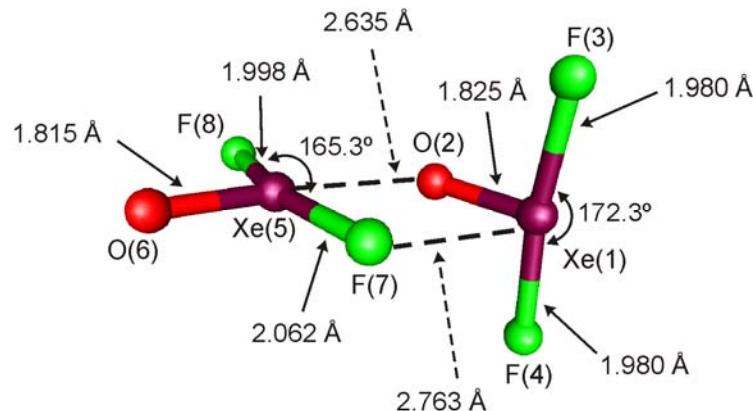
**Table S9.** Calculated Vibrational Frequencies<sup>a</sup> for Xe<sup>16/18</sup>OF<sub>2</sub>·2DF

calc <sup>b</sup>		assgnts
SVWN <sup>c</sup>	Xe <sup>18</sup> OF <sub>2</sub> ·2DF	(C <sub>1</sub> ) symmetry
Xe <sup>16</sup> OF <sub>2</sub> ·2DF		
2431.2(65)[294]	2431.2(65)[294]	v <sub>s</sub> (DF)
2418.1(9)[28]	2418.1(9)[28]	v <sub>as</sub> (DF)
803.0(38)[35]	762.4(34)[32]	v(XeO)
656.0(9)[263]	655.8(9)[264]	δ(F3---D-F5) + δ(F4---D-F7)
635.3(<<1)[57]	635.3(<<1)[57]	δ(F3---D-F5) - δ(F4---D-F7)
510.5(<<1)[116]	510.5(<<1)[116]	D-F5---Xe---F7-D oop wag
502.6(<1)[<<1]	502.6(1)[<<1]	D-F5---Xe---F7-D oop twist
497.7(<1)[214]	497.6(<1)[214]	v <sub>as</sub> (XeF <sub>2</sub> )
457.4(24)[3]	457.4(24)[3]	v <sub>s</sub> (XeF <sub>2</sub> )
323.7(10)[69]	323.6(10)[68]	δ(D-F5---XeF3) + δ(D-F7---XeF4)
319.5(3)[75]	317.5(3)[79]	ρ <sub>rock</sub> (XeOF <sub>2</sub> )
221.5(<1)[29]	213.0(<1)[24]	ρ <sub>rock</sub> (XeOF <sub>2D</sub> )
173.6(<1)[7]	172.5(<1)[6]	δ(XeF <sub>2</sub> ) oop
164.2(<1)[18]	164.0(<1)[18]	v <sub>s</sub> (DF---Xe) + minor δ(XeF <sub>2</sub> ) ip
138.3(<<1)[8]	138.3(<<1)[8]	v <sub>as</sub> (DF---Xe)
125.1(<1)[<<1]	125.0(<1)[<<1]	δ(XeF <sub>2D</sub> ) ip
86.3(1)[3]	83.7(1)[3]	δ(DF---XeF) oop - δ(DF---XeO) oop
20.5(<1)[<<1]	20.5(<1)[<<1]	XeF <sub>2</sub> & XeF <sub>2D</sub> torsions about XeO bond

<sup>a</sup> Frequencies are given in cm<sup>-1</sup>. <sup>b</sup> Values in parentheses denote Raman intensities (Å<sup>4</sup> amu<sup>-1</sup>). Values in square brackets denote infrared intensities (km mol<sup>-1</sup>). <sup>c</sup> SVWN/SDB-cc-pVTZ.

