Supporting Information for

Correlated Ab Initio and Density Functional Studies on H_2 Activation by FeO^+

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Table S1: Key optimized distances r (in Å) and angles θ (in °) obtained at the BP86, TPSS, B3LYP, BHLYP and CASSCF levels with the TZVPP basis set. See Fig. 1 for the definitions of r_i and θ_i in each species.

		^{6}**1** [a]	^{4}**1** [b]	^{6}**TS1** [c]	^{4}**TS1** [b]	^{6}**2** [c]	^{4}**2** [b]	^{6}**TS2** [c]	^{4}**TS2** [d]	^{6}**3** [a]	^{4}**3** [a]	^{6}**FeO$^+$** [e]	^{4}**FeO$^+$** [f]	**H_2O**	**H_2**
BP86	r_1	1.637	1.565	1.731	1.619	1.748	1.685	1.812	1.750	2.090	1.951	1.631	1.601	0.881	0.750
	r_2	0.782	0.846	1.039	0.970	0.980	0.980	0.985	0.980	0.978	0.975				
	r_3	1.963	1.669	1.782	1.695	1.583	1.530	1.665	1.577						
	r_4			1.323	1.402			1.513	1.510						
	θ_1	168.3	96.8	78.4	82.4	142.9	83.4	51.4	53.7	107.7	107.5			120.2	
	θ_2			69.4	69.2	137.5	131.7	170.8	133.3						
TPSS	r_1	1.643	1.566	1.739	1.625	1.744	1.682	1.812	1.760	2.085	1.957	1.635	1.621	0.968	0.743
	r_2	0.772	0.815	1.041	0.981	0.977	0.987	0.982	0.976	0.976	0.972				
	r_3	1.970	1.708	1.781	1.691	1.586	1.507	1.682	1.579						
	r_4			1.301	1.362			1.506	1.497						
	θ_1	168.6	96.6	77.4	81.0	140.7	89.5	50.9	53.0	107.7	107.5			104.1	
	θ_2			70.0	70.2	138.8	128.6	172.1	133.9						
B3LYP	r_1	1.641	1.557	1.725	1.612	1.732	1.685	1.798	1.752	2.103	1.994	1.633	1.691	0.961	0.743
	r_2	0.769	0.798	1.012	0.929	0.969	0.970	0.971	0.967	0.969	0.966				
	r_3	1.992	1.761	1.798	1.678	1.582	1.515	1.712	1.580						
	r_4			1.315	1.429			1.605	1.533						
	θ_1	168.9	98.1	76.6	82.6	139.7	91.3	54.4	54.5	107.7	108.1			104.9	
	θ_2			70.8	68.3	143.4	130.3	173.6	138.1						
BHLYP	r_1	1.730	1.743	1.781	1.751	1.704	1.717	1.809	1.768	2.105	1.993	1.654	1.743	0.949	0.737
	r_2	0.765	0.760	0.826	0.893	0.954	0.955	0.956	0.954	0.958	0.956				
	r_3	1.962	2.05	2.870	1.903	1.576	1.594	1.781	1.638						
	r_4			1.355	1.332			1.726	1.598						
	θ_1	168.8	161.5	48.0	68.3	140.9	87.6	57.5	55.8	107.6	108.3			105.7	
	θ_2			102.4	77.6	153.9	131.4	149.3	137.9						
CASSCF	r_1	1.698	1.595				1.751			2.152		1.698	1.755	0.963	0.755
	r_2	0.774	0.755				0.969			0.948					
	r_3	2.141	2.017				1.599								
	r_4														
	θ_1	169.6	103.5				76.9			107.3				102.9	
	θ_2						128.7								

[a] C_{2v}, A_1 state; [b] C_s, A'' state; [c] C_s, A' state; [d] C_1, A state; [e] $C_{\infty v}$, Σ^+ state; [f] $C_{\infty v}$, Φ state.

Table S2: Key optimized distances r (in Å) and angles θ (in °) of sextet and quartet 3 at the B3LYP/TZVPP level for the lowest state of each symmetry. See Fig. 1 for the definitions of r_i and θ_i in each species. The relative energies ΔE (in kcal/mol) of these states (a) are also reported.

	^{6}**3**				^{4}**3**			
	A_1	**A_2**	**B_1**	**B_2**	**A_1**	**A_2**	**B_1**	**B_2**
r_1	2.103	2.104	2.179	2.116	1.994	1.994	2.037	1.995
r_2	0.969	0.969	0.967	0.968	0.966	0.966	0.965	0.965
θ_1	107.7	107.6	107.1	107.4	108.1	108.1	107.9	107.4
ΔE	6.63	6.68	11.16	8.59	0.00	0.05	3.15	0.89

(a) These states arise from different occupation patterns of the 3d orbitals in Fe^+; see: M. Rosi and C. W. Bauschlicher, Jr., *J. Chem. Phys.* **90**, 7264-7272 (1989). In the following tables, results are given only for the lowest-energy sextet and quartet A_1 states.

Table S3: Comparison of previous and present results for the computed energies (kcal/mol) of the stationary points on the sextet (quartet) surface relative to the energy of $^6FeO^+ + H_2$. The entries are ordered according to the method used (starting with previous results from the given reference).

Ref.[e]	Method	Basis Set[b,c,d,e]	Geometry	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}**1**	^{4}**1**	^{6}**TS1**	^{4}**TS1**	^{6}**2**	^{4}**2**	^{6}**TS2**	^{4}**TS2**	^{6}**3**	^{4}**3**	$Fe^+(^6D) + H_2O$[f]	$Fe^+(^4F) + H_2O$	Δ_1[g]	Δ_2[h]
52	BP86	B1	BP86/B1	0	13	-16	-16	7	**0**	-33	-41	-7	-31	-54	-62	-4	-8	-4	50
	BP86	TZVPP	BP86/TZVPP	0.0	11.4	-16.0	-18.9	7.4	**-2.2**	-32.6	-41.3	-6.4	-29.7	-53.1	-63.4	-17.1	-19.9	-2.8	36.0
	BP86	TZVPP	B3LYP/TZVPP	0.0	12.9	-16.0	-17.9	7.5	**-8.9**	-32.4	-40.6	-6.5	-29.8	-53.0	-63.1	-17.0	-19.8	-2.8	36.0
	BP86	cc-pVQZ	B3LYP/TZVPP	0.0	13.7	-15.8	-16.9	7.5	**-8.4**	-32.2	-41.5	-6.6	-31.4	-53.3	-65.4	-16.5	-22.2	-5.7	36.8
52	B3LYP	B1	B3LYP/B1	0	8	-15	-7	8	1	-38	-41	-13	-34	-73	-79	-39	-41	-2	34
49	B3LYP	B2	B3LYP/B2	0	7	-13	-6	10	1	-34	-38	-11	-30	-66	-75	-33	-37	-4	33
55	B3LYP[i]	6-311++G(3df,p)	B3LYP/6-311++G(3df,p)	0.0	12.4	-12.6	-5.6	9.7	0.8	**-18.9**	-38.3	-11.4	-31.6	-65.1	-74.2	-32.0	-36.9	-4.9	33.1
	B3LYP	TZVPP	B3LYP/TZVPP	0.0	7.8	-14.8	-7.9	9.0	0.0	-37.5	-41.2	-12.7	-33.6	-73.5	-78.9	-39.3	-38.7	0.6	35.5
	B3LYP	ANO	B3LYP/TZVPP	0.0	6.8	-14.7	-9.1	8.9	-1.2	-37.4	-41.9	-13.7	-35.0	-73.0	-75.8	-43.3	-53.7	-10.4	29.7
	B3LYP	cc-pVTZ	B3LYP/TZVPP	0.0	7.3	-14.8	-8.3	9.0	-0.6	-37.1	-41.4	-12.6	-34.1	-72.8	-81.4	-35.9	-39.6	-3.7	36.9
	B3LYP	cc-pVQZ	B3LYP/TZVPP	0.0	7.1	-14.8	-8.5	9.0	-0.8	-37.4	-41.9	-13.0	-34.5	-73.2	-81.7	-38.0	-41.7	-3.7	35.2
	B3LYP+DKH2	cc-pVQZ	B3LYP/TZVPP	0.0	8.3	-15.4	-8.5	9.0	-0.8	-39.5	-42.4	-12.6	-32.9	-73.3	-76.5	-38.0	-34.6	3.4	35.5
	B3LYP	cc-pwCVTZ	B3LYP/TZVPP	0.0	7.3	-14.8	-8.5	9.0	-0.7	-37.0	-41.5	-12.6	-34.1	-72.7	-81.2	-35.8	-39.4	-3.6	36.9
	B3LYP	cc-pwCVQZ	B3LYP/TZVPP	0.0	7.1	-14.8	-8.6	9.0	-0.8	-37.3	-41.9	-13.0	-34.5	-73.2	-81.8	-38.0	-41.8	-3.8	35.2
	B3LYP	def2-QZVPP	B3LYP/TZVPP	0.0	7.1	-14.8	-8.5	9.0	-0.7	-37.4	-41.8	-13.0	-34.5	-73.2	-81.7	-38.9	-42.7	-3.8	34.3
	B3LYP+DKH2	def2-QZVPP	B3LYP/TZVPP	0.0	8.3	-15.3	-7.9	9.2	-0.3	-39.4	-42.0	-12.6	-32.6	-73.7	-76.6	-39.6	-35.6	4.0	34.1
52	FT97	B1	FT97/B1	0	16	-12	-12	12	-1	-26	-34	4	-21	-38	-50	-8	-14	-6	30
	TPSS	TZVPP	TPSS/TZVPP	0.0	8.0	-15.5	-17.2	9.4	**0.3**	-30.6	-39.1	-3.6	-27.1	-51.3	-62.1	-15.2	-20.0	-4.8	36.1
	TPSS	TZVPP	B3LYP/TZVPP	0.0	11.0	-15.4	-16.9	9.4	**-6.7**	-30.5	-39.0	-3.9	-27.1	-51.2	-61.9	-15.1	-19.9	-4.8	36.1
	TPSS	cc-pVQZ	B3LYP/TZVPP	0.0	9.8	-15.3	-17.4	9.4	**-7.7**	-30.2	-39.8	-4.1	-29.4	-50.9	-65.6	-13.9	-23.8	-9.9	37.0
	BHLYP	TZVPP	BHLYP/TZVPP	0.0	-9.6	-20.9	-23.8	-2.0	**-8.0**	-48.8	-46.8	-29.0	-43.4	-102.7	-100.3	-69.9	-61.5	8.4	32.8
	BHLYP	TZVPP	B3LYP/TZVPP	0.0	-9.0	-18.7	-7.0	5.7	**-0.3**	-48.5	-46.0	-28.8	-43.0	-102.7	-100.3	-68.9	-61.5	8.4	32.8
	BHLYP	cc-pVQZ	B3LYP/TZVPP	0.0	-9.6	-18.8	-7.3	5.4	-0.8	-48.7	-46.5	-29.0	-43.4	-101.9	-100.3	-67.1	-63.2	3.9	34.8

Table S3: Continued

Ref.[e]	Method	Basis Set[b,c,d,e]	Geometry	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}**1**	^{4}**1**	^{6}**TS1**	^{4}**TS1**	^{6}**2**	^{4}**2**	^{6}**TS2**	^{4}**TS2**	^{6}**3**	^{4}**3**	$Fe^+(^6D) + H_2O$[f]	$Fe^+(^4F) + H_2O$	Δ_1[g]	Δ_2[h]
	CASSCF	TZVPP	CASSCF/TZVPP	0.0	5.4	-9.3	**-9.2**							-95.5		-66.8	-28.4	38.4	28.7
	CASSCF	ANO	BP86/TZVPP	0.0	8.9	-8.6	**-3.0**	13.7	**3.5**	-33.3	-30.0	-6.8	-26.4	-96.2	-72.0	-66.4	-28.5	37.9	29.8
	CASSCF	TZVPP	BP86/TZVPP	0.0	9.0	-8.4	**-1.9**	14.4	**10.0**	-31.4	-29.3	-5.9	-25.8	-95.3	-77.2	-68.0	-28.4	39.6	27.3
	CASSCF	TZVPP	B3LYP/TZVPP	0.0	3.0	-8.9	**-6.4**	12.8	10.0	-31.4	-28.3	-6.6	-26.1	-97.3	-77.6	-68.0	-27.3	40.7	29.3
	CASSCF	cc-pVTZ	B3LYP/TZVPP	0.0	2.5	-8.9	-7.0	12.7	9.8	-32.1	-28.2	-6.3	-25.9	-96.1	-76.6	-64.4	-25.7	38.7	31.7
	CASSCF	cc-pVQZ	B3LYP/TZVPP	0.0	2.2	-8.9	-7.5	12.7	9.7	-32.8	-28.7	-6.9	-26.5	-96.5	-77.0	-65.4	-26.7	38.7	31.1
50	CASPT2D[j]	ANO	NLSD/DZP	0	19	-5	3	19	6	-14	-25								
	CASPT2D	ANO	BP86/TZVPP	0.0	13.3	-14.0	-	16.7	8.4	-15.9	-27.8	3.7	-20.5		-61.2	-30.4	-29.6	0.8	
	CASPT2D	TZVPP	BP86/TZVPP	0.0	15.5	-12.5	3.3	15.8	9.6	-22.5	-25.1	2.4	-18.7	-69.1	-61.3	-34.2	-25.0	9.2	34.9
	CASPT2D	Δ(ANO-TZVPP)	BP86/TZVPP	0.0	-2.2	-1.5		0.9	-1.2	6.6	-2.7	1.3	-1.8		0.1	3.8	-4.6	-8.4	
	CASPT2	TZVPP	BP86/TZVPP	0.0	15.5	-12.5	3.3	15.8	9.6	-22.5	-25.1	2.4	-18.7	-69.1	-61.2	-34.9	-25.0	9.9	34.2
	CASPT2	TZVPP	CASSCF/TZVPP	0.0	31.2	-12.5	-4.1							-72.6		-36.6	-26.7	9.9	36.0
	CASPT2	TZVPP	B3LYP/TZVPP	0.0	13.7	-12.8	-0.5	15.9	9.1	-23.6	-24.7	2.5	-19.0	-69.9	-61.7	-35.0	-26.8	8.2	34.9
	CASPT2	cc-pVTZ	B3LYP/TZVPP	0.0	14.7	-13.4	15.1	16.4	7.4	-18.0	-26.0	4.0	-19.8	-68.5	-62.4	-30.2	-30.4	-0.2	38.3
	CASPT2	cc-pVQZ	B3LYP/TZVPP	0.0	14.3	-13.8	4.5	17.8	6.2	-17.5	-27.7	3.4	-21.4	-68.7	-64.8	-30.9	-33.5	-2.6	37.8
	CASPT2	Δ(cc-pVQZ-TZVPP)	B3LYP/TZVPP	0.0	0.6	-1.0	5.0	1.9	-2.9	6.1	-3.0	0.9	-2.4	1.2	-3.1	4.1	-6.7	-10.8	2.9
54	DMC	B3	B3LYP/B1	0.0	8.3	-12.7	0.0	12.9	1.4	-50.0	-49.4	-21.9	-18.9	-82.1	-93.6	-49.8	-42.4	7.4	32.3
	CCSD	TZVPP	B3LYP/TZVPP	0.0	6.4	-13.2	-0.7	13.4	6.6	-41.6	-33.8	-14.8	-30.3	-88.3	-76.7	-56.9	-43.2	13.7	31.4
	CCSD(T)	TZVPP	B3LYP/TZVPP	0.0	12.2	-12.8	-1.8	13.1	6.0	-37.6	-31.7	-9.4	-26.7	-79.1	-68.8	-47.4	-34.8	12.6	31.7
	CCSD(T)+ZPE[k]	TZVPP	B3LYP/TZVPP	0.0	12.0	-10.6	1.5	13.8	7.7	-34.3	-28.2	-8.1	-23.7	-71.9	-61.3	-41.6	-29.0	12.6	30.3
49	CCSD(T)+ZPE	B2	B3LYP/B2	0	13	-12	0	13	8	-31	-30	-7	-22	-70	-67	-37	-32	5	33
	CCSD(T)+CV+DKH2+ZPE[l]	cc-pVTZ	B3LYP/TZVPP	0.0	12.0	-12.4	-3.6	10.8	2.3	-34.3	-33.0	-8.6	-25.4	-71.4	-65.3	-37.5	-26.4	11.1	33.9
55	CCSD(T)+CV+DKH2+ZPE[m]	aug-cc-pVTZ	B3LYP/6-311++G(3df,p)	0.0	14.4	-12.8	-5.9	10.7	0.6	-33.0	-33.4	-8.1	-24.6	-69.9	-65.7	-37.5	-27.7	9.8	32.4
	CCSD(T)+CV+DKH2+ZPE[l]	cc-pVQZ	B3LYP/TZVPP	0.0	11.5	-12.9	-5.4	10.2	0.7	-35.2	-35.3	-10.1	-27.6	-72.1	-68.0	-38.8	-29.6	9.2	33.3
55	CCSD(T) +CV+DKH2+ZPE[n]	aug-cc-pVQZ	B3LYP/6-311++G(3df,p)	0.0	13.3	-12.9	-7.1	10.4	-0.5	-33.4	-34.8	-9.0	-26.1	-70.7	-67.8	-37.9	-29.9	8	32.8
	CCSD(T)+CV+DKH2+ZPE	CBS[o]	B3LYP/TZVPP	0.0	11.6	-13.3	-6.5	9.9	-0.4	-35.6	-36.7	-10.9	-29.0	-72.5	-69.8	-39.4	-31.6	7.8	33.1
55	CCSD(T) +CV+DKH2+ZPE	CBS[p]	B3LYP/6-311++G(3df,p)	0.0	12.6	-13.0	-7.9	10.1	-1.4	-33.5	-35.7	-9.5	-27.2	-71.1	-69.1	-38.0	-31.3	6.7	33.1

