Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

May there be a Multi-bond between Noble Gas and Metal? A Theoretical Study of F_2XeMoF_2

Kunqi Gao and Li Sheng

Table S1. The optimized equilibrium geometry parameters of F_2XeMoF_2, $FXeMoF_3$,transition states and products (Bond lengths are given in angstroms and bond angles are given in degrees, the F atoms transferring to the Mo atom is denoted as F^1 in TS1, and the F atoms transferring to the Mo atom is denoted as F^2 in TS2).

	B3LYP	M06	MP2	CCSD(T)
$F^1F^2XeMoF_2$				
F^1-Xe	2.125	2.064	2.147	2.093
Xe-Mo	2.534	2.561	2.462	2.518
Mo-F	1.806	1.806	1.792	1.813
F^1-Xe-Mo	102.1	99.4	104.1	101.1
Xe-Mo-F	110.0	106.2	110.5	108.4
TS1				
F^2-Xe	2.130	2.050	2.186	
F^1-Xe	2.251	2.148	2.297	
Xe-Mo	2.571	2.669	2.497	
Mo-F	1.819	1.811	1.784	
F^2-Xe-Mo	117.9	117.9	114.5	
F^1-Xe-Mo	72.0	69.3	76.4	
Xe-Mo-F	103.5	112.9	107.0	
$F^2XeMoF^1F_2$				
F^2-Xe	2.208	2.172	2.158	
Xe-Mo	2.761	2.732	2.692	
Mo-F	1.813	1.821	1.813	
Mo-F^1	1.853	1.803	1.882	
Xe-Mo-F	97.4	94.6	91.8	

Table S1. (Continued)

	B3LYP	M06	MP2	CCSD(T)
TS2				
F^2-Xe	2.367	2.326	2.310	
Xe-Mo	2.632	2.606	2.560	
Mo-F	1.836	1.803	1.821	
F^2-Xe-Mo	91.6	91.9	95.5	
Xe-Mo-F	104.3	106.6	106.8	
XeF_2				
Xe-F	2.010	1.976	1.988	1.988
F-Xe-F	180.0	180.0	180.0	180.0
XeF_4				
Xe-F	1.971	1.941	1.953	1.949
F-Xe-F	90.0	90.0	90.0	90.0
MoF_2				
Mo-F	1.885	1.879	1.889	1.894
F-Mo-F	132.1	132.2	135.8	136.6
MoF_4				
Mo-F	1.864	1.854	1.858	1.860
F-Mo-F	109.6	109.6	109.4	109.4

Table S2. The IR frequencies (cm^{-1}), IR intensities (km mol^{-1}, in parentheses, the former) and Raman activities ($Å^4$ amu^{-1}, in parentheses, the latter) of F_2XeMoF_2, $FXeMoF_3$, transition states and products; among them, only Raman activities of F_2XeMoF_2 and $FXeMoF_3$ are listed.

		B3LYP	MP2
F_2XeMoF_2			
	Xe-Mo str	227.0(0.3, 11.5)	287.1(37.2, 43.8)
	Xe-F sy. str	364.9(114.0, 36.9)	372.3(54.2, 113.1)
	Xe-F as. str	441.6(196.1, 13.9)	449.3(197.9, 50.0)
	Mo-F sy. str	713.8(70.0, 6.8)	762.0(57.9, 24.9)
	Mo-F as. str	723.7(228.4, 0.0)	791.1(220.8, 2.4)
	Sy. bend	121.2(7.6, 4.1)	131.3(14.8, 0.2)
	As. bend	147.7(35.0, 0.1)	167.8(11.9, 0.9)
	F-Xe-Mo as. bend	77.4(0.4, 0.5)	88.2(0.1, 0.3)
	F-Mo-Xe as. bend	68.3(2.5, 4.1)	108.2(8.9, 4.6)
	Torsion	47.0(0.0, 1.0)	104.3(0.0, 1.7)
	Mo-Xe-F torsion	149.7(13.5, 0.0)	146.7(8.9, 0.9)
	Xe-Mo-F torsion	179.5(2.5, 4.9)	196.3(2.1, 3.2)
$FXeMoF_3$			
	Xe-Mo str	206.5(6.6, 32.1)	220.4(0.2, 113.6)
	Xe-F str	372.4(215.7, 61.3)	412.6(383.0, 146.9)
	Mo-F sy. str	690.9(61.5, 12.6)	712.5(104.8, 33.3)
	Mo-F as. str	593.3(158.3, 3.6)	686.1(122.2, 17.4)
	Mo-F as. str	750.0(203.7, 1.2)	733.5(286.4, 1.8)
	Mo-Xe-F bend	75.3(6.7, 3.8)	74.9(8.0, 5.1)
	Mo-Xe-F bend	112.9(2.4, 2.0)	115.7(6.7, 2.7)
	Xe-Mo-F as. bend	141.6(0.9, 5.6)	131.4(1.3, 5.2)
	Xe-Mo-F as. bend	36.4(14.4, 1.4)	66.0(3.7, 2.6)
	Xe-Mo-F sy. bend	116.9(3.4, 0.6)	130.0(1.0, 2.7)