**Table S10.** Calculated Vibrational Frequencies<sup>a</sup> for  $(\text{Xe}^{16/18}\text{OF}_2)_2$  Dimer

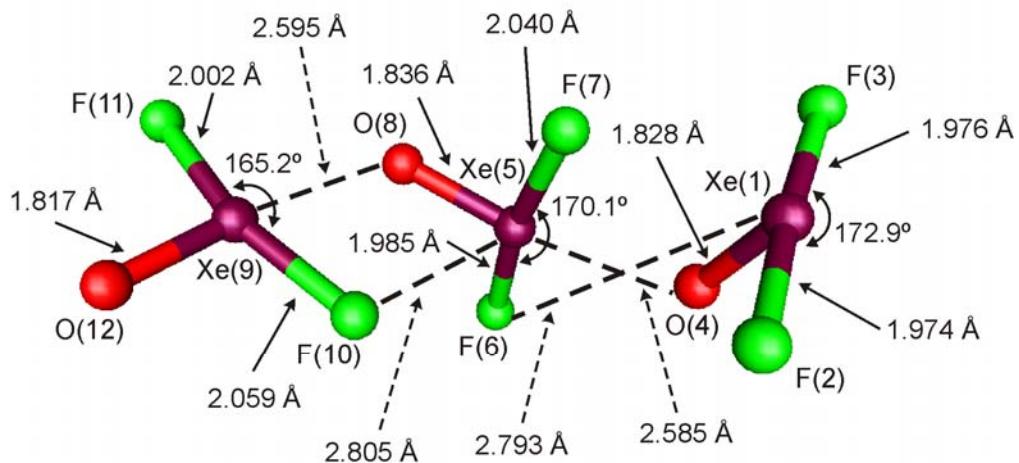
calc <sup>b</sup>		assgnts (C <sub>1</sub> ) symmetry
SVWN <sup>c</sup> (Xe <sup>16</sup> OF <sub>2</sub> ) <sub>2</sub>	(Xe <sup>18</sup> OF <sub>2</sub> ) <sub>2</sub>	
790.9(82)[59]	752.0(73)[55]	v(Xe5O6)
756.8(48)[72]	719.4(48)[66]	v(Xe1O2)
586.0(2)[198]	587.5(1)[199]	v(Xe1F <sub>3</sub> – Xe1F <sub>4</sub> )
540.9(8)[177]	542.0(8)[179]	v(Xe5F <sub>7</sub> – Xe5F <sub>8</sub> )
516.4(32)[23]	516.3(31)[23]	v(Xe1F <sub>3</sub> + Xe1F <sub>4</sub> )
457.3(21)[31]	457.3(22)[30]	v(Xe5F <sub>8</sub> + Xe5F <sub>7</sub> )
260.3(3)[6]	250.2(3)[6]	$\rho_{\text{rock}}(\text{Xe1OF}_2)$
238.2(14)[21]	228.9(14)[15]	$\rho_{\text{rock}}(\text{Xe5OF}_2) - v(\text{Xe1O}_2 + \text{Xe5O}_2)$
230.0(<1)[25]	224.3(1)[34]	$\rho_{\text{rock}}(\text{Xe5OF}_2) + v(\text{Xe1O}_2 + \text{Xe5O}_2)$
202.8(<1)[15]	202.4(<1)[14]	$\delta(\text{Xe5F}_2)$ oop
200.5(3)[24]	198.0(4)[19]	$\delta(\text{Xe5F}_2)$ ip + $\delta(\text{Xe1F}_2)$ oop
191.4(1)[3]	189.6(1)[3]	$\delta(\text{Xe1F}_2)$ oop + minor $\delta(\text{Xe5F}_2)$ ip
169.3(<1)[17]	169.3(<1)[18]	$\delta(\text{Xe1F}_2)$ ip
94.6(<1)[<1]	94.1(<1)[<1]	coupled deformations
89.2(1)[2]	86.4(1)[1]	
63.4(<1)[1]	63.2(<1)[2]	
35.8(1)[<1]	35.6(2)[<1]	
22.4(2)[<<1]	22.2(3)[<<1]	



<sup>a</sup> Frequencies are given in  $\text{cm}^{-1}$ . <sup>b</sup> Values in parentheses denote Raman intensities ( $\text{\AA}^4 \text{ amu}^{-1}$ ). Values in square brackets denote infrared intensities ( $\text{km mol}^{-1}$ ). <sup>c</sup> SVWN/SDB-cc-pVTZ.