Table S3: Continued (Footnotes)

(a) If no reference is given, the results were obtained in the present study.

(b) B1: Wachters [8s6p4d] basis for Fe, Dunning TZ2P basis for H and O

(c) B2: Modified Ahlrichs TZVP basis for Fe, 6-311++G(2df,2p) for H and O

(d) B3: Stuttgart pseudopotentials that include relativistic corrections for Fe and O, 6-311++G(2df,2p) for H; Slater-Jastrow type guiding wave functions

(e) ANO: [8s7p6d4f2g], [3s2p1d] and [5s4p3d2f] ANO basis sets for Fe, H and O, respectively

(f) Experimental (including ZPE): -34.9 $\pm$ 0.5 kcal/mol (refs. 122 and 123); computational target without ZPE: -40.7 $\pm$ 0.5 kcal/mol.

(g) Excitation energy of Fe^+ [$\Delta_1 = E(^4F) - E(^6D)$]. Experimental: 5.8 kcal/mol (refs. 49 and 124)

(h) Dissociation energy of ^{6}**3** [$\Delta_2 = E(Fe^+) + E(H_2O) - E(Fe\text{-}OH_2^+)$]. Experimental value at 0 K (including ZPE): 30.6 $\pm$ 1.5 kcal/mol (ref. 125); computational target without ZPE: 32.0 $\pm$ 1.5 kcal/mol.

(i) The bold number must be a typing error.

(j) As the ^{6}**3** and "$^6Fe^+ + H_2O$" energies of -67 and -36 kcal/mol given in ref. 50 were computed at the MCPF/[8s6p4d1f] level, they are not shown in this table to avoid misleading comparisons.

(k) ZPE corrections were calculated at the B3LYP/TZVPP level.

(l) Basis sets: cc-pwCVQZ for the CV correction, def2-QZVPP for the DKH2 correction, and TZVPP (at the B3LYP level) for the ZPE; UKS-B3LYP orbitals were used as the reference.

(m) Basis sets: aug-cc-pwCVTZ for the CV and DKH2 corrections, and 6-311++G(3df,p) (at the B3LYP level) for the ZPE; RO-B3LYP orbitals were used as the reference.

(n) Basis sets: aug-cc-pwCVQZ for the CV and DKH2 corrections, and 6-311++G(3df,p) (at the B3LYP level) for the ZPE; RO-B3LYP orbitals were used as the reference.

(o) Extrapolation to the complete basis set limit using the data of (l)

(p) Extrapolation to the complete basis set limit using the data from (m) and (n)

Table S4: CC reaction profiles (kcal/mol) using UHF reference orbitals.

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
CCSD	TZVPP	0.0	6.4	-13.2	-0.7	13.4	6.6	-41.6	-33.8	-14.8	-30.3	-88.3	-76.7	-56.9	-43.2	13.7	31.4
CCSD[T]	TZVPP	0.0	16.8	-12.2	-2	14.2	7.8	-34.3	-27.7	-4.2	-22.3	-72.3	-64.1	-40.5	-28	12.5	31.8
CCSD(T)	TZVPP	0.0	12.2	-12.8	-1.8	13.1	6.0	-37.6	-31.7	-9.4	-26.7	-79.1	-68.8	-47.4	-34.8	12.6	31.7
CCSDT	TZVPP	0.0	10.8	-13.2	-3.5	11.4	4.3	-36.5	-32.0	-9.1	-26.8	-77.4	-67.5	-45.6	-32.9	12.7	31.8
CCSDT[Q]	TZVPP	0.0	12.4	-13.0	-3.3	11.1	5.2	-34.1	-30.4	-7.7	-25.6	-76.3	-66.1	-44.6	-31.9	12.7	31.7
CCSDT(Q)	TZVPP	0.0	13.2	-12.9	-4.1	11.3	5.1	-33.5	-29.5	-5.9	-24.1	-73.4	-63.6	-41.6	-29.0	12.6	31.8
CCSD	cc-pVDZ	0.0	7.4	-13.8	-1.2	14.3	7.2	-36.5	-31.5	-11.3	-27.4	-84.9	-78.3	-45.1	-36.7	8.4	39.8
CCSD[T]	cc-pVDZ	0.0	16.7	-12.9	-2.6	16.0	8.3	-29.9	-25.3	-0.3	-19.2	-68.2	-64.2	-27.6	-20.3	7.3	40.6
CCSD(T)	cc-pVDZ	0.0	12.1	-13.5	-2.5	14.2	6.4	-33.1	-29.5	-5.9	-23.8	-76.0	-70.5	-35.5	-27.9	7.6	40.5
CCSDT	cc-pVDZ	0.0	9.8	-13.9	-4.8	12.4	4.0	-33.1	-30.9	-6.7	-25.0	-75.2	-70.1	-34.7	-27.2	7.5	40.5
CCSDT[Q]	cc-pVDZ	0.0	11.5	-13.7	-4.8	12.0	4.9	-30.4	-29.3	-5.2	-23.8	-74.2	-68.8	-33.8	-26.2	7.6	40.4
CCSDT(Q)	cc-pVDZ	0.0	11.7	-13.6	-5.7	12.6	4.5	-30.6	-28.9	-3.8	-22.6	-71.5	-66.5	-30.9	-23.5	7.4	40.6
T-(T)	cc-pVDZ	0.0	-2.3	-0.4	-2.3	-1.8	-2.4	0.0	-1.4	-0.8	-1.2	0.8	0.4	0.8	0.7	-0.1	0.0
+**(Q)**	cc-pVDZ	0.0	1.9	0.3	-0.9	0.2	0.5	2.5	2.0	2.9	2.4	3.7	3.6	3.8	3.7	-0.1	0.1
T-(T)+(Q)	cc-pVDZ	0.0	-0.4	-0.1	-3.2	-1.6	-1.9	2.5	0.6	2.1	1.2	4.5	4.0	4.6	4.4	-0.2	0.1
CCSD	cc-pVTZ	0.0	4.9	-13.7	-2.9	11.8	4.3	-39.8	-35.8	-15.1	-32.5	-88.2	-83.3	-53.7	-46.9	6.8	34.5
CCSD[T]	cc-pVTZ	0.0	14.7	-12.9	-5.2	13.3	4.3	-33.1	-30.9	-4.6	-25.5	-71.8	-70.4	-36.7	-32.0	4.7	35.1
CCSD(T)	cc-pVTZ	0.0	10.6	-13.4	-4.8	11.7	3.0	-35.6	-34.2	-9.5	-29.3	-78.6	-76.2	-43.5	-38.7	4.8	35.1
CCSDT	cc-pVTZ	0.0	9.1	-13.8	-6.7	10.5	1.2	-34.6	-34.5	-9.0	-29.4	-76.7	-74.4	-41.6	-36.7	4.9	35.1
CCSDT[Q]	cc-pVTZ	0.0	10.6	-13.6	-6.6	11.1	2.0	-32.2	-32.9	-7.7	-28.3	-75.9	-73.2	-40.9	-35.8	5.1	40.1
CCSDT(Q)	cc-pVTZ	0.0	11.3	-13.5	-7.7	10.8	1.7	-31.7	-32.1	-5.7	-26.7	-72.3	-70.3	-37.4	-32.5	4.9	39.8
+(T)	cc-pVTZ	0.0	5.7	0.3	-1.9	-0.1	-1.3	4.2	1.6	5.6	3.2	9.6	7.1	10.2	8.2	-2.0	0.6
+T	cc-pVTZ	0.0	4.2	-0.1	-3.8	-1.3	-3.1	5.2	1.3	6.1	3.1	11.5	8.9	12.1	10.2	-1.9	0.6
+T-(T)	cc-pVTZ	0.0	-1.5	-0.4	-1.9	-1.2	-1.8	1.0	-0.3	0.5	-0.1	1.9	1.8	1.9	2.0	0.1	0.0
+**(Q)**	cc-pVTZ	0.0	2.2	0.3	-1.0	0.3	0.5	2.9	2.4	3.3	2.7	4.4	4.1	4.2	4.2	0.0	4.7
+T-(T)+(Q)	cc-pVTZ	0.0	0.7	-0.1	-2.9	-0.9	-1.3	3.9	2.1	3.8	2.6	6.3	5.9	6.1	6.2	0.1	4.7
CCSD	cc-pVQZ	0.0	3.8	-14.2	-4.5	11.1	2.6	-41.2	-38.3	-17.2	-35.0	-89.7	-86.4	-55.8	-50.6	5.2	33.9
CCSD[T]	cc-pVQZ	0.0	13.5	-13.4	-7.4	12.5	2.1	-34.8	-34.0	-7.0	-28.5	-73.5	-73.9	-39.0	-36.3	2.7	34.9
CCSD(T)	cc-pVQZ	0.0	9.7	-13.9	-6.8	10.9	1.0	-37.0	-37.0	-11.7	-32.0	-79.9	-79.6	-45.5	-42.6	2.9	34.4
+(T)	cc-pVQZ	0.0	5.9	0.3	-2.3	-0.2	-1.6	4.2	1.3	5.5	3.0	9.8	6.8	10.3	8.0	-2.3	0.5
CCSDT	cc-pVQZ	0.0	8.4					-35.6		-10.7		-77.7	-77.3	-43.2	-40.2	3.0	34.5
+T-(T)	cc-pVQZ	0.0	-1.3					1.4		1.0		2.2	2.3	2.3	2.4	0.1	0.1
CCSD(T)+DKH2	cc-pVQZ	0.0	11.9	-14.9	-5.4	11.5	2.1	-39.0	-36.4	-10.2	-29.4	-78.5	-73.8	-44.0	-34.0	10.0	34.5
+DKH2	cc-pVQZ	0.0	2.2	-1.0	1.4	0.6	1.1	-2.0	0.6	1.5	2.6	1.4	5.8	1.5	8.6	7.1	0.1