Table S2. (Continued)

		B3LYP	MP2
TS1			
	Mo-Xe-F bend	-141.9(1.3)	-149.6(5.7)
	Xe-Mo str	197.6(2.2)	246.6(60.2)
	Xe-F sy. str	312.1(109.4)	423.8(28.6)
	Xe-F as. str	420.4(192.9)	383.6(161.3)
	Mo-F sy. str	677.9(86.5)	799.9(44.0)
	Mo-F as. str	718.0(222.7)	760.8(232.3)
TS2			
	Mo-Xe-F bend	-97.5(3.0)	-112.2(4.6)
	Xe-Mo str	242.9(45.4)	252.0(199.4)
	Xe-F str	298.8(81.1)	323.9(127.2)
	Mo-F sy str	686.9(174.5)	701.0(179.3)
	Mo-F as str	664.2(129.5)	692.8(141.6)
	Mo-F as. str	737.5(172.7)	762.7(217.4)
	Xe-Mo-F as. bend	103.0(2.6)	106.6(0.6)
	Xe-Mo-F as. bend	131.2(7.2)	125.7(7.4)
	Xe-Mo-F sy. bend	146.8(0.2)	142.3(3.6)
XeF_2			
	Xe-F sy. str	509.5(0.0)	529.3(0.0)
	Xe-F as. str	549.5(246.6)	575.8(261.0)
	F-Xe-F bend	221.7(15.6)	216.0(15.8)
MoF_2			
	Mo-F sy. str	627.2(58.2)	618.5(70.9)
	Mo-F as. str	658.7(199.6)	663.7(242.0)
	F-Mo-F bend	148.1(9.2)	123.8(12.5)

Table S2. (Continued)

		B3LYP	MP2
XeF_4			
	Xe-F sy. str	546.9(0.0)	558.4(0.0)
	Xe-F as. str	503.1(0.0)	522.7(0.0)
	Xe-F as. str	576.4(269.1)	603.3(267.3)
	F-Xe-F sy. bend in-plane	215.6(0.0)	215.9(0.0)
	F-Xe-F as. bend in-plane	161.2(1.3)	159.1(1.9)
	F-Xe-F sy. bend out-of-plane	290.8(33.4)	191.9(33.6)
	F-Xe-F as. bend out-of-plane	170.3(0.0)	168.5(0.0)
MoF_4			
	Mo-F sy. str	688.1(1.3)	699.6(0.0)
	Mo-F sy. str	673.4(183.6)	688.9(215.8)
	F-Mo-F sy. bend	133.6(0.6)	144.1(0.0)
	F-Mo-F as. bend	115.9(31.2)	112.9(34.9)

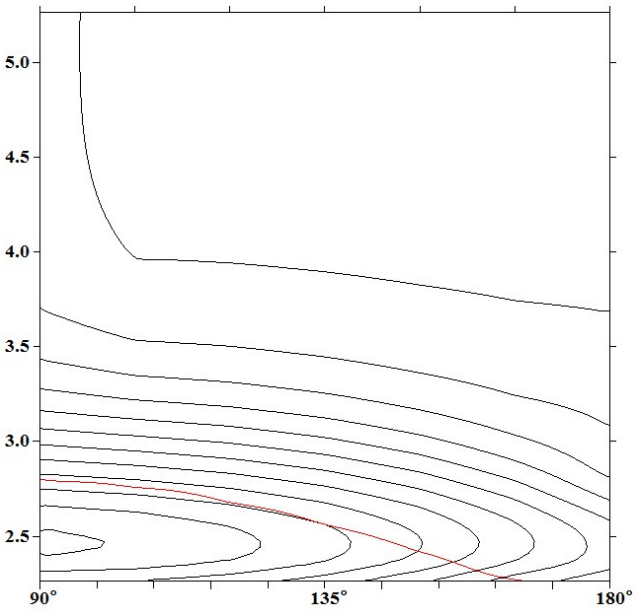

Figure S1. Contour plots of the MP2/AVTZ potential energy surfaces of F_2XeMoF_2 as a function of D_{FXeMoF} and R_{XeMo}. The contours are drawn by 5 kcal mol^{-1}. The red line is the intersection line between singlet and quintet PES.