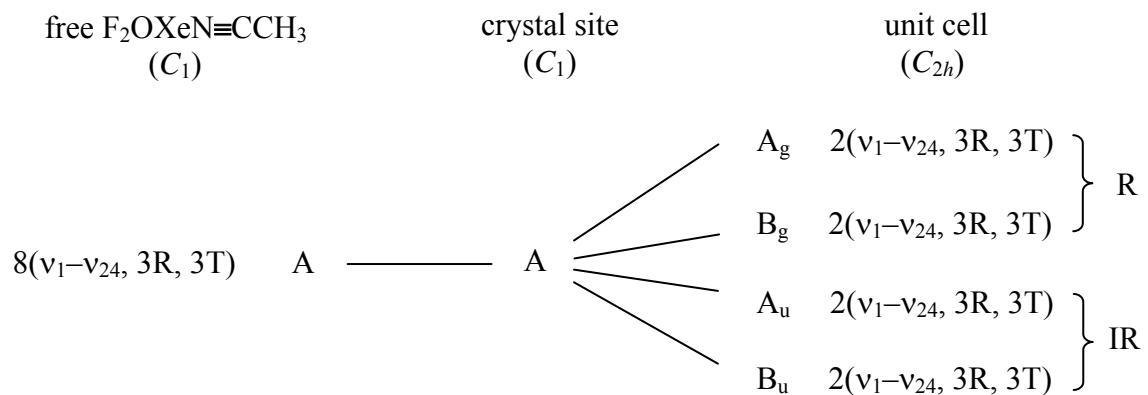
**Table S11.** Calculated Vibrational Frequencies<sup>a</sup> and Geometries for  $(\text{Xe}^{16/18}\text{OF}_2)_3$

calc <sup>b</sup>		assgnts (C <sub>1</sub> ) symmetry
SVWN <sup>c</sup>	(Xe <sup>18</sup> OF <sub>2</sub> ) <sub>3</sub>	
(Xe <sup>16</sup> OF <sub>2</sub> ) <sub>3</sub>		v(Xe9O12)
787.3(103)[66]	748.6(94)[62]	
753.9(9)[28]	716.5(8)[26]	v(Xe1O4 – Xe5O4) + v(Xe9O8 – Xe5O8)
734.4(345)[259]	698.4(307)[238]	v(Xe1O4 – Xe5O4) – v(Xe9O8 – Xe5O8)
592.1(1)[190]	593.7(1)[191]	v(Xe1F2 – Xe1F3)
553.3(10)[178]	554.5(10)[179]	v(Xe5F6 – Xe5F7)
537.3(9)[188]	538.4(9)[190]	v(Xe9F10 – Xe9F11)
521.9(22)[30]	521.9(22)[31]	v(Xe1F2 + Xe1F3)
471.2(82)[39]	471.2(84)[37]	v(Xe5F6 + Xe5F7)
458.0(12)[15]	457.9(12)[14]	v(Xe9F10 + Xe9F11)
272.5(13)[27]	261.2(11)[25]	v(Xe9O8 + Xe5O8) + ρ <sub>rock</sub> (Xe1OF <sub>2</sub> )
253.3(17)[12]	243.0(13)[11]	ρ <sub>rock</sub> (Xe1OF <sub>2</sub> )
248.6(17)[15]	239.3(16)[9]	v(Xe1O4 + Xe5O4) + ρ <sub>rock</sub> (Xe5OF <sub>2</sub> )
239.5(<1)[33]	231.1(<1)[39]	v(Xe1O4 + Xe5O4) + v(Xe9O8 + Xe5O8)
228.2(3)[8]	221.7(4)[12]	ρ <sub>rock</sub> (Xe9OF <sub>2</sub> )
209.6(6)[23]	209.1(6)[21]	δ(Xe9F <sub>2</sub> ) oop
202.7(1)[6]	202.3(1)[5]	δ(Xe5F <sub>2</sub> ) ip + δ(Xe1F <sub>2</sub> ) oop + δ(Xe9F <sub>2</sub> ) oop
197.8(5)[16]	195.8(6)[13]	δ(Xe1F <sub>2</sub> ) oop + δ(Xe9F <sub>2</sub> ) oop
193.6(5)[24]	191.7(4)[22]	δ(Xe9F <sub>2</sub> ) ip + δ(Xe5F <sub>2</sub> ) oop
186.2(2)[16]	184.9(3)[14]	δ(Xe5F <sub>2</sub> ) oop
168.9(1)[20]	168.8(1)[20]	Coupled deformation modes
111.0(<1)[<1]	110.0(<1)[<1]	
95.2(<1)[<1]	93.4(<1)[<1]	
85.0(1)[1]	84.0(1)[1]	
67.2(1)[<1]	66.9(1)[<1]	
60.5(<1)[2]	60.3(1)[2]	
48.4(2)[<1]	48.1(2)[<1]	
37.6(3)[<1]	37.3(3)[<1]	
25.6(1)[<<1]	25.6(1)[<<1]	
19.5(2)[<<1]	19.5(2)[<<1]	
10.4(1)[<1]	10.4(1)[<1]	



<sup>a</sup> Frequencies are given in  $\text{cm}^{-1}$ . <sup>b</sup> Values in parentheses denote Raman intensities ( $\text{\AA}^4 \text{ amu}^{-1}$ ). Values in square brackets denote infrared intensities ( $\text{km mol}^{-1}$ ). <sup>c</sup> SVWN/SDB-cc-pVTZ.