Table S4: Continued

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
CCSD(T)	cc-pVTZ	0.0	10.6	-13.4	-4.8	11.7	3.0	-35.6	-34.2	-9.5	-29.3	-78.6	-76.2	-43.5	-38.7	4.8	35.1
CCSD(T)	cc-pVQZ	0.0	9.7	-13.9	-6.8	10.9	1.0	-37.0	-37.0	-11.7	-32.0	-79.9	-79.6	-45.5	-42.6	2.9	34.4
CCSD(T)	CBS	0.0	9.1	-14.3	-8.2	10.3	-0.4	-37.9	-39.0	-13.1	-33.9	-81.0	-82.1	-46.7	-45.1	1.6	34.3
CCSD-nofc	cc-pVQZ	0.0	3.7	-14.8	-5.5	10.0	1.0	-42.5	-40.8	-19.2	-37.8	-91.1	-90.1	-56.6	-52.9	3.7	34.5
CCSD[T]-nofc	cc-pVQZ	0.0	15.4	-13.8	-8.3	11.9	0.8	-36.1	-35.8	-6.9	-30	-71.4	-75.0	-36.0	-35.1	0.9	35.4
CCSD(T)-nofc	cc-pVQZ	0.0	10.5	-14.5	-8	10.1	-0.7	-37.9	-39.4	-12.6	-34	-79.8	-81.7	-44.5	-43.2	1.3	35.3
CCSD	def2-QZVPP	0.0	5.6	-12.7	-2.7	12.4	4.5	-40.2	-36.7	-15.6	-33.3	-88.2	-85.4	-54.9	-48.9	6.0	33.3
CCSD(T)	def2-QZVPP	0.0	10.8	-13.0	-5.4	11.6	2.3	-36.7	-35.9	-10.8	-30.9	-79.2	-76.4	-45.5	-41.5	4.0	33.7
CCSD+DKH2	def2-QZVPP	0.0	6.7	-13.3	-2.3	12.2	4.7	-43.4	-36.9	-14.9	-31.5	-88.3	-78.4	-55.0	-41.5	13.5	33.3
CCSD(T)+DKH2	def2-QZVPP	0.0	12	-13.6	-4.7	11.3	2.7	-39.5	-36	-10.3	-29.0	-79.2	-72.2	-45.4	-34.1	11.3	33.8
+DKH2	def2-QZVPP	0.0	1.2	-0.6	0.7	-0.3	0.4	-2.8	-0.1	0.5	1.9	0.0	4.2	0.1	7.4	7.3	0.1
CCSD	cc-pwCVTZ	0.0	5.7	-13.4	-2.1	13.2	5.0	-38	-35	-14.0	-31.7	-86.9	-84	-52.4	-46.3	6.1	34.5
CCSD(T)	cc-pwCVTZ	0.0	10.9	-13.8	-4.8	12.5	3.0	-34.4	-34.1	-8.9	-29	-77.7	-74.5	-42.6	-38.6	4.0	35.1
CCSD+CV	cc-pwCVTZ	0.0	5.5	-13.5	-1.4	13.2	5.3	-38.8	-35.7	-14.9	-32.7	-88.6	-87.3	-54.2	-48.4	5.8	34.4
CCSD(T)+CV	cc-pwCVTZ	0.0	12.2	-13.9	-3.8	13.2	3.7	-34	-34.1	-8.3	-28.8	-77.3	-72.8	-42.2	-38.5	3.7	35.1
+CV (CCSD)	cc-pwCVTZ	0.0	-0.2	-0.1	0.7	0.0	0.3	-0.8	-0.7	-0.9	-1.0	-1.7	-3.3	-1.8	-2.1	-0.3	-0.1
+CV (CCSD(T))	cc-pwCVTZ	0.0	1.3	-0.1	1.0	0.7	0.7	0.4	0.0	0.6	0.2	0.4	1.7	0.4	0.1	-0.3	0.0
CCSD+DKH2	cc-pwCVTZ	0.0	6.8	-13.9	-1.6	13	5.4	-41.2	-35.2	-13.3	-29.9	-87	-81.2	-52.5	-38.9	13.6	34.5
CCSD(T)+DKH2	cc-pwCVTZ	0.0	12.1	-14.3	-4.0	12.2	3.4	-37.3	-34.1	-8.5	-27.3	-77.8	-72.2	-42.7	-31.3	11.4	35.1
CCSD+CV+DKH2	cc-pwCVTZ	0.0	6.7	-14	-0.9	13	5.6	-41.7	-35.8	-14.3	-30.9	-88.8	-83.9	-54.4	-41	13.4	34.4
CCSD(T)+CV+DKH2	cc-pwCVTZ	0.0	13.4	-14.4	-2.9	12.9	4.1	-36.7	-34	-8.0	-26.9	-77.5	-71	-42.4	-31.2	11.2	35.1
+DKH2 (CCSD)-nocv	cc-pwCVTZ	0.0	1.1	-0.5	0.5	-0.2	0.4	-3.2	-0.2	0.7	1.8	-0.1	2.8	-0.1	7.4	7.5	0.0
+DKH2 (CCSD(T))-nocv	cc-pwCVTZ	0.0	1.2	-0.5	0.8	-0.3	0.4	-2.9	0.0	0.4	1.7	-0.1	2.3	-0.1	7.3	7.4	0.0
+DKH2 (CCSD)-withcv	cc-pwCVTZ	0.0	1.2	-0.5	0.5	-0.2	0.3	-2.9	-0.1	0.6	1.8	-0.2	3.4	-0.2	7.4	7.6	0.0
+DKH2 (CCSD(T))-withcv	cc-pwCVTZ	0.0	1.2	-0.5	0.9	-0.3	0.4	-2.7	0.1	0.3	1.9	-0.2	1.8	-0.2	7.3	7.5	0.0
+CV (CCSD)	cc-pwCVTZ	0.0	-0.1	-0.1	0.7	0.0	0.2	-0.5	-0.6	-1.0	-1.0	-1.8	-2.7	-1.9	-2.1	-0.2	-0.1
+CV (CCSD(T))	cc-pwCVTZ	0.0	1.3	-0.1	1.1	0.7	0.7	0.6	0.1	0.5	0.4	0.3	1.2	0.3	0.1	-0.2	0.0

Table S4: Continued

Method	**Basis Set**	$^{6}FeO^{+}$ + H_2	$^{4}FeO^{+}$ + H_2	**^{6}1**	**^{4}1**	**^{6}TS1**	**^{4}TS1**	**^{6}2**	**^{4}2**	**^{6}TS2**	**^{4}TS2**	**^{6}3**	**^{4}3**	$Fe^{+}(^{6}D)$ + H_2O	$Fe^{+}(^{4}F)$ + H_2O	**Δ_1**	**Δ_2**
CCSD	cc-pwCVQZ	0.0	5.0	-13.8	-3.3	12.6	3.8	-39.4	-37.1	-15.7	-33.7	-88.2	-86.0	-54.2	-49.6	4.6	34
CCSD(T)	cc-pwCVQZ	0.0	10.5	-14.2	-6.1	12.1	1.8	-35.5	-36.1	-10.5	-31.0	-78.7	-76.4	-44.2	-41.8	2.4	34.5
CCSD+CV	cc-pwCVQZ	0.0	4.8	-13.9	-2.8	12.5	3.9	-39.8	-37.9	-16.7	-35.0	-88.8	-89.9	-55.9	-52.3	3.6	32.9
CCSD(T)+CV	cc-pwCVQZ	0.0	11.8	-14.4	-5.2	12.9	2.4	-34.8	-36.2	-9.9	-31.0	-78.2	-74.9	-43.6	-42.4	1.2	34.6
+CV (CCSD(T))	cc-pwCVQZ	0.0	1.3	-0.2	0.9	0.8	0.6	0.7	-0.1	0.6	0.0	0.5	1.5	0.6	-0.6	-1.2	0.1
CCSD+DKH2	cc-pwCVQZ	0.0	6.2	-14.3	-2.9	12.4	4.2	-42.6	-37.3	-15.0	-32.0	-88.3	-83.2	-54.4	-42.2	12.2	33.9
CCSD(T)+DKH2	cc-pwCVQZ	0.0	11.7	-14.8	-5.3	11.8	2.2	-38.4	-36.2	-10.0	-29.3	-78.8	-74.0	-44.3	-34.5	9.8	34.5
+DKH2 (CCSD(T))	cc-pwCVQZ	0.0	1.2	-0.6	0.8	-0.3	0.4	-2.9	-0.1	0.5	1.7	-0.1	2.4	-0.1	7.3	7.4	0.0
+CV+DKH2	cc-pwCVQZ	0.0	2.5	-0.8	1.7	0.5	1.0	-2.2	-0.2	1.1	1.7	0.4	3.9	0.5	6.7	6.2	0.1
CCSD+CV+DKH2	cc-pwCVQZ	0.0	5.9	-14.4	-2.3	12.4	4.3	-42.8	-38.1	-16.0	-33.2	-90.0	-86.4	-56.2	-45.0	11.2	33.8
CCSD(T)+CV+DKH2	cc-pwCVQZ	0.0	13.0	-14.9	-4.3	12.6	2.8	-37.4	-36.2	-9.6	-29.2	-78.5	-73.1	-43.8	-35.1	8.7	34.7
+CV+DKH2	cc-pwCVQZ	0.0	2.5	-0.7	1.8	0.5	1.0	-1.9	-0.1	0.9	1.8	0.2	3.3	0.4	6.7	6.3	0.2
CCSD(T)	cc-pwCVTZ	0.0	10.9	-13.8	-4.8	12.5	3	-34.4	-34.1	-8.9	-29.0	-77.7	-74.5	-42.6	-38.6	4.0	35.1
CCSD(T)	cc-pwCVQZ	0.0	10.5	-14.2	-6.1	12.1	1.8	-35.5	-36.1	-10.5	-31.0	-78.7	-76.4	-44.2	-41.8	2.4	34.5
CCSD(T)	CBS	0.0	10.5	-14.6	-6.8	12.0	1.1	-36.1	-37.4	-11.5	-32.3	-79.3	-77.7	-45.0	-43.7	1.3	34.3
+CV (CCSD(T))	cc-pwCVQZ	0.0	1.3	-0.2	0.9	0.8	0.6	0.7	-0.1	0.4	0.1	0.5	1.5	0.6	-0.6	-1.2	0.1
+DKH2	def2-QZVPP	0.0	1.2	-0.6	0.7	-0.3	0.4	-2.8	-0.1	0.5	1.9	0.0	4.2	0.1	7.4	7.3	0.1
T-(T)	cc-pVTZ	0.0	-1.5	-0.4	-1.9	-1.2	-1.8	1.0	-0.3	0.5	-0.1	1.9	1.8	1.9	2.0	0.1	0.0
+**(Q)**	cc-pVTZ	0.0	2.2	0.3	-1.0	0.3	0.5	2.9	2.4	3.3	2.7	4.4	4.1	4.2	4.2	0.0	-0.2
+ZPE	TZVPP	0.0	-0.2	2.2	3.3	0.7	1.7	3.4	3.5	1.3	2.9	7.2	7.5	5.8	5.8	0.0	-1.4
CCSDT(Q)+CV+DKH2	CBS	0.0	13.7	-15.5	-8.1	11.6	0.8	-34.3	-35.5	-6.8	-27.7	-72.5	-66.1	-38.2	-30.7	7.5	34.3
CCSDT(Q)+CV+DKH2+ZPE	CBS	0.0	13.5	-13.3	-4.8	12.3	2.5	-30.9	-32.0	-5.5	-24.8	-65.3	-58.6	-32.4	-24.9	7.5	32.9

Table S5: CC reaction profiles (kcal/mol) using UKS (B3LYP) orbitals.

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
CCSD	cc-pVTZ	0.0	4.7	-13.6	1.5	11.0	7.2	-41.1	-36.5	-16.9	-33.9	-92.1	-86.0	-57.9	-50.1	7.8	34.2
CCSD(T)	cc-pVTZ	0.0	10.2	-13.8	-6.2	9.9	1.1	-36.1	-35.8	-10.7	-30.7	-79.1	-76.3	-44.1	-38.6	5.5	35.0
+(T)	cc-pVTZ	0.0	5.5	-0.2	-7.7	-1.1	-6.1	5.0	0.7	6.2	3.2	13.0	9.7	13.8	11.5	-2.3	0.8
Δ(UKS-U HF)	cc-pVTZ	0.0	-0.4	-0.4	-1.4	-1.8	-1.9	-0.5	-1.6	-1.2	-1.4	-0.5	-0.1	-0.6	0.1	0.7	-0.1
CCSD	cc-pVQZ	0.0	3.8	-14.0	-0.1	10.5	5.6	-42.2	-38.9	-18.7	-36.2	-93.3	-88.8	-59.7	-53.5	6.2	33.6
CCSD(T)	cc-pVQZ	0.0	9.7	-14.3	-8.0	9.3	-0.5	-37.0	-38.1	-12.2	-32.9	-79.8	-79.0	-45.4	-41.8	3.6	34.4
+(T)	cc-pVQZ	0.0	5.9	-0.3	-7.9	-1.2	-6.1	5.2	0.8	6.5	3.3	13.5	9.8	14.3	11.7	-2.6	0.8
Δ(UKS-U HF)	cc-pVQZ	0.0	0.0	-0.4	-1.2	-1.6	-1.5	0.0	-1.1	-0.5	-0.9	0.1	0.6	0.1	0.8	0.7	0.0
CCSD(T)	CBS	0.0	9.8	-14.7	-9.1	9.0	-1.6	-37.4	-39.5	-13.0	-34.3	-80.2	-80.8	-46.0	-43.8	2.2	34.2
CCSD	cc-pwCVTZ	0.0	4.2	-13.6	0.9	11.1	6.5	-40.7	-37.0	-17.1	-34.4	-92.2	-86.7	-57.9	-50.9	7.9	34.3
CCSD(T)	cc-pwCVTZ	0.0	10.0	-13.8	-6.9	10.0	0.5	-35.5	-36.2	-10.6	-31.1	-78.7	-76.7	-43.6	-38.9	4.7	35.1
+(T)	cc-pwCVTZ	0.0	5.8	-0.2	-7.8	-1.1	-6.0	5.2	0.8	6.5	3.3	13.5	10.0	14.3	12.0	-3.2	0.8
Δ(UKS-U HF)	cc-pwCVTZ	0.0	-0.9	0.0	-2.1	-2.5	-2.5	-1.1	-2.1	-1.7	-2.1	-1.0	-2.2	-1.0	-0.3	0.7	0.0
CCSD	cc-pwCVQZ	0.0	3.6	-14.0	-0.5	10.6	5.3	-41.9	-39.1	-18.7	-36.4	-93.3	-89.3	-59.6	-54.0	6.6	33.7
CCSD(T)	cc-pwCVQZ	0.0	9.6	-14.3	-8.4	9.5	-0.9	-36.6	-38.3	-12.1	-33.1	-79.6	-79.3	-45.1	-42.1	3.0	34.5
+(T)	cc-pwCVQZ	0.0	6.0	-0.3	-7.9	-1.1	-6.2	5.3	0.8	6.6	3.3	13.7	10.0	14.5	11.9	-3.6	0.8
Δ(UKS-U HF)	cc-pwCVQZ	0.0	-0.9	-0.1	-2.3	-2.6	-2.7	-1.1	-2.2	-1.6	-2.1	-0.9	-2.9	-0.9	-0.3	0.6	0.0
CCSD(T)	CBS	0.0	9.6	-14.6	-9.3	9.1	-1.8	-37.2	-39.6	-13.0	-34.4	-80.2	-81.1	-46.0	-44.0	2.0	34.2
Δ(UKS-U HF)	CBS	0.0	-0.9	0.0	-2.5	-2.9	-2.9	-1.1	-2.2	-1.5	-2.1	-0.9	-3.4	-1.0	-0.3	0.7	-0.1
CCSD+CV	cc-pwCVQZ	0.0	3.2	-14.2	-0.8	10.7	5.0	-41.4	-39.9	-19.5	-37.7	-95.4	-93.5	-61.7	-57.8	3.9	33.7
CCSD(T)+CV	cc-pwCVQZ	0.0	10.4	-14.6	-9.5	9.9	-1.6	-35.3	-38.9	-11.5	-33.6	-79.2	-81.5	-44.5	-43.4	1.1	34.7
+CV (CCSD(T))	cc-pwCVQZ	0.0	0.8	-0.3	-1.1	0.4	-0.7	1.3	-0.6	0.6	0.5	0.4	-2.2	0.6	-1.3	-1.9	0.2
CCSD+DKH2	cc-pwCVQZ	0.0	4.6	-14.7	0.0	10.2	5.4	-45.3	-39.5	-18.3	-34.8	-93.6	-83.6	-59.9	-46.7	13.2	33.7
CCSD(T)+DKH2	cc-pwCVQZ	0.0	10.9	-14.8	-7.8	9.3	-0.5	-39.5	-38.4	-11.9	-31.3	-79.7	-73.7	-45.2	-34.7	10.5	34.5
+DKH2 (CCSD(T))	cc-pwCVQZ	0.0	1.3	-0.5	0.6	-0.2	0.4	-2.9	-0.1	0.2	1.8	-0.1	5.6	-0.1	7.4	7.5	0.0

Table S5: Continued

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
CCSD	def2-QZVPP	0.0	4.1	-14.0	0.3	10.3	6.0	-42.7	-38.7	-18.7	-36.0	-93.4	-88.1	-60.4	-53.4	7.0	33.0
CCSD(T)	def2-QZVPP	0.0	10.0	-14.3	-7.5	9.2	-0.1	-37.5	-38.0	-12.4	-32.8	-80.2	-78.5	-46.5	-42.0	4.5	33.7
+(T)	def2-QZVPP	0.0	5.9	-0.3	-7.8	-1.1	-6.1	5.2	0.7	6.3	3.2	13.2	9.6	13.9	11.4	-2.5	0.7
Δ(UKS-U HF)	def2-QZVPP	0.0	-0.8	-1.3	-2.1	-2.4	-2.4	-0.8	-2.1	-1.6	-1.9	-1.0	-2.1	-1.0	-0.5	0.5	0.0
CCSD+DKH2	def2-QZVPP	0.0	5.1	-14.7	0.7	10.0	6.0	-46.1	-39.2	-18.4	-34.4	-93.5	-82.5	-60.5	-46.0	14.5	33.0
CCSD(T)+DKH2	def2-QZVPP	0.0	11.2	-14.8	-7.1	9.0	0.1	-40.4	-38.1	-12.2	-30.9	-80.1	-72.8	-46.3	-34.3	12.0	33.8
+DKH2 (CCSD(T))	def2-QZVPP	0.0	1.2	-0.5	0.4	-0.2	0.2	-2.9	-0.1	0.2	1.9	0.1	5.7	0.2	7.7	7.5	0.1

1) The choice of reference orbitals (HF vs B3LYP) does not affect the CCSD(T) results much.
2) The DKH2 corrections calculated with cc-pVQZ and def2-QZVPP agree to within 1.5 kcal/mol.
3) The core-valence and DKH2 corrections are essentially additive.
4) The contributions from the perturbative quadruples (Q) computed with the cc-pVTZ and cc-pVQZ basis sets are nearly the same.