In order to determine the transition state in reaction (2), the singlet and quintet potential energy surfaces (PESs) are scanned by changing the bond length of Xe – Mo and dihedral angle (D) of F – Xe – Mo – F. The bond lengths of Xe – F and Mo – F bonds and the bond angles of F – Xe – Mo and Xe – Mo – F are fixed considering their relatively weak influences on the results of calculation. Figure S1 shows the singlet state PES, with the intersection line between the singlet and quintet PESs being presented in red at the MP2 level of theory. The intersection line is tangent to the equi-potential line of 11 kcal mol^{-1} at about 2.7 Å of R_{XeMo} and 130° of D_{FXeMoF}. The tangency point is corresponding to transition state of reaction (2), i.e. the lowest energy point of the intersection line. The energy barrier is thus approximately 11 kcal mol^{-1}.

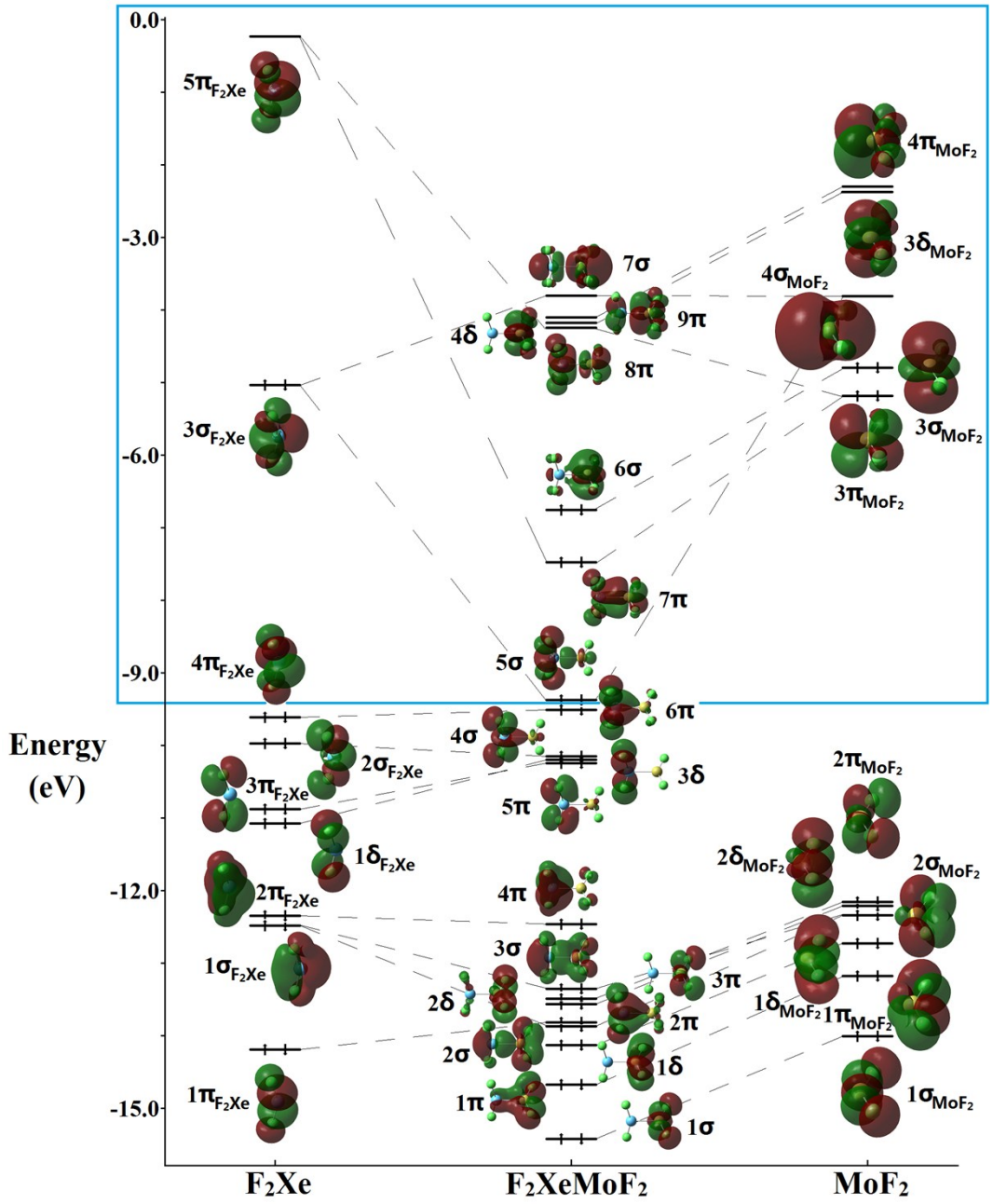

Figure S2. Energy graph of NMOs about F_2XeMoF_2, the NMOs correlated to the Xe-Mo bonding are framed by the blue line.