**Table S12.** Factor-Group Analysis for  $\text{F}_2\text{OXeN}\equiv\text{CCH}_3$



There are two crystallographically unique  $\text{F}_2\text{OXeN}\equiv\text{CCH}_3$  molecules in the asymmetric unit of the unit cell, both having  $C_1$  site symmetry. Each structure type is distinguished by its non-linear Xe-N-C angle which lies either in or out of the  $\text{XeOF}_2$  plane. The present factor-group analysis correlates the gas-phase molecular symmetry of both conformations ( $C_1$ ) to their site symmetries ( $C_1$ ) which, in turn, are correlated to the unit cell symmetry ( $C_{2h}$ ) for a total of 8 molecules per unit cell. The present analysis has been simplified by assuming a single adduct conformation. Consequently, no provision has been made for coupling between different conformers. The analysis reveals that each Raman and infrared band will be split, as a result of coupling within the unit cell, into a maximum of four components,  $2A_g + 2B_g$  in the Raman spectrum and  $2A_u + 2B_u$  in the infrared spectrum.

**Table S13.** Comparison of Calculated Vibrational Frequencies and Geometries for XeOF<sub>2</sub> Using Different Levels of Theory and Basis Sets

Frequencies (cm <sup>-1</sup> )												
exptl	B3LYP				SVWN				MP2			CCSD(T)
	321G	ccpVTZ	SDDAll	DZVP	ccpVTZ	ccpVQZ	SDDAll	DZVP	ccpVTZ	ccpVQZ	SDDAll	ccpVTZ
750.0(60)	727(3)	734(13)	713(12)	653(11)	795(22)	809(23)	788(23)	753(22)	939(60)	947(60)	928(64)	747
n.o.	658(34)	556(240)	558(261)	559(210)	572(213)	578(223)	573(234)	572(188)	582(252)	587(267)	582(9)	581
468.0(100)	563(3)	494(6)	496(7)	480(6)	505(7)	514(8)	506(9)	489(8)	509(7)	525(8)	507(9)	517
297.8(11)	271(6)	258(3)	253(3)	230(4)	244(3)	249(3)	240(3)	224(5)	283(3)	285(3)	279(4)	267
256.1(1) 251.6, sh	235(18)	209(23)	209(23)	211(24)	200(21)	204(19)	199(21)	193(22)	218(25)	219(22)	216(25)	217
175.5(1) 153.3(6)	218(15)	175(17)	177(18)	173(20)	155(14)	161(13)	153(14)	155(16)	176(19)	180(18)	173(20)	188
Geometrical Parameters												
Xe-O Å	1.885	1.817	1.828	1.881	1.809	1.795	1.818	1.851	1.770	1.763	1.782	1.811
Xe-F Å	1.978	1.999	1.999	2.050	1.996	1.975	1.998	2.039	1.980	1.963	1.990	1.974
F-Xe-F °	171.9	169.4	169.9	180.0	167.1	167.4	167.2	167.4	168.2	168.7	167.8	170.7
O-Xe-F °	94.0	95.3	95.1	94.7	96.4	96.3	96.4	96.3	95.9	95.7	96.1	94.6