Table S6: T_1-diagnostic values at the CCSD(T)/cc-pwCVQZ level using UHF and UKS (B3LYP) orbitals.

Reference	$^6FeO^+$	$^4FeO^+$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	Fe^+ (^{6}D)	Fe^+ (^{4}F)
UHF	0.068	0.047	0.057	0.106	0.057	0.082	0.045	0.062	0.051	0.056	0.014	0.091	0.012	0.012
UKS	0.012	0.023	0.018	0.023	0.017	0.020	0.024	0.019	0.023	0.018	0.019	0.016	0.018	0.014

Table S7: DFT reaction profiles (kcal/mol).

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
GGA functionals																	
BP86	cc-pVQZ	0.0	13.7	-15.8	-16.9	7.5	-8.4	-32.2	-41.5	-6.6	-31.4	-53.3	-65.4	-16.5	-22.2	-5.7	36.8
PBE	cc-pVQZ	0.0	14.3	-16.4	-17.9	6.0	-9.7	-33.2	-42.5	-8.1	-32.7	-54.2	-66.3	-16.7	-22.2	-5.5	37.5
BLYP	cc-pVQZ	0.0	11.2	-14.5	-16.4	10.8	-5.8	-29.3	-40.0	-3.4	-28.8	-49.9	-65.3	-13.6	-22.6	-9.0	36.3
+DKH2	cc-pVQZ	0.0	1.2	-0.6	0.2	0.4	0.3	-1.6	-0.2	0.1	1.7	-0.1	4.8	-0.2	6.4	6.6	-0.1
BLYP+DKH2	cc-pVQZ	0.0	12.4	-15.1	-16.2	11.2	-5.5	-30.9	-40.2	-3.3	-27.1	-50.0	-60.5	-13.8	-16.2	-2.4	36.2
XLYP	cc-pVQZ	0.0	10.3	-14.6	-16.7	11.1	-5.7	-29.2	-40.0	-3.3	-28.8	-50.1	-65.9	-13.4	-23.1	-9.7	36.7
OLYP	cc-pVQZ	0.0	17.8	-10.7	-6.2	13.1	3.2	-26.1	-31.2	1.9	-22.2	-46.0	-59.9	-12.7	-24.2	-11.5	33.3
Hybrid functionals																	
B3LYP	TZVPP	0.0	7.8	-14.8	-7.9	9.0	0.0	-37.5	-41.2	-12.7	-33.6	-73.5	-78.9	-39.3	-38.7	0.6	39.6
B3LYP	cc-pVTZ	0.0	7.3	-14.8	-8.3	9.0	-0.6	-37.1	-41.4	-12.6	-34.1	-72.8	-81.4	-35.9	-39.6	-3.7	36.9
B3LYP	cc-pVQZ	0.0	7.1	-14.8	-8.5	9.0	-0.8	-37.4	-41.9	-13.0	-34.5	-73.2	-81.7	-38.0	-41.7	-3.7	35.2
B3LYP+DKH2	cc-pVQZ	0.0	8.3	-15.4	-8.5	9.0	-0.8	-39.5	-42.4	-12.6	-32.9	-73.3	-76.5	-38.0	-34.6	3.4	35.5
+DKH2	cc-pVQZ	0.0	1.2	-0.6	0.0	0.1	0.0	-2.1	-0.5	0.4	1.6	-0.1	5.2	0.0	7.1	7.1	0.1
B3LYP	cc-pwCVTZ	0.0	7.3	-14.8	-8.5	9.0	-0.7	-37.0	-41.5	-12.6	-34.1	-72.7	-81.2	-35.8	-39.4	-3.6	36.9
B3LYP	cc-pwCVQZ	0.0	7.1	-14.8	-8.6	9.0	-0.8	-37.3	-41.9	-13.0	-34.5	-73.2	-81.8	-38.0	-41.8	-3.8	35.2
B3LYP	def2-QZVPP	0.0	7.1	-14.8	-8.5	9.0	-0.7	-37.4	-41.8	-13.0	-34.5	-73.2	-81.7	-38.9	-42.7	-3.8	34.3
B3LYP+DKH2	def2-QZVPP	0.0	8.3	-15.3	-7.9	9.2	-0.3	-39.4	-42.0	-12.6	-32.6	-73.7	-76.6	-39.6	-35.6	4.0	34.1
+DKH2	def2-QZVPP	0.0	1.2	-0.5	0.6	0.2	0.4	-2.0	-0.2	0.4	1.9	-0.5	5.1	-0.7	7.1	7.8	-0.2
B3LYP	ANO	0.0	6.8	-14.7	-9.1	8.9	-1.2	-37.4	-41.9	-13.7	-35.0	-73.0	-75.8	-43.3	-53.7	-10.4	29.7
B1LYP	cc-pVQZ	0.0	4.1	-14.6	-6.4	9.1	0.8	-38.8	-41.9	-15.2	-35.3	-78.1	-84.8	-43.3	-45.6	-2.3	34.8
CAM-B3LYP	cc-pVQZ	0.0	4.2	-16.4	-1.8	6.7	2.7	-41.7	-39.5	-18.1	-38.8	-72.0	-75.2	-43.7	-48.7	-5.0	28.3
O3LYP	cc-pVQZ	0.0	16.5	-15.2	-9.6	5.4	-3.3	-37.2	-41.4	-11.2	-34.8	-65.0	-76.0	-27.7	-34.2	-6.5	37.3
X3LYP	cc-pVQZ	0.0	6.3	-15.3	-8.7	7.9	-1.3	-38.8	-43.0	-14.8	-36.0	-75.7	-83.7	-39.8	-43.0	-3.2	35.9
B1P	cc-pVQZ	0.0	5.6	-15.7	-7.2	5.9	-2.2	-41.5	-43.6	-18.4	-38.2	-81.4	-85.2	-46.1	-45.6	0.5	35.3
B3P	cc-pVQZ	0.0	8.4	-15.7	-9.0	6.4	-3.1	-39.6	-43.3	-15.6	-36.9	-75.9	-82.0	-40.2	-41.6	-1.4	35.7
PBE0	cc-pVQZ	0.0	6.2	-15.8	-7.5	5.0	-2.8	-42.1	-44.0	-19.2	-38.8	-82.1	-85.6	-46.7	-45.8	0.9	35.4
BHLYP	cc-pVQZ	0.0	-9.6	-18.8	-7.3	5.4	-0.8	-48.7	-46.5	-29.0	-43.4	-101.9	-100.3	-67.1	-63.2	3.9	34.8

Table S7: Continued

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
Meta and hybrid-meta GGAs																	
M05	cc-pVQZ	0.0	15.1	-12.2	2.1	9.2	9.2	-36.4	-34.3	-4.7	-29.1	-57.8	-75.4	-24.5	-32.9	-8.4	33.3
M06	cc-pVQZ	0.0	12.5	-14.8	-1.1	7.3	4.2	-41.0	-39.2	-10.0	-33.2	-67.4	-75.6	-33.4	-34.1	-0.7	34.0
M06L	cc-pVQZ	0.0	13.2	-16.6	-9.7	5.2	-1.7	-39.9	-39.2	-6.2	-29.3	-56.5	-66.1	-17.1	-25.4	-8.3	39.4
M062X	cc-pVQZ	0.0	-6.0	-17.1	-7.4	0.1	-3.1	-53.0	-49.9	-33.1	-49.8	-102.7	-103.7	-62.2	-63.6	-1.4	40.5
M06HF	cc-pVQZ	0.0	-36.2	-16.7	-7.0	-20.9	-6.0	-69.5	-74.7	-67.7	-81.4	-145.7	-145.5	-102.1	-93.8	8.3	43.6
A																	
TPSS	cc-pVQZ	0.0	9.8	-15.3	-17.4	9.4	-7.7	-30.2	-39.8	-4.1	-29.4	-50.9	-65.6	-13.9	-23.8	-9.9	37.0
TPSSh	cc-pVQZ	0.0	7.8	-15.2	-13.0	8.7	-4.7	-33.9	-40.4	-8.7	-31.9	-62.4	-73.6	-26.4	-33.4	-7.0	36.0
TPSS0	cc-pVQZ	0.0	1.9	-15.1	-7.5	7.5	-1.6	-39.5	-42.2	-16.6	-36.3	-78.5	-84.6	-43.4	-46.4	-3.0	35.1
+DKH2	cc-pVQZ	0.0	1.3	-0.7	0.1	0.1	0.0	-2.4	-0.6	0.7	1.6	-0.1	5.8	-0.1	7.5	7.6	0.0
TPSS0+DKH2	cc-pVQZ	0.0	3.2	-15.8	-7.4	7.6	-1.6	-41.9	-42.8	-15.9	-34.7	-78.6	-78.8	-43.5	-38.9	4.6	35.1
Double hybrid functionals																	
B2PLYP	cc-pVQZ	0.0	17.0	-1.4	7.4	19.8	12.2	-30.7	-33.0	-5.7	-26.8	-70.6	-80.4	-35.5	-40.7	-5.2	35.1
+DKH2	cc-pVQZ	0.0	1.8	0.0	0.7	0.0	0.5	-1.6	0.1	1.2	2.3	0.6	5.9	0.8	7.9	7.1	0.2
B2PLYP+DKH2	cc-pVQZ	0.0	18.8	-1.4	8.1	19.8	12.7	-32.3	-32.9	-4.5	-24.5	-70.0	-74.5	-34.7	-32.8	1.9	35.3
B2PLYP-D3	cc-pVQZ	0.0	17.0	-1.6	7.1	19.6	12.1	-31.1	-33.5	-6.2	-27.2	-71.8	-81.4	-35.5	-40.7	-5.2	36.3
ZPE (B3LYP)	TZVPP	0.0	-0.2	2.2	3.3	0.7	1.7	3.4	3.5	1.3	2.9	7.2	7.5	5.8	5.8	0.0	-1.4
CCSD(T) (without ZPE)	CBS	0.0	13.7	-15.5	-8.1	11.6	0.8	-34.3	-35.5	-6.8	-27.7	-72.5	-66.1	-38.2	-30.7	7.5	34.3

1) Hybrid functionals give much better results than GGA functionals.

2) The quartet $^4\Phi$ state of FeO^+ is not the lowest quartet root for GGA functionals. The results listed above always refer to the $^4\Phi$ state.

Table 8: CASSCF reaction profiles (kcal/mol).

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}**1**	^{4}**1**	^{6}**TS1**	^{4}**TS1**	^{6}**2**	^{4}**2**	^{6}**TS2**	^{4}**TS2**	^{6}**3**	^{4}**3**	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
CASSCF	TZVPP	0.0	3.0	-8.9	-6.4	12.8	10.0	-31.4	-28.3	-6.6	-26.1	-97.3	-77.6	-68.0	-27.3	40.7	29.3
+DKH2	TZVPP	0.0	1.1	2.6	1.4	0.4	1.0	1.6	1.6	0.9	2.1	0.6	1.8	0.5	8.2	7.7	-0.1
CASSCF+DKH2	TZVPP	0.0	4.1	-6.3	-5.0	13.2	11.0	-29.8	-26.7	-5.7	-24.0	-96.7	-75.8	-67.5	-19.1	48.4	29.2
CASSCF	cc-pVTZ	0.0	2.5	-8.9	-7.0	12.7	9.8	-32.1	-28.2	-6.3	-25.9	-96.1	-76.6	-64.4	-25.7	38.7	31.7
CASSCF	cc-pVQZ	0.0	2.2	-8.9	-7.5	12.7	9.7	-32.8	-28.7	-6.9	-26.5	-96.5	-77.0	-65.4	-26.7	38.7	31.1
CASSCF	CBS	0.0	2.1	-8.9	-7.6	12.7	9.6	-33.0	-28.8	-7.0	-26.7	-96.6	-77.1	-65.6	-27.0	38.6	31.0
+DKH2	cc-pVQZ	0.0	1.2	-0.4	0.9	0.3	0.5	-4.1	-0.1	1.2	1.7	1.0	2.0	1.0	8.0	7.0	0.0
CASSCF+DKH2	cc-pVQZ	0.0	3.4	-9.3	-6.6	13.0	10.2	-36.9	-28.8	-5.7	-24.8	-95.5	-75	-64.4	-18.7	45.7	31.1
Δ(cc-pVQZ-TZVPP)		0.0	-0.8	0.0	-1.1	-0.1	-0.3	-1.4	-0.4	-0.3	-0.4	0.8	0.6	2.6	0.6	-2.0	1.8
Δ(cc-pVQZ-TZVPP)+DKH2		0.0	-0.7	-3.0	-1.6	-0.2	-0.8	-7.1	-2.1	0	-0.8	1.2	0.8	3.1	0.4	-2.7	1.9
CASSCF	def2-QZVPP	0.0	2.2	-8.9	-7.4	12.7	9.7	-32.7	-28.7	-6.8	-26.4	-96.4	-77.0	-65.8	-27.1	38.7	30.6
+DKH2	def2-QZVPP	0.0	1.2	**-6.7**	1.2	1.8	0.8	-3.9	1.5	0.7	1.9	0.5	1.7	0.4	7.8	7.4	-0.1
CASSCF+DKH2	def2-QZVPP	0.0	3.4	**-15.6**	-6.2	14.5	10.5	-36.6	-27.2	-6.1	-24.5	-95.9	-75.3	-65.4	-19.3	46.1	30.5
CASSCF	cc-pwCVTZ	0.0	2.4	-8.9	-7.2	12.7	9.7	-32.3	-28.4	-6.4	-26.1	-96.2	-76.7	-64.4	-25.7	38.7	31.8
+DKH2	cc-pwCVTZ	0.0	1.2	-0.3	1.3	0.4	0.8	-3.8	0.3	1.0	2.0	0.5	1.7	0.4	7.8	7.4	-0.1
CASSCF+DKH2	cc-pwCVTZ	0.0	3.6	-9.2	-5.9	13.1	10.5	-36.1	-28.1	-5.4	-24.1	-95.7	-75.0	-64.0	-17.9	46.1	31.7
CASSCF	cc-pwCVQZ	0.0	2.2	-8.9	-7.5	12.7	9.6	-32.8	-28.7	-6.9	-26.5	-96.5	-77.0	-65.3	-26.7	38.6	31.2
+DKH2	cc-pwCVQZ	0.0	1.2	-0.3	1.3	0.4	0.9	-3.9	0.3	1.2	2	0.6	1.7	0.3	7.8	7.5	-0.3
CASSCF+DKH2	cc-pwCVQZ	0.0	3.4	-9.2	-6.2	13.1	10.5	-36.7	-28.4	-5.7	-24.5	-95.9	-75.3	-65.0	-18.9	46.1	30.9

1) The CASSCF results are not very sensitive to the choice of basis set dependent.