**Table S14.** Calculated Vibrational Frequencies<sup>a</sup> and Geometries for XeF<sub>4</sub> (*D*<sub>4h</sub>)

frequencies			
exptl <sup>b</sup>	SVWN <sup>c</sup>	MP2 <sup>c</sup>	assgnts <sup>d</sup>
586	590(225)	603(245)	v(E <sub>u</sub> ), v <sub>as</sub> (XeF <sub>t</sub> – XeF <sub>t</sub> )
543	547(<<1)	545(0)	v(A <sub>1g</sub> ), v <sub>s</sub> (XeF <sub>4</sub> )
502	514(<<1)	513(0)	v(B <sub>1g</sub> ), v <sub>as</sub> (XeF <sub>2t</sub> – XeF <sub>2t</sub> )
291	272(31)	295(39)	v(A <sub>2u</sub> ), δ(XeF <sub>4</sub> ) oop, umbrella mode
235	196(0)	217(0)	v(B <sub>2g</sub> ), δ(XeF <sub>2c</sub> + XeF <sub>2c</sub> )
(221)	150(0)	166(0)	v(B <sub>2u</sub> ), δ(XeF <sub>2t</sub> ) oop – δ(XeF <sub>2t</sub> ) oop
123	140(0)	160(3)	v(E <sub>u</sub> ), δ(XeF <sub>2t</sub> ) ip
Bond Lengths (Å)			
Xe-F	1.971	1.960	

<sup>a</sup> Frequencies are given in cm<sup>-1</sup>. <sup>b</sup> From *Mol. Phys.* **1965**, 9, 449-454. <sup>c</sup> Values in parentheses denote infrared intensities (km mol<sup>-1</sup>). <sup>c</sup> (SDB-)cc-pVTZ. <sup>d</sup> The abbreviations denote trans (t), cis (c), symmetric (s), asymmetric (as), stretch (v), bend (δ), in-plane bend (ip), and out-of-plane bend (oop). The in-plane and out-of-plane mode descriptions are relative to the XeF<sub>4</sub> plane.

**Table S15.** Natural Bond Orbital (NBO) Charges, Valencies and Bond Orders for the two Experimental Conformers of  $\text{F}_2\text{OXeN}\equiv\text{CCH}_3$

Charges [Valencies]									
	in-plane					out-of-plane			
	SVWN		MP2			SVWN		MP2	
Xe(1)	2.088	[1.487]	2.168	[1.499]	Xe(2)	2.068	[1.586]	2.172	[1.503]
O(1)	-0.904	[0.742]	-0.944	[0.739]	O(2)	-0.893	[0.762]	-0.947	[0.740]
F(1)	-0.607	[0.294]	-0.620	[0.301]	F(3)	-0.601	[0.323]	-0.622	[0.301]
F(2)	-0.601	[0.300]	-0.615	[0.304]	F(4)	-0.601	[0.321]	-0.615	[0.306]
N(1)	-0.410	[2.040]	-0.415	[1.998]	N(2)	-0.406	[2.090]	-0.414	[1.986]
C(10)	0.376	[3.011]	0.378	[2.910]	C(20)	0.375	[3.033]	0.379	[2.919]
C(11)	-0.744	[3.342]	-0.634	[3.324]	C(21)	-0.741	[3.339]	-0.643	[3.335]
H	0.268	[0.827]	0.228	[0.837]	H	0.267	[0.826]	0.230	[0.837]
Bond Orders									
Xe(1)–O(1)	0.783		0.787		Xe(2)–O(2)	0.800		0.788	
Xe(1)–F(1)	0.313		0.325		Xe(2)–F(3)	0.340		0.324	
Xe(1)–F(2)	0.319		0.326		Xe(2)–F(4)	0.338		0.329	
Xe(1)---N(1)	0.069		0.055		Xe(2)---N(2)	0.094		0.057	
N(1)–C(10)	1.958		1.923		N(2)–C(20)	1.981		1.909	
C(10)–C(11)	0.983		0.922		C(20)–C(21)	0.974		0.940	
C(11)–H	0.780		0.793		C(21)–H	0.782		0.791	

**Table S16.** Energies (Hartrees) for  $\text{Xe}^{16/18}\text{OF}_2$ ,  $\text{F}_2^{16/18}\text{OXeN}\equiv\text{CCH}_3$ ,  $\text{CH}_3\text{C}\equiv\text{N}$ ,  $\text{Xe}^{16/18}\text{OF}_2\cdot{}^{1/2}\text{HF}$  (O---H Coordinated),  $\text{Xe}^{16/18}\text{OF}_2\cdot{}^{1/2}\text{HF}$  (F---H Coordinated),  $\text{Xe}^{16/18}\text{OF}_2\cdot{}2^{1/2}\text{HF}$ ,  $(\text{Xe}^{16/18}\text{OF}_2)_2$ ,  $(\text{Xe}^{16/18}\text{OF}_2)_3$ , and  $\text{XeF}_4$

	level	energy
$\text{Xe}^{16}\text{OF}_2$	SVWN	-289.111888
	MP2	-289.693725
$\text{Xe}^{18}\text{OF}_2$	SVWN	-289.111995
	MP2	-289.693852
$\text{F}_2^{16}\text{OXe-N}\equiv\text{CCH}_3$	SVWN	-421.139885
	MP2	-421.139982
$\text{F}_2^{16}\text{OXe-N}\equiv\text{CCH}_3$	SVWN	-422.153240
	MP2	-422.153374
$\text{CH}_3\text{C}\equiv\text{N}$	SVWN	-132.006544
	MP2	-132.443603
$\text{Xe}^{16}\text{OF}_2\cdot\text{HF}$ (O---H coordinated)	SVWN	-389.155952
	MP2	-390.024148
$\text{Xe}^{18}\text{OF}_2\cdot\text{HF}$ (O---H coordinated)	SVWN	-389.155948
	MP2	-390.024300
$\text{Xe}^{16}\text{OF}_2\cdot\text{DF}$ (O---D coordinated)	SVWN	-389.159092
	MP2	-390.027402
$\text{Xe}^{18}\text{OF}_2\cdot\text{DF}$ (O---D coordinated)	SVWN	-389.159234
	MP2	-390.027563
$\text{Xe}^{16}\text{OF}_2\cdot\text{HF}$ (F---H coordinated)	SVWN	-389.158920
	MP2	-390.024754
$\text{Xe}^{18}\text{OF}_2\cdot\text{HF}$ (F---H coordinated)	SVWN	-389.159035
	MP2	-390.024887
$\text{Xe}^{16}\text{OF}_2\cdot\text{DF}$ (F---D coordinated)	SVWN	-389.162019
	MP2	-390.027871
$\text{Xe}^{18}\text{OF}_2\cdot\text{DF}$ (F---D coordinated)	SVWN	-389.162140
	MP2	-390.028107
$\text{Xe}^{16}\text{OF}_2\cdot{}2\text{HF}$	SVWN	-489.199468
	MP2	-490.352720
$\text{Xe}^{18}\text{OF}_2\cdot{}2\text{HF}$	SVWN	-489.199585
	MP2	-490.352852
$\text{Xe}^{16}\text{OF}_2\cdot{}2\text{DF}$	SVWN	-489.205693
$\text{Xe}^{18}\text{OF}_2\cdot{}2\text{DF}$	SVWN	-489.205820
$(\text{Xe}^{16}\text{OF}_2)_2$ dimer	SVWN	-578.249060
	MP2	-579.405429
$(\text{Xe}^{18}\text{OF}_2)_2$ dimer	SVWN	-578.249305
	MP2	-579.405710
$(\text{Xe}^{16}\text{OF}_2)_3$	SVWN	-867.388133
$(\text{Xe}^{18}\text{OF}_2)_3$	SVWN	-867.388510
$\text{XeF}_4$	SVWN	-413.119699
	MP2	-414.039912

**Table S17.** Cartesian Coordinates for  $\text{XeOF}_2$ ,  $\text{F}_2\text{OXe-N}\equiv\text{CCH}_3$ ,  $\text{CH}_3\text{C}\equiv\text{N}$ ,  $\text{XeOF}_2\cdot\text{HF}$  (O---H Coordinated),  $\text{XeOF}_2\cdot\text{HF}$  (F---H Coordinated),  $\text{XeOF}_2\cdot2\text{HF}$ ,  $(\text{XeOF}_2)_2$ ,  $(\text{XeOF}_2)_3$ , and  $\text{XeF}_4$