2) The large DKH2 correction with def2-QZVPP for sextet **1** (in boldface) is probably a computational artifact.

Table S9: Effects of MRCI thresholds on the reaction profile (kcal/mol).

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2	Thresholds
MRCI	TZVPP	0.0	11.0	-8.0	3.0	17.1	12.6	-25.6	-24.5	2.3	-20.3	-77.5	-64.1	-52.7	-36.8	15.9	24.8	$T_{sel}=10^{-6}$; $T_{pre}=10^{-4}$
MRCI+Q	TZVPP	0.0	13.1	-9.7	4.1	16.1	12.2	-27.3	-24.9	-1.7	-19.4	-74.2	-63.6	-45.3	-30.8	14.5	28.9	
MRCI	TZVPP	0.0	11.4	-8.3	3.5	18.7	13.2	-24.4	-23.7	0.0	-18.1	-76.7	-63.2	-51.6	-35.7	15.9	25.1	$T_{sel}=10^{-7}$; $T_{pre}=10^{-4}$
MRCI+Q	TZVPP	0.0	13.6	-10.4	3.6	16.8	11.8	-27.0	-24.9	-0.8	-18.5	-72.9	-62.4	-43.2	-28.8	14.4	29.7	
MRCI	TZVPP	0.0	11.5	-8.8	2.2	17.1	11.5	-25.9	-25.1	-0.9	-19.2	-76.4	-63.3	-50.9	-35.0	15.9	25.5	$T_{sel}=10^{-8}$; $T_{pre}=10^{-4}$
MRCI+Q	TZVPP	0.0	13.6	-11.1	1.6	14.4	9.2	-29.5	-26.9	-2.3	-20.1	-72.3	-62.2	-42.0	-27.5	14.5	30.3	
MRCI	cc-pVQZ	0.0	9.9	-9.1	-2.9	13.5	6.7	-25.1	-30.3	-3.8	-29.1	-76.3	-67.1	-50.8	-42.7	8.1	25.5	$T_{sel}=10^{-6}$; $T_{pre}=10^{-4}$
MRCI+Q	cc-pVQZ	0.0	12.0	-10.8	-0.9	13.7	7.2	-25.1	-29.7	-3.0	-26.4	-72.9	-67.4	-42.9	-36.9	6.0	30.0	
Δ(cc-pVQZ-TZVPP)		0.0	-1.1	-1.1	-5.0	-2.4	-5.0	2.2	-4.8	-1.3	-7.0	1.3	-3.8	2.4	-6.1	-8.5	1.1	
MRCI	cc-pVQZ	0.0	9.9	-9.3	-1.2	17.9	8.8	-21.7	-27.6	-0.3	-22	-75.3	-65.2	-49.9	-41.7	8.2	25.4	$T_{sel}=10^{-8}$; $T_{pre}=10^{-5}$
+Q	cc-pVQZ	0.0	2.2	-2.4	0.1	-1.4	-1.4	-3.1	-1.1	-0.7	-0.1	4.0	-0.2	10.2	8.0	-2.2	6.2	
MRCI+Q	cc-pVQZ	0.0	12.1	-11.7	-1.1	16.5	7.4	-24.8	-28.7	-1	-22.1	-71.3	-65.4	-39.7	-33.7	6.0	31.6	
MRCI	cc-pVQZ	0.0	9.8	-9.4	-1.5	17.6	8.3	-22.7	-27.9	-0.7	-22.4	-75.3	-65.3	-49.9	-41.7	8.2	25.4	$T_{sel}=10^{-8}$; $T_{pre}=10^{-6}$
+Q	cc-pVQZ	0.0	2.2	-2.3	0.2	-1.3	-1.1	-1.8	-1.0	-0.5	0.0	4.0	-0.2	10.2	8.0	-2.2	6.2	
MRCI+Q	cc-pVQZ	0.0	12	-11.7	-1.3	16.3	7.2	-24.5	-28.9	-1.2	-22.4	-71.3	-65.5	-39.7	-33.7	6.0	31.6	

1) The MRCI absolute energies with $T_{sel}=10^{-8}$ and $T_{pre}=10^{-5}$ or $T_{pre}=10^{-6}$ are almost identical and very close to the corresponding CCSD(T) results. With less stringent thresholds, the MRCI absolute energies still differ significantly from the converged values, while MRCI reaction energies are already close to those obtained with $T_{sel}=10^{-8}$ and $T_{pre}=10^{-5}$ or $T_{pre}=10^{-6}$ (see above).
2) There is a significant basis set effect when going from TZVPP to cc-pVQZ.

Table S10: MRCI reaction profiles (kcal/mol) with $T_{sel}=10^{-6}$ and $T_{pre}=10^{-4}$ ($T_{nat}=10^{-5}$).

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+ (^6D) + H_2O$	$Fe^+ (^4F) + H_2O$	Δ_1	Δ_2
MRCI	TZVPP	0.0	11.0	-8.0	3.0	17.1	12.6	-25.6	-24.5	2.3	-20.3	-77.5	-64.1	-52.7	-36.8	15.9	24.8
MRCI+Q	TZVPP	0.0	13.1	-9.7	4.1	16.1	12.2	-27.3	-24.9	-1.7	-19.4	-74.2	-63.6	-45.3	-30.8	14.5	28.9
MRCI	cc-pVQZ	0.0	9.9	-9.1	-2.9	13.5	6.7	-25.1	-30.3	-3.8	-29.1	-76.3	-67.1	-50.8	-42.7	8.1	25.5
MRCI+Q	cc-pVQZ	0.0	12.0	-10.8	-0.9	13.7	7.2	-25.1	-29.7	-3.0	-26.4	-72.9	-67.4	-42.9	-36.9	6.0	30.0
Δ(cc-pVQZ-TZVPP)		0.0	-1.1	-1.1	-5.0	-2.4	-5.0	2.2	-4.8	-1.3	-7.0	1.3	-3.8	2.4	-6.1	-8.5	1.1
MRCI+3sp	cc-pVQZ	0.0	9.2	-9.3	-7.8	8.4	2.2	-29.1	-34.8	-9.2	-41.1	-78.9	-68.9	-64.1	-47.7	16.4	14.8
+Q	cc-pVQZ	0.0	2.8	-1.6	5.4	2.8	3.0	3.1	3.2	2.9	7.3	3.2	0.4	13.3	11.3	-2.0	10.1
MRCI+Q+3sp	cc-pVQZ	0.0	12.0	-10.9	-2.4	11.2	5.2	-26	-31.6	-6.3	-33.8	-75.7	-68.5	-50.8	-36.4	14.4	24.9
+3sp	cc-pVQZ	0.0	0.0	-0.1	-1.5	-2.5	-2	-0.9	-1.9	-3.3	-7.4	-2.8	-1.1	-7.9	0.5	8.4	-5.1
MRCI+DKH2	cc-pVQZ	0.0	11.1	-9.5	-2.4	13.3	6.9	-27.6	-30.5	-3.7	-27.5	-75.9	-64.5	-50.5	-35	15.5	25.4
+Q	cc-pVQZ	0.0	2.4	-1.5	2.2	0.3	0.6	0.5	0.8	0.9	2.9	3.6	0.4	8.1	5.9	-2.2	4.5
MRCI+Q+DKH2	cc-pVQZ	0.0	13.5	-11	-0.2	13.6	7.5	-27.1	-29.7	-2.8	-24.6	-72.3	-64.1	-42.4	-29.1	13.3	29.9
+DKH2	cc-pVQZ	0.0	1.5	-0.2	0.7	-0.1	0.3	-2.0	0.0	0.2	1.8	0.6	3.3	0.5	7.8	7.3	-0.1
MRCI+3sp+DKH2	cc-pVQZ	0.0	9.8	-10.3	-7.7	7.9	1.9	-32.2	-35.4	-9.5	-39.9	-79.2	-67	-65.8	-39.9	25.9	13.4
+Q	cc-pVQZ	0.0	3.1	-1.2	5.8	3.1	3.3	3.9	3.6	3.0	7.7	3.6	1.3	15.1	10.4	-4.7	11.5
MRCI+Q+3sp+DKH2	cc-pVQZ	0.0	12.9	-11.5	-1.9	11	5.2	-28.3	-31.8	-6.5	-32.2	-75.6	-65.7	-50.7	-29.5	21.2	24.9
+3sp	cc-pVQZ	0.0	-0.6	-0.5	-1.7	-2.6	-2.3	-1.2	-2.1	-3.7	-7.6	-3.3	-1.6	-8.3	-0.4	7.9	-5.0
+DKH2	cc-pVQZ	0.0	0.9	-0.6	0.5	-0.2	0.0	-2.3	-0.2	-0.2	1.6	0.1	2.8	0.1	6.9	6.8	0.0
MRCI-nofc	cc-pVQZ	0.0	9.6	-9.8	-10.5	5.6	-0.7	-32.5	-38.2	-12.7	-46.1	-80.5	-70.0	-64.1	-48.1	16.0	16.4
+Q	cc-pVQZ	0.0	2.9	-1.5	6.3	3.7	3.8	4.1	4.0	3.8	8.8	3.3	0.8	13.3	11.1	-2.2	10.0
MRCI+Q-nofc	cc-pVQZ	0.0	12.5	-11.3	-4.2	9.3	3.1	-28.4	-34.2	-8.9	-37.3	-77.2	-69.2	-50.8	-37.0	13.8	26.4
+CV	cc-pVQZ	0.0	0.5	-0.5	-3.3	-4.4	-4.1	-3.3	-4.5	-5.9	-10.9	-4.3	-1.8	0.1	7.9	7.8	4.4
MRCI	def2-QZVPP	0.0	9.8	-9.2	-2.4	13	7.1	-26.0	-30.0	-4	-28.1	-77.3	-67.4	-52.4	-43.3	9.1	24.9
+Q	def2-QZVPP	0.0	2.5	-1.3	2.3	0.4	0.6	0.2	0.7	1.1	2.6	3.6	-0.2	8.0	5.9	-2.1	4.4
MRCI+Q	def2-QZVPP	0.0	12.3	-10.5	-0.1	13.4	7.7	-25.8	-29.3	-2.9	-25.5	-73.7	-67.6	-44.4	-37.4	7.0	29.3
Δ(cc-pVQZ-def2-QZVPP)		0.0	-0.3	-0.3	-0.8	0.3	-0.5	0.7	-0.4	-0.1	-0.9	0.8	0.2	1.5	0.5	-1.0	0.7

Table S10: Continued

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
MRCI+3sp	def2-QZVPP	0.0	9.1	-10.3	-7.7	8.3	2.1	-29.8	-35.1	-8.2	-37.6	-78.1	-68.4	-62.4	-45	17.4	15.7
+Q	def2-QZVPP	0.0	3.3	-1.1	5.4	2.7	2.9	3.0	2.9	2.9	6.5	3.7	0.7	13.4	11.1	-2.3	9.7
MRCI+Q+3sp	def2-QZVPP	0.0	12.4	-11.4	-2.3	11.0	5	-26.8	-32.2	-5.3	-31.1	-74.4	-67.7	-49	-33.9	15.1	25.4
+3sp	def2-QZVPP	0.0	0.1	-0.9	-2.2	-2.4	-2.7	-1	-2.9	-2.4	-5.6	-0.7	-0.1	-4.6	3.5	8.1	-3.9
MRCI+DKH2	def2-QZVPP	0.0	11.2	-10.5	-1.5	13.4	7.5	-28.2	-30.1	-1.1	-26.3	-76.9	-65	-52.2	-35.7	16.5	24.7
+Q	def2-QZVPP	0.0	2.0	-0.7	1.8	0.1	0.1	0.1	0.3	0.5	2.3	3.1	-0.2	7.6	5.5	-2.1	4.5
MRCI+Q+DKH2	def2-QZVPP	0.0	13.2	-11.2	0.3	13.5	7.6	-28.1	-29.8	-0.6	-24	-73.8	-65.2	-44.6	-30.2	14.4	29.2
+DKH2	def2-QZVPP	0.0	0.9	-0.7	0.4	0.1	-0.1	-2.3	-0.5	2.3	1.5	-0.1	2.4	-0.2	7.2	7.4	-0.1
MRCI+3sp+DKH2	def2-QZVPP	0.0	11.1	-10	-4.9	9.9	5.1	-31.1	-33.5	-5	-35.4	-80.3	-65.5	-65.9	-39.4	26.5	14.4
+Q	def2-QZVPP	0.0	2.3	-0.5	4.6	2.3	2.0	2.7	2.0	2.7	6.2	3.3	-0.1	13.4	10.1	-3.3	10.1
MRCI+Q+3sp+DKH2	def2-QZVPP	0.0	13.4	-10.5	-0.3	12.2	7.1	-28.4	-31.5	-2.3	-29.2	-77	-65.6	-52.5	-29.3	23.2	24.5
+3sp	def2-QZVPP	0.0	0.2	0.7	-0.6	-1.3	-0.5	-0.3	-1.7	-1.7	-5.2	-3.2	-0.4	-7.9	0.9	8.8	-4.7
+DKH2	def2-QZVPP	0.0	1.0	0.9	2	1.2	2.1	-1.6	0.7	3	1.9	-2.6	2.1	-3.5	4.6	8.1	-0.9
MRAQCC	def2-QZVPP	0.0	11.7	-11	-0.9	13.2	7.8	-26.5	-29.7	-3.9	-25.7	-75.1	-71.5	-43.8	-35.8	8.0	31.3
MRAQCC+DKH2	def2-QZVPP	0.0	12.6	-12.1	-0.6	13.0	7.5	-29	-30.2	-2.9	-24.3	-75.3	-68.4	-44.2	-28.8	15.4	31.1
MRAQCC+3sp	def2-QZVPP	0.0	12.5	-11.8	-2	11.2	6.1	-28.6	-32.4	-6.8	-30.4	-75.7	-74.5	-45.5	-30.3	15.2	30.2
MRAQCC+3sp+DKH2	def2-QZVPP	0.0	13.1	-11.6	-0.5	11.5	7.6	-30.9	-31.9	-6.2	-29	-78.8	-71.3	-49.6	-26.2	23.4	29.2
+DKH2 (without 3sp)	def2-QZVPP	0.0	0.9	-1.1	0.3	-0.2	-0.3	-2.5	-0.5	1.0	1.4	-0.2	3.1	-0.4	7.0	7.4	-0.2
+DKH2 (with 3sp)	def2-QZVPP	0.0	0.6	0.2	1.5	0.3	1.5	-2.3	0.5	0.6	1.4	-3.1	3.2	-4.1	4.1	8.2	-1.0
+3sp (without DKH2)	def2-QZVPP	0.0	0.8	-0.8	-1.1	-2	-1.7	-2.1	-2.7	-2.9	-4.7	-0.6	-3	-1.7	5.5	7.2	-1.1
+3sp (with DKH2)	def2-QZVPP	0.0	0.5	0.5	0.1	-1.5	0.1	-1.9	-1.7	-3.3	-4.7	-3.5	-2.9	-5.4	2.6	8.0	-1.9
SORCI	TZVPP	0.0	11.5	-8.3	1.6	15.0	9.9	-27.0	-27.0	-1.5	-23.5	-75.5	-64.4	-50.4	-34.5	15.9	25.1
SORCI+Q	TZVPP	0.0	13.9	-10.1	1.9	14.0	9.8	-28.4	-27.4	-1.6	-22.8	-71.8	-63.5	-42.6	-28.2	14.4	29.2
SORCI	cc-pVQZ	0.0	7.8	-9.3	-7.9	11.1	3.1	-27.1	-35.6	-2.9	-31.9	-70.2	-66.2	-41.4	-34.6	6.8	28.8
SORCI+Q	cc-pVQZ	0.0	10.3	-11.5	-7.4	10.2	3.2	-27.6	-35.8	-2.4	-30.5	-66.6	-66.8	-32.8	-28.2	4.5	33.8
Δ(cc-pVQZ-TZVPP)		0.0	-3.6	-1.4	-9.3	-3.8	-6.6	0.8	-8.4	-0.8	-7.7	5.2	-3.3	9.8	0.0	-9.9	4.6

Table S10: Continued

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
SORCP	TZVPP	0.0	13.7	-10.9	1.9	14.5	10.3	-28.8	-27.3	-1.9	-22.3	-72.8	-64.5	-42.1	-27.4	14.7	30.7
SORCP	cc-pVQZ	0.0	9.8	-12.2	-7.6	10.3	3.3	-28.8	-36.2	-3.6	-30.6	-68.1	-69.7	-32.4	-27.3	5.1	35.7
Δ(cc-pVQZ-TZVPP)		0.0	-3.9	-1.3	-9.5	-4.2	-7.0	0.0	-8.9	-1.7	-8.3	4.7	-5.2	9.7	0.1	-9.6	5.0
MR-AQCC	TZVPP	0.0	12.9	-10.2	3.9	16.3	12.7	-27.4	-24.9	-2.0	-19.0	-75.1	-65.0	-44.8	-29.6	15.2	30.3
MR-AQCC+DKH2	TZVPP	0.0	14.3	-10.8	5.5	16.2	13.4	-32.6	-24.8	-1.6	-16.9	-74.5	-61.9	-44.2	-21.1	23.1	30.3
+DKH2	TZVPP	0.0	1.4	-0.6	1.6	-0.1	0.7	-5.2	0.1	0.4	2.1	0.6	3.1	0.6	8.5	7.9	0.0
MR-AQCC+3sd	TZVPP	0.0	13.4	-10.1	5.6	18.1	14.8	-27.4	-23.8	-1.4	-18.5	-75	-66.4	-46.9	-23.5	23.5	28.1
MR-AQCC+3sd+DKH	TZVPP	0.0	14.2	-10.8	6.4	17.3	15.1	-33.1	-24.7	-1.6	-16.9	-75.8	-63.1	-47.5	-15.5	32.0	28.2
+3sd	TZVPP	0.0	0.5	0.1	1.7	1.8	2.1	0.0	1.1	0.6	0.5	0.1	-1.4	-2.1	6.1	8.3	-2.2
+DKH2	TZVPP	0.0	0.8	-0.7	0.8	-0.8	0.3	-5.7	-0.9	-0.2	1.6	-0.8	3.3	-0.6	8.0	8.5	0.1
MR-AQCC-nofc	TZVPP	0.0	14.2	-10.2	5.9	18.0	15.0	-28.1	-23.9	-1.5	-18.6	-74.7	-67.1	-46.9	-23.9	23.1	27.8
Δ(nofc-3sd)	TZVPP	0.0	0.8	-0.1	0.3	-0.1	0.2	-0.7	-0.1	-0.1	-0.1	0.3	-0.7	0.0	-0.4	-0.4	-0.3
MR-AQCC	cc-pVQZ	0.0	11.4	-11.3	-1.5	13.4	7.2	-25.8	-30.2	-4.0	-26.8	-74.3	-71.0	-42.4	-35.4	7.0	31.9
MR-AQCC+DKH	cc-pVQZ	0.0	13.1	-11.2	-0.9	13.6	7.7	-27.7	-30	-3.7	-24.7	-73.6	-67.1	-41.6	-27.4	14.2	32.0
+DKH2	cc-pVQZ	0.0	1.7	0.1	0.6	0.2	0.5	-1.9	0.2	0.3	2.1	0.7	3.9	0.8	8.0	7.2	0.1
Δ(cc-pVQZ-TZVPP)		0.0	-1.5	-1.1	-5.4	-2.9	-5.5	1.6	-5.3	-2.0	-7.8	0.8	-6.0	2.4	-5.8	-8.2	1.6
MR-AQCC+3sd	cc-pVQZ	0.0	12.0	-11.6	-2.1	11.3	6.2	-28.1	-32.0	-8.1	-33.3	-77.2	-75.1	-47.2	-33.0	14.2	32.0
MR-AQCC+3sd+DKH2	cc-pVQZ	0.0	13.4	-11.7	-1.3	11.5	6.6	-30	-31.8	-7.7	-31.1	-76.6	-70.7	-46.7	-25.3	21.4	29.9
+3sd	cc-pVQZ	0.0	0.6	-0.3	-0.7	-2.1	-1.0	-2.3	-1.8	-4.1	-6.5	-2.9	-4.1	-4.8	2.4	7.2	0.1
+DKH2	cc-pVQZ	0.0	1.4	-0.1	0.8	0.2	0.4	-1.9	0.2	0.4	2.2	0.6	4.4	0.5	7.7	7.2	-2.1
Δ(cc-pVQZ-TZVPP)		0.0	-1.4	-1.5	-7.7	-6.8	-8.6	-0.7	-8.2	-6.7	-14.8	-2.2	-8.7	-0.3	-9.5	-9.3	3.9
MR-AQCC-nofc	cc-pVQZ	0.0	13.0	-11.7	-2.4	10.3	5.3	-30.1	-33.6	-10.1	-35.1	-77.8	-76.7	-47.2	-33.3	13.9	30.6
MR-MP2	TZVPP	0.0	17.8	-13.2	2.6	14.4	7.1	-24.6	-26.5	1.8	-20.8	-66.1	-52.8	-32.0	-24.4	7.6	34.1
MR-MP2	cc-pVQZ	0.0	18.0	-14.5	-1.3	14.3	3.5	-18.5	-29.7	2.9	-23.2	-63.6	-53.3	-26.9	-31.1	-4.2	36.6
Δ(cc-pVQZ-TZVPP)		0.0	0.2	-1.3	-3.9	-0.1	-3.6	6.1	-3.2	1.1	-2.4	2.5	-0.5	5.1	-6.7	-11.8	2.5

The MRCI/TZVPP relative energies tend to be too small. The MRCI/cc-pVQZ and MRCI/def2-QZVPP results are almost identical.

Table S11: MRCI reaction profiles (kcal/mol) with $T_{sel}=10^{-8}$ and $T_{pre}=10^{-6}$ ($T_{nat}=10^{-7}$).

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
MRCI	cc-pVTZ	0.0	10.5	-9.2	-0.1	17.2	8.9	-22.9	-26.7	-0.1	-21.1	-74.7	-64.1	-47.8	-38.0	9.8	26.9
+Q	cc-pVTZ	0.0	2.3	-2.2	0.4	-1.3	-1.0	-1.7	-0.9	-0.3	0.2	4.2	0.1	10.0	7.8	-2.2	5.8
MRCI+Q	cc-pVTZ	0.0	12.8	-11.4	0.3	15.9	7.9	-24.6	-27.6	-0.4	-20.9	-70.5	-64.0	-37.8	-30.2	7.6	32.7
MRCI	cc-pVQZ	0.0	9.8	-9.4	-1.5	17.6	8.3	-22.7	-27.9	-0.7	-22.4	-75.3	-65.3	-49.9	-41.7	8.2	25.4
+Q	cc-pVQZ	0.0	2.2	-2.3	0.2	-1.3	-1.1	-1.8	-1.0	-0.5	0.0	4.0	-0.2	10.2	8.0	-2.2	6.2
MRCI+Q	cc-pVQZ	0.0	12.0	-11.7	-1.3	16.3	7.2	-24.5	-28.9	-1.2	-22.4	-71.3	-65.5	-39.7	-33.7	6.0	31.6
MRCI+Q	CBS	0.0	11.6	-12.0	-2.3	16.6	6.8	-24.0	-29.6	-1.5	-23.2	-71.7	-66.4	-40.8	-35.9	4.9	30.9
MRCI+3sp	cc-pVQZ	0.0	8.2	-8.0	-0.8	20.6	10.1	-18.5	-26.0	1.5	-21.3	-76.6	-65.3	-64.2	-47.7	16.5	12.4
+Q	cc-pVQZ	0.0	2.4	-3.0	0.7	-1.1	-1.3	-1.4	-1.2	-0.4	0.2	4.2	-0.4	17.2	14.1	-3.1	13.0
MRCI+Q+3sp	cc-pVQZ	0.0	10.6	-11	-0.1	19.5	8.8	-19.9	-27.2	1.1	-21.1	-72.4	-65.7	-47	-33.6	13.4	25.4
+3sp	cc-pVQZ	0.0	-1.4	0.7	1.2	3.2	1.6	4.6	1.7	2.3	1.3	-1.1	-0.2	-7.3	0.1	7.4	-6.2
MRCI+DKH2	cc-pVQZ	0.0	11.3	-9.8	-0.8	17.6	8.7	-25.1	-27.9	-0.4	-20.7	-74.8	-62.5	-49.4	-34.0	15.4	25.4
+Q	cc-pVQZ	0.0	2.4	-2.2	0.3	-1.2	-1.0	-1.2	-0.9	-0.5	0.2	4.1	0.5	10.3	8.1	-2.2	6.2
MRCI+Q+DKH2	cc-pVQZ	0.0	13.7	-12	-0.5	16.4	7.7	-26.3	-28.8	-0.9	-20.5	-70.7	-62.0	-39.1	-25.9	13.2	31.6
+DKH2	cc-pVQZ	0.0	1.7	-0.3	0.8	0.1	0.5	-1.8	0.1	0.3	1.9	0.6	3.5	0.6	7.8	7.2	0.0
MRCI+3sp+DKH2	cc-pVQZ	0.0	9.5	-8.4	-0.1	20.7	10.5	-21.1	-25.8	1.7	-19.5	-76.1	-62.7	-64.1	-39.7	24.4	12.0
+Q	cc-pVQZ	0.0	2.6	-2.9	0.8	-1.0	-1.2	-0.9	-1.2	-0.3	0.3	4.3	0.4	17.2	14.3	-2.9	12.9
MRCI+Q+3sp+DKH2	cc-pVQZ	0.0	12.1	-11.3	0.7	19.7	9.3	-22.0	-27.0	1.4	-19.2	-71.8	-62.3	-46.9	-25.4	21.5	24.9
+3sp	cc-pVQZ	0.0	-1.6	0.7	1.2	3.3	1.6	4.3	1.8	2.3	1.3	-1.1	-0.3	-7.8	0.5	8.3	-6.7
+DKH2	cc-pVQZ	0.0	1.5	-0.3	0.8	0.2	0.5	-2.1	0.2	0.3	1.9	0.6	3.4	0.1	8.2	8.1	-0.5
MRCI-nofc	cc-pVQZ	0.0	8.2	-8.0	-1.4	20.4	9.7	-19.0	-26.8	0.7	-22.4	-77.9	-66.2			16.7	
+Q	cc-pVQZ	0.0	2.5	-3.0	0.8	-1.2	-1.5	-1.4	-1.4	-0.4	0.0	3.9	-0.4			-3.1	
MRCI+Q-nofc	cc-pVQZ	0.0	10.7	-11.0	-0.6	19.2	8.2	-20.4	-28.2	0.3	-22.4	-74.0	-66.6			13.6	
+CV	cc-pVQZ	0.0	-1.3	0.7	0.7	2.9	1.0	4.1	0.7	1.5	0.0	-2.7	-0.1			7.6	
MRAQCC	cc-pVTZ	0.0	12.9	-12.6	-0.7	14.9	7.3	-25.8	-28.2	-1.2	-21.5	-70.8	-67.5	-36.2	-27.6	8.6	34.6
MRAQCC	cc-pVQZ	0.0	12.1	-13.0	-2.4	15.3	6.7	-25.7	-29.6	-1.9	-22.9	-71.7	-69.3	-38	-30.9	7.1	33.7
MRAQCC	CBS	0.0	11.6	-13.3	-3.4	15.6	6.2	-25.4	-30.4	-2.3	-23.8	-72.2	-70.5	-38.9	-32.9	7.0	33.3