	level	atom	x	y	z
$\text{Xe}^{16}\text{OF}_2$	SVWN	Xe	0.000000	-0.130590	0.000000
		O	0.000000	1.678085	0.000000
		F	1.982995	-0.354046	0.000000
		F	-1.982995	-0.354046	0.000000
	MP2	Xe	0.000000	0.000000	0.131170
		O	0.000000	0.000000	-1.638788
		F	0.000000	1.969466	0.334840
		F	0.000000	-1.969466	0.334840
$\text{F}_2^{16}\text{OXeN}\equiv\text{CCH}_3$	SVWN	Xe	0.785561	-0.000069	-0.000686
		O	2.598529	-0.002694	0.011510
		F	0.564445	-2.000940	-0.001958
		F	0.570206	2.001409	-0.001925
		N	-1.915902	0.002400	-0.013732
		C	-3.067799	0.000530	-0.003741
		C	-4.495887	0.000133	0.009707
		H	-4.880231	-0.898144	-0.493270
		H	-4.880590	0.888197	-0.510969
		H	-4.866136	0.010255	1.044486
	MP2	Xe	0.827398	-0.000088	-0.000457
		O	2.601730	-0.002978	0.008378
		F	0.631390	-1.983650	-0.001324
		F	0.637832	1.984075	-0.001297
		N	-2.055348	0.003086	-0.010948
		C	-3.222234	0.000917	-0.002976
		C	-4.677293	-0.000186	0.007442
		H	-5.047035	-0.891061	-0.492967
		H	-5.048222	0.880975	-0.508974
		H	-5.036446	0.008831	1.032999
$\text{CH}_3\text{C}\equiv\text{N}$	SVWN	N	0.000003	1.426012	0.000000
		C	0.000000	0.271414	0.000000
		C	-0.000002	-1.161785	0.000000
		H	-0.514665	-1.546621	0.891420
		H	1.029322	-1.546621	0.000000
		H	-0.514665	-1.546621	-0.891420
		N	0.000000	0.000000	1.444067
	MP2	C	0.000000	0.000000	0.274857
		C	0.000000	0.000000	-1.182621
		H	0.000000	1.021324	-1.553963
		H	-0.884493	-0.510662	-1.553963
		H	0.884493	-0.510662	-1.553963
		N	0.000000	0.000000	1.444067
		C	0.000000	0.000000	0.274857
$\text{Xe}^{16}\text{OF}_2\cdot\text{HF}$ (O---H Coordinated)	SVWN	Xe	-0.397923	0.000223	-0.055760
		O	0.812339	-0.000766	1.309989
		F	-0.520883	-1.973794	-0.165136
		F	-0.518589	1.974420	-0.164873
		H	2.095075	-0.001437	0.353633
		F	2.472143	-0.001126	-0.539161
		N	0.427392	0.000413	-0.061650
	MP2	O	-0.743818	-0.001120	1.282340
		F	0.533893	1.962232	-0.169764
		F	0.538668	-1.961109	-0.170091
		H	-2.281751	-0.002656	0.354895
		F	-2.722213	-0.002311	-0.469535
		N	0.427392	0.000413	-0.061650
		C	-0.743818	-0.001120	1.282340

**Table S17.** (continued ...)

	level	atom	x	y	z
Xe <sup>16</sup> OF <sub>2</sub> ·HF (F---H Coordinated)	SVWN	Xe	0.203973	-0.012944	-0.000055
		O	1.360447	-1.403549	0.000373
		F	1.550716	1.446025	-0.000066
		F	-1.532699	-1.196385	-0.000216
		F	-2.195845	1.065445	0.000280
		H	-2.297671	0.091600	-0.000007
	MP2	Xe	0.233428	-0.004981	-0.000010
		O	1.495412	-1.243034	0.000057
		F	1.443843	1.551747	-0.000001
		F	-1.318184	-1.320053	-0.000026
		F	-2.570289	0.906084	0.000033
		H	-2.566732	-0.026753	0.000033
Xe <sup>16</sup> OF <sub>2</sub> ·2HF	SVWN	Xe	0.000002	-0.307929	-0.000116
		O	0.000016	-2.115941	0.000534
		F	-2.074616	-0.263955	0.000027
		F	2.074623	-0.263931	-0.000177
		F	-1.355989	1.985633	0.000066
		H	-2.019089	1.282498	-0.000227
		F	1.355958	1.985662	0.000318
		H	2.019067	1.282540	0.000141
	MP2	Xe	-0.382953	-0.001255	-0.001265
		O	-2.150053	-0.013719	0.007070
		F	-0.188804	-1.938007	-0.519252
		F	-0.210321	1.938032	0.514833
		F	2.141827	-1.631718	0.589402
		H	1.534293	-2.189063	0.162786
		F	2.127433	1.649819	-0.583955
		H	1.514403	2.203439	-0.160314
(Xe <sup>16</sup> OF <sub>2</sub> ) <sub>2</sub> dimer	SVWN	Xe(1)	-2.001425	-0.000032	0.019101
		O(2)	-0.565307	-0.001536	1.144767
		F(3)	-2.114476	1.975443	-0.049412
		F(4)	-2.114502	-1.975320	-0.054615
		Xe(5)	1.791802	0.000045	-0.033191
		O(6)	3.211632	0.001577	-1.163023
		F(7)	0.320778	0.002109	-1.478389
		F(8)	2.813651	-0.002347	1.683183
(Xe <sup>16</sup> OF <sub>2</sub> ) <sub>3</sub>	SVWN	Xe(1)	3.459347	-0.624152	0.134155
		F(2)	2.975179	-2.138840	-1.034679
		F(3)	4.083907	0.733930	1.426446
		O(4)	2.551549	0.598435	-0.877542
		Xe(5)	0.118101	1.088239	-0.155990
		F(6)	0.891999	-0.255024	1.169655
		F(7)	-0.325815	2.381263	-1.595236
		O(8)	-1.487193	1.242697	0.722246
		Xe(9)	-3.313273	-0.485881	0.081576
		F(10)	-1.644499	-0.901872	-1.050923
		F(11)	-4.636300	0.295609	1.365246
		O(12)	-4.360065	-1.823467	-0.563530