Table S11: Continued

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
MRAQCC+DKH2	cc-pVQZ	0.0	13.8	-13.3	-1.6	15.3	7.2	-27.5	-29.5	-1.7	-21.0	-71.0	-64.9	-37.2	-23.0	14.2	33.8
MRAQCC+3sp	cc-pVQZ	0.0	11.8	-13.0	-0.2	18.9	9.2	-21.7	-27.5	1.0	-20.5	-70.3	-76.2	-38.6	-25.3	13.3	31.7
MRAQCC+3sp+DKH2	cc-pVQZ	0.0	13.5	-13.2	0.7	19.2	9.9	-23.5	-27.1	1.5	-18.4	-69.6	-69.9	-38.3	-16.8	21.5	31.3
MRAQCC-nofc	cc-pVQZ	0.0	12.9	-12.9	0.6		9.9	-21.8	-27.5	1.2		-69.7	-83.3			12.6	
+DKH2 (without 3sp)	cc-pVQZ	0.0	1.7	-0.3	0.8	0.0	0.5	-1.8	0.1	0.2	1.9	0.7	4.4	0.8	7.9	7.1	0.1
+DKH2 (with 3sp)	cc-pVQZ	0.0	1.7	-0.2	0.9	0.3	0.7	-1.8	0.4	0.5		0.7	6.3	0.3	8.5	8.2	-0.4
+3sp (without DKH2)	cc-pVQZ	0.0	-0.3	0.0	2.2	3.6	2.5	4.0	2.1	2.9		1.4	-6.9	-0.6	5.6	6.2	-2.0
+3sp (with DKH2)	cc-pVQZ	0.0	-0.3	0.1	2.3	3.9	2.7	4.0	2.4	3.2		1.4	-5.0	-1.1	6.2	7.3	-2.5
SORCI	cc-pVTZ	0.0	10.1	-9.7	-2.1	14.6	6.3	-25.9	-29.2	-2.1	-23.6	-74.6	-64.2	-47.7	-37.7	10.0	26.9
+Q	cc-pVTZ	0.0	2.3	-2.3	-0.5	-2.0	-1.5	-2.5	-1.6	-0.7	-0.3	4.1	0.1	9.9	7.8	-2.1	5.8
SORCI+Q	cc-pVTZ	0.0	12.4	-12.0	-2.6	12.6	4.8	-28.4	-30.8	-2.8	-23.9	-70.5	-64.1	-37.8	-29.9	7.9	32.7
SORCI	cc-pVQZ	0.0	9.4	-10.0	-4.7	13.9	4.6	-26.4	-31.7	-3.1	-26.3	-75.1	-65.1	-49.4	-40.9	8.5	25.7
+Q	cc-pVQZ	0.0	2.2	-2.7	-0.8	-2.2	-2.0	-2.6	-1.9	-0.9	-0.6	4.0	-0.3	10.2	8.0	-2.2	6.2
SORCI+Q	cc-pVQZ	0.0	11.6	-12.7	-5.5	11.7	2.6	-29.0	-33.6	-4.0	-26.9	-71.1	-65.8	-39.2	-32.9	6.3	31.9
SORCI+Q	CBS	0.0	11.2	-13.2	-7.5	11.1	1.1	-29.2	-35.4	-4.6	-28.8	-71.3	-66.5	-39.9	-34.7	5.2	31.4
SORCP	cc-pVTZ	0.0	10.7	-12.3	-4.0	10.8	3.0	-28.5	-31.8	-2.6	-29.0	-70.9	-69.5	-36.8	-29.3	7.5	34.1
SORCP	cc-pVQZ	0.0	10.4	-13.2	-9.7	6.5	-0.1	-31.7	-39.2	-6.1	-36.0	-68.3	-71.4	-31.7	-26.3	5.4	36.6
SORCP	CBS	0.0	10.3	-14.0	-13.6	3.4	-2.4	-33.7	-44.4	-8.4	-40.8	-66.2	-72.6	-27.5	-23.8	3.7	38.7
MRMP2	cc-pVTZ	0.0	17.8	-11.4	4.3	18.5	10.8	-14.1	-24.2	6.5	-18.0	-61.9	-50.9	-34.8	-36.8	-2.0	27.1
MRMP2	cc-pVQZ	0.0	17.6	-12.0	2.0	18.1	7.6	-13.9	-26.3	5.5	-19.8	-62.0	-52.1	-34.7	-38.8	-4.1	27.3
MRMP2	CBS	0.0	17.6	-12.5	0.5	17.8	5.3	-13.6	-27.7	5.1	-20.9	-62.0	-52.9	-34.1	-39.9	-5.8	27.9
NEVPT2-nofc	TZVPP	0.0	12.3	-12.0	-5.9	14.3	0.0	-23.5	-33.5	-1.1	-26.8	-71.7	-57.3	-40.1	-34.5	5.6	31.6
NEVPT2-nofc	cc-pVTZ	0.0	11.7	-12.7	-8.8	14.1	-2.4	-17.7	-35.5	-0.9	-29.0	-71.6	-58.8	-36.6	-43.6	-7.0	35.0
NEVPT2-nofc	cc-pVQZ	0.0	11.5	-12.9	-10.1	13.5	-4.5	-17.5	-38.0	-1.6	-31.0	-70.8	-59.3	-36.5	-46.5	-10.0	34.3
NEVPT2-nofc	CBS	0.0	11.4	-13.0	-11.0	13.1	-5.9	-17.0	-39.6	-1.8	-32.3	-70.1	-59.5	-36.1	-48.2	-12.1	34.0
+DKH2	cc-pVQZ	0.0	1.2	-0.4	0.3	-0.2	0.4	-1.0	-0.2	-0.8	2.0	0.3	2.1	0.4	9.6	9.2	0.1
NEVPT2+DKH2	cc-pVQZ	0.0	12.7	-13.3	-9.8	13.3	-4.1	-18.5	-38.2	-2.4	-29	-70.5	-57.2	-36.1	-36.9	-0.8	34.4
Δ(cc-pVQZ-TZVPP)		0.0	-0.8	-0.9	-4.2	-0.8	-4.5	6.0	-4.5	-0.5	-4.2	0.9	-2.0	3.6	-12.0	-15.6	2.7

Table S11: Continued

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
NEVPT2	def2-QZVPP	0.0	11.9	-13.4	-11.7	12.2	-6.0	-20.6	-40.0	-2.4	-32.1	-69.9	-58.5	-35.5	-40.4	-4.9	34.4
+DKH2	def2-QZVPP	0.0	1.0	1.3	3.9	2.2	3.7	1.4	2.0	7.1	4.3	-2.1	-0.1	-3.2	-0.2	3.0	-1.1
NEVPT2+DKH2	def2-QZVPP	0.0	12.9	-12.1	7.8	14.4	-2.3	-19.2	-38.0	4.7	-27.8	-72.0	-59	-38.7	-40.6	-1.9	33.3
NEVPT2	cc-pwCVTZ	0.0	11.6	-12.1	-8.1	15.1	-1.8	-15.5	-34.4	0.5	-27.9	-70.0	-57.8	-36.2	-42.0	-5.8	33.8
NEVPT2+DKH2	cc-pwCVTZ	0.0	12.8	-12.4	-6.7	14.9	-1.1	-16.3	-34.2	-0.5	-25.6	-70.4	-56.0	-36.2	-35.5	0.7	34.2
+DKH2	cc-pwCVTZ	0.0	1.2	-0.3	1.4	-0.2	0.7	-0.8	0.2	-1.0	2.3	-0.4	1.8	0.0	6.5	6.5	0.4
CASPT2	TZVPP	0.0	13.7	-12.8	-0.5	15.9	9.1	-23.6	-24.7	2.5	-19.0	-69.9	-61.7	-35.0	-26.8	8.2	34.9
CASPT2	cc-pVTZ	0.0	14.7	-13.4	15.1	16.4	7.4	-18.0	-26.0	4.0	-19.8	-68.5	-62.4	-30.2	-30.4	-0.2	38.3
CASPT2	cc-pVQZ	0.0	14.3	-13.8	4.5	17.8	6.2	-17.5	-27.7	3.4	-21.4	-68.7	-64.8	-30.9	-33.5	-2.6	37.8
CASPT2	CBS	0.0	14.1	-14.2	-4.9	18.3	5.4	-16.9	-28.8	3.2	-22.3	-68.7	-66.3	-31.0	-35.3	-4.3	37.7
MRCI	cc-pwCVTZ	0.0	10.4	-9.2	-0.9	17.9	8.6	-21.6	-26.9	0.4	-21	-73.7	-63.5	-47.3	-38.3	9.0	26.4
+Q	cc-pwCVTZ	0.0	2.3	-2.1	0.2	-1.2	-1.0	-1.8	-0.9	-0.2	0.1	4.4	0.2	10.2	8.1	-2.1	5.8
MRCI+Q	cc-pwCVTZ	0.0	12.7	-11.3	-0.7	16.7	7.6	-23.4	-27.8	0.2	-20.9	-69.3	-63.3	-37.1	-30.2	6.9	32.2
Δ(cc-pVQZ-cc-pwCVTZ)		0.0	0.7	0.4	0.6	0.4	0.4	1.1	1.1	1.4	1.5	2.0	2.2	2.6	3.5	0.9	0.6
MRCI+CV	cc-pwCVTZ	0.0	8.6	-7.4	0.2	21.0	10.9	-18.0	-24.7	2.6	-19.8	-77.0	-64.5			18.5	
+Q	cc-pwCVTZ	0.0	2.6	-2.8	0.7	-1.0	-1.3	-1.4	-1.2	-0.1	0.2	4.3	0.3	25.2		-2.7	
MRCI+Q+CV	cc-pwCVTZ	0.0	11.2	-10.2	0.9	20.0	9.6	-19.4	-25.9	2.5	-19.6	-72.7	-64.2			15.8	
+CV	cc-pwCVTZ	0.0	-1.5	1.1	1.6	3.3	2.0	4.0	1.9	2.3	1.3	-3.4	-0.9			8.9	
MRCI+DKH2	cc-pwCVTZ	0.0	11.4	-9.8	-0.4	17.7	9.0	-24.2	-26.9	0.2	-19.4	-74.3	-61.7	-47.7	-31.1	16.6	26.6
+Q	cc-pwCVTZ	0.0	2.2	-2.3	0.0	-1.4	-1.2	-1.5	-1.1	-0.5	0.1	4.1	0.6	10.2	7.9	-2.3	6.1
MRCI+Q+DKH2	cc-pwCVTZ	0.0	13.6	-12.1	-0.4	16.3	7.8	-25.7	-28.0	-0.3	-19.3	-70.2	-61.1	-37.5	-23.2	14.3	32.7
+DKH2	cc-pwCVTZ	0.0	0.9	-0.8	0.3	-0.4	0.2	-2.3	-0.2	-0.5	1.6	-0.9	2.2	-0.4	7.0	7.4	0.5
MRCI+CV+DKH2	cc-pwCVTZ	0.0	9.4	-8.1	1.0	20.9	11.2	-20.8	-24.7	2.3	-18.2	-77.4	-62.7			26.3	
+Q	cc-pwCVTZ	0.0	2.4	-3.0	0.5	-1.3	-1.5	-1.3	-1.4	-0.4	-0.1	4.0	0.6	24.9	22.2	-2.7	
MRCI+Q+CV+DKH2	cc-pwCVTZ	0.0	11.8	-11.1	1.5	19.6	9.7	-22.1	-26.1	1.9	-18.3	-73.4	-62.1			23.6	
+DKH2	cc-pwCVTZ	0.0	0.6	-0.9	0.6	-0.4	0.1	-2.7	-0.2	-0.6	1.3	-0.7	2.1			7.8	
+CV	cc-pwCVTZ	0.0	-1.8	1.0	1.9	3.3	1.9	3.6	1.9	2.2	1.0	-3.2	-1.0			9.3	

Table S11: Continued

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
MRAQCC	cc-pwCVTZ	0.0	12.8	-12.5	-1.7	15.7	7.1	-24.6	-28.5	-0.7	-21.4	-69.6	-66.7	-35.5	-27.6	7.9	34.1
MRAQCC+DKH2	cc-pwCVTZ	0.0	13.7	-13.4	-1.5	15.2	7.2	-26.9	-28.8	-1.1	-19.9	-70.5	-63.6	-36.0	-20.5	15.5	34.5
MRAQCC+CV	cc-pwCVTZ	0.0	12.9	-12.0	1.1	19.6	10.3	-21.0	-25.9	2.8	-18.6	-69.7	-72.3			15.8	
MRAQCC+CV+DKH2	cc-pwCVTZ	0.0	13.3	-13.3	1.3	18.8	10.1	-23.9	-26.5	2.1	-17.6	-70.7	-67.9			23.5	
+DKH2 (without cv)	cc-pwCVTZ	0.0	0.9	-0.9	0.2	-0.5	0.1	-2.3	-0.3	-0.4	1.5	-0.9	3.1	-0.5	7.1	7.6	0.4
+DKH2 (with cv)	cc-pwCVTZ	0.0	0.4	-1.3	0.2	-0.8	-0.2	-2.9	-0.6	-0.7	1.0	-1.0	4.4			7.7	
+CV (without DKH2)	cc-pwCVTZ	0.0	0.1	0.5	2.8	3.9	3.2	3.6	2.6	3.5	2.8	-0.1	-5.6			7.9	
+CV (with DKH2)	cc-pwCVTZ	0.0	-0.4	0.1	2.8	3.6	2.9	3.0	2.3	3.2	2.3	-0.2	-4.3			8.0	
NEVPT2	cc-pwCVQZ	0.0	11.3	-12.5	-10.1	14.5	-3.3	-15.6	-36.7	-0.6	-29.9	-70.6	-59.1	-36.7	-48.5	-11.8	33.9
NEVPT2	CBS	0.0	11.2	-12.9	-11.3	14.0	-4.4	-15.5	-38.1	-1.2	-31.2	-71.0	-60.0	-36.8	-52.8	-16.0	34.2
+DKH2	cc-pwCVQZ	0.0	1.3	-0.4	-1.0	-0.2	0.7	-0.9	0.2	-0.9	2.2	-0.2	1.7	-0.2	7.9	8.1	0.0
NEVPT2+DKH2	cc-pwCVQZ	0.0	12.6	-12.9	-8.5	14.3	-2.6	-16.5	-36.5	-1.5	-27.7	-70.8	-57.4	-36.9	-40.6	-3.7	33.9
MRCI	cc-pwCVQZ	0.0	10.0	-9.2	-2.0	18.1	8.3	-21.8	-27.9	-0.3	-22.3	-74.8	-64.8	-49.5	-41.7	7.8	25.3
+Q	cc-pwCVQZ	0.0	2.3	-2.2	0.4	-1.2	-1.0	-1.6	-0.9	-0.4	0.2	4.1	-0.2	10.4	8.1	-2.3	6.3
MRCI+Q	cc-pwCVQZ	0.0	12.3	-11.4	-1.6	16.9	7.3	-23.4	-28.8	-0.7	-22.1	-70.7	-65.0	-39.1	-33.6	5.5	31.6
MRCI+Q	CBS	0.0	12.2	-11.5	-2.2	17.1	7.1	-23.2	-29.4	-1.1	-22.9	-71.6	-66.0	-40.2	-35.6	4.6	31.4
Δ(cc-pwCVQZ-cc-pwCVTZ)		0.0	-0.4	-0.1	-0.9	0.2	-0.3	0.0	-1.0	-0.9	-1.2	-1.4	-1.7	-2.0	-3.4	-1.4	-0.6
Δ(cc-pwCVQZ-cc-pVQZ)		0.0	0.3	0.3	-0.3	0.6	0.1	1.1	0.1	0.5	0.3	0.6	0.5	0.6	0.1	-0.5	0.0
MRCI+CV	cc-pwCVQZ	0.0	8.2	-7.4	-0.1	21.6	11.1	-17.5	-25.4	1.9	-20.9	-77.8	-65.8			16.5	
+Q	cc-pwCVQZ	0.0	2.7	-2.8	0.9	-1.0	1.2	-1.2	-1.2	-0.3	0.2	4.0	-0.1			-2.9	
MRCI+Q+CV	cc-pwCVQZ	0.0	10.9	-10.2	0.8	20.6	9.9	-18.7	-26.6	1.6	-20.7	-73.8	-65.9			13.6	
+CV	cc-pwCVQZ	0.0	-1.4	1.2	2.4	3.7	2.6	4.7	2.2	2.3	1.4	-3.1	-0.9			8.1	
MRCI+DKH2	cc-pwCVQZ	0.0	11.2	-9.6	-0.8	18.0	8.8	-24.2	-27.7	-0.2	-20.5	-74.9	-62.8	-49.7	-34.4	15.3	25.2
+Q	cc-pwCVQZ	0.0	2.4	-2.2	0.4	-1.2	-1.0	-1.2	-1.0	-0.5	0.2	4.1	0.4	10.4	8.1	-2.3	6.3
MRCI+Q+DKH2	cc-pwCVQZ	0.0	13.6	-11.8	-0.4	16.8	7.8	-25.4	-28.7	-0.7	-20.3	-70.8	-62.4	-39.3	-26.3	13.0	31.5
+DKH2	cc-pwCVQZ	0.0	1.3	-0.4	1.2	-0.1	0.5	-2.0	0.1	0.0	1.8	-0.1	2.6	-0.2	7.3	7.5	-0.1
MRCI+CV+DKH2	cc-pwCVQZ	0.0	9.3	-7.8	0.9	21.7	11.7	-20.1		2.1	-19.1	-77.9	-63.8			24.2	
+Q	cc-pwCVQZ	0.0				-1.1	-1.3			0.4	0.2					2.9	
MRCI+Q+CV+DKH2	cc-pwCVQZ	0.0	12.0	-10.7	1.8	20.6	10.4	-21.0		1.7	-18.9	-74.0	-63.5			21.3	
+DKH2	cc-pwCVQZ	0.0	1.1	-0.5	1.0	0.0	0.5	-2.3		0.1	1.8	-0.2	2.4			7.7	
+CV	cc-pwCVQZ	0.0	-1.6	1.1	2.2	3.8	2.6	4.4		2.4	1.4	-3.2	-1.1			8.3	