**Table S17.** (continued ...)

XeF <sub>4</sub>		level	atom	x	y	z
		SVWN	Xe	0.000000	0.000000	0.000000
			F	0.000000	1.971036	0.000000
			F	0.000000	-1.971036	0.000000
			F	1.971036	0.000000	0.000000
			F	-1.971036	0.000000	0.000000
MP2		Xe	Xe	0.000000	0.000000	0.000000
			F	0.000000	1.959594	0.000000
			F	0.000000	-1.959594	0.000000
			F	1.959594	0.000000	0.000000
			F	-1.959594	0.000000	0.000000

**Synthesis of High-Purity Deuterium Fluoride.** Calcium fluoride powder (J.T. Baker, 98.2%) was dried in a glass vessel under dynamic vacuum at 200–250 °C for 24 h and stored in a drybox until used. Sulfuric acid-*d*<sub>2</sub> (Aldrich, 99.5 atom % <sup>2</sup>H) was used without further purification.

Deuterium fluoride was prepared by the reaction of 25.59 g (0.2556 mol) of D<sub>2</sub>SO<sub>4</sub> with 20.09 g (0.3400 mol) of CaF<sub>2</sub> powder. The reaction was carried out in a ¾-in. o.d. FEP reaction vessel fitted with a Kel-F valve. The DF was initially vacuum distilled from the reaction slurry at room temperature into –196 °C cold trap comprised of a U-tube constructed from ½-in. o.d. FEP tubing and equipped with Kel-F valves. Throughout, the reaction vessel was periodically agitated until the slurry solidified, whereupon the reaction vessel was incrementally heated to no more than 105 °C in a silicone oil bath over a period of 2 h and the DF was collected in the U-tube until DF evolution ceased. The crude DF was then statically distilled at room temperature into an FEP vessel containing 1.06 g of XeF<sub>2</sub> at –196 °C. Upon warming to room temperature, XeF<sub>2</sub> dissolved and any D<sub>2</sub>O that had transferred or SO<sub>2</sub> that formed in the course of the acid displacement reaction was converted to DF and O<sub>2</sub>, and SO<sub>2</sub>F<sub>2</sub>, respectively. After standing at room temperature for 1 h, the mixture was cooled to –78 °C and DF was distilled under dynamic vacuum into a second FEP U-tube at –196 °C. The sample was warmed to room temperature and a portion was condensed into a 4-mm o.d. FEP NMR tube at –196 °C. The room temperature <sup>19</sup>F NMR spectrum revealed a small amount (1.3 mole %) of SO<sub>2</sub>F<sub>2</sub> ( $\delta(^{19}\text{F})$ , 29.3 ppm;  ${}^1\Delta^{19}\text{F}({}^{34/32}\text{S})$ , –0.0482 ppm) but no other fluorine-containing species other than DF could be detected under high-gain conditions. The remaining DF was stored by condensing it into a Kel-F vessel containing 0.140 g of resublimed BiF<sub>5</sub> (Ozark Mahoning Co.) to remove trace amounts of D<sub>2</sub>O that may still be present. The yield of pure anhydrous DF was 8.93 g (83.1% based on D<sub>2</sub>SO<sub>4</sub> as the limiting reagent). Transfer of DF was accomplished by vacuum distillation from the Kel-F storage vessel, on a metal vacuum line, through connections constructed of FEP.

**Complete reference 61.** Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; *Gaussian 98*, Revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2003.