Table S11: Continued

Method	Basis Set	$^6FeO^+ + H_2$	$^4FeO^+ + H_2$	^{6}1	^{4}1	^{6}TS1	^{4}TS1	^{6}2	^{4}2	^{6}TS2	^{4}TS2	^{6}3	^{4}3	$Fe^+(^6D) + H_2O$	$Fe^+(^4F) + H_2O$	Δ_1	Δ_2
MRAQCC	cc-pwCVQZ	0.0	12.4	-12.6	-2.6	15.9	6.8	-24.7	-29.5	-1.4	-22.7	-71.1	-68.8	-37.3	-30.8	6.5	33.8
MRAQCC	CBS	0.0	12.2	-12.7	-3.2	16.1	6.6	-24.5	-30.2	-1.8	-23.4	-72.0	-70.2	-38.3	-32.6	5.7	33.7
MRAQCC+DKH2	cc-pwCVQZ	0.0	13.8	-13.1	-1.5	15.8	7.3	-26.6	-29.4	-1.5	-20.9	-71.2	-65.2	-37.5	-23.4	14.1	33.7
+DKH2	cc-pwCVQZ	0.0	1.4	-0.5	1.1	-0.1	0.5	-1.9	0.1	-0.1	1.8	-0.1	3.6	-0.2	7.4	7.6	-0.1
MRAQCC+CV	cc-pwCVQZ	0.0	12.6	-12.0	1.3	20.5	10.8	-20.3	-26.5	1.8	-19.6	-71.2	-74.1			13.6	
+CV	cc-pwCVQZ	0.0	0.2	0.6	3.9	4.6	4.0	4.4	3.0	3.2	3.1	-0.1	-5.3			7.1	
+CV+DKH2	cc-pwCVQZ	0.0	1.6	0.1	5.0	4.5	4.5	2.5	3.1	3.1	4.9	-0.2	-1.7			14.7	
MRAQCC+CV+DKH2	cc-pwCVQZ	0.0	13.7	-12.7	2.1	20.4	11.3	-22.6	-26.3	1.8	-17.9	-71.4	-70.3			21.2	
+CV+DKH2	cc-pwCVQZ	0.0	1.3	-0.1	4.7	4.5	4.5	2.1	3.2	3.2	4.8	-0.3	-1.5			14.7	
MRCI	def2-QZVPP	0.0	10.3	-9.2	-1.0	17.4	8.8	-23.4	-27.6	-0.7	-22.2	-75.6	-65.3	-50.7	-41.6	9.1	24.9
+Q	def2-QZVPP	0.0	2.3	-2.2	0.4	-1.2	-0.9	-1.7	-0.8	-0.4	0.1	4.1	-0.1	10.1	7.9	-2.2	6.0
MRCI+Q	def2-QZVPP	0.0	12.6	-11.4	-0.6	16.2	7.9	-25.1	-28.4	-1.1	-22.1	-71.5	-65.4	-40.6	-33.7	6.9	30.9
MRCI+3sp	def2-QZVPP	0.0	9.0	-8.5	-1.5	19.4	8.8	-20.5	-27.5	1.1	-22.0	-74.8	-63.9	-61.2	-43.6	17.6	13.6
+Q	def2-QZVPP	0.0	2.6	-2.7	0.8	-0.9	-1.1	-1.3	-1.2	-0.1	0.3	4.6	-0.3	16.6	13.7	-2.9	12.0
MRCI+Q+3sp	def2-QZVPP	0.0	11.6	-11.2	-0.7	18.5	7.7	-21.8	-28.7	1.0	-21.7	-70.2	-64.2	-44.6	-29.9	14.7	25.6
+3sp	def2-QZVPP	0.0	-1.0	0.2	-0.1	2.3	-0.2	3.3	-0.3	2.1	0.4	1.3	1.2	-4.0	3.8	7.8	-5.3
MRCI+DKH2	def2-QZVPP	0.0	11.2	-10.7	-0.1	17.6	9.0	-25.8	-28.2	2.7	-20.5	-75.6	-63.4	-51.0	-34.4	16.6	24.6
+Q	def2-QZVPP	0.0	2.3	-1.2	0.3	-1.6	-1.0	-1.4	-0.9	-0.7	0.0	4.0	0.3	10.1	7.8	-2.3	6.1
MRCI+Q+DKH2	def2-QZVPP	0.0	13.5	-11.9	0.2	16.0	8.0	-27.2	-29.1	2.0	-20.5	-71.6	-63.1	-40.9	-26.6	14.3	30.7
+DKH2	def2-QZVPP	0.0	0.9	-0.5	0.8	-0.2	0.1	-2.1	-0.7	3.1	1.6	-0.1	2.3	-0.3	7.1	7.4	-0.2
MRCI+DKH2+3sp	def2-QZVPP	0.0	9.5	-9.1	0.7	20.8	11.0	-22.1	-26.7	5.0	-19.1	-77.0	-63.2	-65.4	-39.9	25.5	11.5
+Q	def2-QZVPP	0.0	2.5	-1.2	0.6	-1.5	-1.2	-1.2	-1.3	-0.1	0.2	4.2	0.3	16.6	13.8	-2.8	12.5
MRCI+Q+DKH2+3sp	def2-QZVPP	0.0	12.0	-10.3	1.3	19.3	9.8	-23.3	-28.0	4.9	-18.9	-72.8	-62.9	-48.8	-26.1	22.7	24.0
+3sp+DKH2	def2-QZVPP	0.0	-0.6	1.1	1.9	3.1	1.9	1.8	0.4	6.0	3.2	-1.3	2.5	-8.2	7.6	15.8	-6.9
MRAQCC	def2-QZVPP	0.0	12.7	-12.7	-1.6	15.2	7.3	-26.4	-29.1	-1.8	-22.6	-71.9	-69.1	-38.9	-30.9	8.0	33.0
MRAQCC+DKH2	def2-QZVPP	0.0	13.6	-13.1	-1.0	15.0	7.4	-28.5	-29.7	-0.6	-21.1	-72.0	-65.9	-39.2	-23.8	15.4	32.8
+DKH2	def2-QZVPP	0.0	0.9	-0.4	0.6	-0.2	0.1	-2.1	-0.6	1.2	1.5	-0.1	3.2	-0.3	7.1	7.4	-0.2
MRAQCC+3sp	def2-QZVPP	0.0	12.9	-12.9	-0.7	18.1	8.3	-23.4	-28.7	1.1	-21.0	-67.9	-74.9	-36.5	-21.9	14.6	31.4
+3sp	def2-QZVPP	0.0	0.2	-0.2	0.9	2.9	1.0	3.0	0.4	2.9	1.6	4.0	-5.8	2.4	9.0	6.6	-1.6
+3sp+DKH2	def2-QZVPP	0.0	1.1	-0.6	1.5	2.7	1.1	0.9	-0.2	4.1	3.1	3.9	-2.6	2.1	16.1	14.0	-3.6
MRAQCC+3sp+DKH2	def2-QZVPP	0.0	13.2	-11.8	1.0	18.4	10.1	-25.0	-27.9	0.5	-18.4	-70.8	-69.9	-40.6	-18.0	22.6	30.2
+3sp+DKH2	def2-QZVPP	0.0	0.5	0.9	2.6	3.2	2.8	1.4	1.2	2.3	4.2	1.1	-0.8	-1.7	12.9	14.6	-2.8

Table S12: Effect of the active space on Fe^+ splitting Δ_1 (kcal/mol) using the cc-pVQZ basis set. Standard small CAS of ^{6}D and ^{4}F: (7,6) and (7,5); large CAS of ^{6}D and ^{4}F: (7,11) and (7,10).

Method	Small CAS		Large CAS	
	FC[a]	+CV	FC[a]	+CV
MRCI+Q	6.0	13.4	5.5	4.5
MRCI+Q+DKH2	13.2	21.5	11.8	11.3
MRAQCC	7.1	13.3	6.6	4.3
MRAQCC+DKH2	14.2	21.5	13.6	13.2

[a] Standard calculations with the core orbitals frozen (1s, 2s, 2p, 3s, and 3p orbitals of Fe^+)

Table S13: Optimized Cartesian coordinates (Å) of all stationary points

A. B3LYP/TZVPP geometries

$^6FeO^+$

Fe	0.0000000000	0.0000000000	0.0000000000
O	0.0000000000	0.0000000000	1.6332936501

^{6}1

Fe	0.0000000000	0.0000000000	-0.3020811962
O	0.0000000000	0.0000000000	1.3387291839
H	0.0000000000	0.3844810282	-2.2563521298
H	0.0000000000	-0.3844810282	-2.2563521298

^{6}TS1

Fe	0.0000000000	0.0270487395	-0.3981509487
O	0.0000000000	0.0867285577	1.3258415360
H	0.0000000000	-1.7061983248	0.0783279409
H	0.0000000000	-1.1691671086	0.9364814484

^{6}2

Fe	0.0000000000	0.0256659048	-0.3928135838
O	0.0000000000	0.0088570093	1.3393961636
H	0.0000000000	-0.9867167462	-1.6080423044
H	0.0000000000	-0.5759463313	2.1119663910

$^4FeO^+$

Fe	0.0000000000	0.0000000000	0.0000000000
O	0.0000000000	0.0000000000	1.6914479404

^{4}1

Fe	0.0000000000	-0.0719023257	-0.3258120280
O	0.0000000000	0.0493172182	1.2261408880
H	-0.3990078924	1.6005333988	-0.7053466437
H	0.3990078924	1.6005333988	-0.7053466437

^{4}TS1

Fe	0.0000000000	0.0316928299	-0.3677739449
O	0.0000000000	0.0717781580	1.2435134345
H	0.0000000000	-1.6266393801	-0.1093216204
H	0.0000000000	-1.2687283231	0.7478543100

^{4}2

Fe	0.0000000000	0.0223509541	-0.3966893570
O	0.0000000000	0.0580771817	1.2881032560
H	0.0000000000	-1.4921061742	-0.3980943124
H	0.0000000000	-0.6681749748	1.9309546979

Table S13 (A): Continued

^{6}TS2

Fe	0.0000000000	0.0101440725	-0.4411038547
O	0.0000000000	0.0521953082	1.3562681184
H	0.0000000000	-1.3572639527	0.5882287010
H	0.0000000000	-0.0333045656	2.3235029802

^{6}3 (A1)

Fe	0.0000000000	0.0000000000	-0.5284778170
O	0.0000000000	0.0000000000	1.5743015930
H	0.0000000000	0.7822783606	2.1459708527
H	0.0000000000	-0.7822783606	2.1459708527

^{6}3 (A2)

Fe	0.0000000000	0.0000000000	-0.5287439095
O	0.0000000000	0.0000000000	1.5750978502
H	0.0000000000	0.7820922675	2.1470229284
H	0.0000000000	-0.7820922675	2.1470229284

^{6}3 (B1)

Fe	0.0000000000	0.0000000000	-0.5471145768
O	0.0000000000	0.0000000000	1.6317788534
H	0.0000000000	0.7780768581	2.2060961873
H	0.0000000000	-0.7780768581	2.2060961873

^{6}3 (B2)

Fe	0.0000000000	0.0000000000	-0.5318284337
O	0.0000000000	0.0000000000	1.5845337762
H	0.0000000000	0.7802183711	2.1575851859
H	0.0000000000	-0.7802183711	2.1575851859

H_2O

O	0.0000000000	0.0000000000	-0.0655205502
H	0.0000000000	0.7617124906	0.5200158205
H	0.0000000000	-0.7617124906	0.5200158205

^{4}TS2

Fe	-0.0040395631	-0.0069955782	-0.4264530090
O	0.0285009367	-0.0777486808	1.3241007906
H	0.1444002769	1.2340751578	0.5396889357
H	-0.3729857218	0.3876625442	2.0708861151

^{4}3 (A1)

Fe	0.0000000000	0.0000000000	-0.5017417699
O	0.0000000000	0.0000000000	1.4919555201
H	0.0000000000	0.7820139720	2.0588425271
H	0.0000000000	-0.7820139720	2.0588425271

^{4}3 (A2)

Fe	0.0000000000	0.0000000000	-0.5018808551
O	0.0000000000	0.0000000000	1.4923538249
H	0.0000000000	0.7818157047	2.0595344532
H	0.0000000000	-0.7818157047	2.0595344532

^{4}3 (B1)

Fe	0.0000000000	0.0000000000	-0.5123946368
O	0.0000000000	0.0000000000	1.5248573332
H	0.0000000000	0.7796082922	2.0928333387
H	0.0000000000	-0.7796082922	2.0928333387

^{4}3 (B2)

Fe	0.0000000000	0.0000000000	-0.5021576561
O	0.0000000000	0.0000000000	1.4927259042
H	0.0000000000	0.7778980518	2.0642497450
H	0.0000000000	-0.7778980518	2.0642497450

H_2

H	0.0000000000	0.0000000000	0.0000000000
H	0.0000000000	0.0000000000	0.7428893704

B. BP86/TZVPP geometries

$^{6}FeO^{+}$

Fe	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.631242

$^{6}1$

Fe	0.256895	-0.000474	-0.000005
O	-1.379997	0.000811	0.000008
H	2.181143	-0.388312	0.000029
H	2.179559	0.394156	0.000028

$^{6}TS1$

Fe	-0.154938	-0.820369	-0.401171
O	1.017072	0.195713	0.366607
H	-0.069686	0.886008	0.061343
H	-0.999592	0.748643	-0.381670

$^{6}2$

Fe	1.495615	-0.547713	0.404349
O	0.898404	1.088616	0.541152
H	1.118776	-1.989266	-0.130692
H	0.090205	1.586363	0.295190

$^{6}TS2$

Fe	-0.201125	-0.915575	-0.424009
O	0.898872	0.270839	0.389822
H	1.374016	1.015387	0.826251
H	-0.518532	0.654611	0.028225

$^{6}3$

Fe	0.020025	0.000000	0.000078
O	2.109649	-0.000001	-0.000358
H	2.686977	0.790254	0.000139
H	2.686978	-0.790255	0.000139

H_2O

O	-0.045010	0.090276	0.000000
H	0.905582	0.103433	0.000000
H	-0.462386	0.785478	0.000000

$^{4}FeO^{+}$

Fe	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.600852

$^{4}1$

Fe	0.195458	0.021643	0.096352
O	-0.223571	0.029135	-1.412479
H	1.844953	0.004854	-0.156740
H	1.645145	0.825461	-0.097174

$^{4}TS1$

Fe	-0.129745	-0.756311	-0.377532
O	1.008626	0.136037	0.348089
H	-0.117894	0.913668	0.049215
H	-0.968131	0.716601	-0.374663

$^{4}2$

Fe	1.897380	-0.536809	0.591764
O	0.946291	0.850527	0.505155
H	0.706095	-1.182842	-0.119314
H	0.053235	1.007123	0.132395

$^{4}TS2$

Fe	0.461718	-0.545790	-0.342330
O	1.454910	0.679768	0.416414
H	1.409024	1.143269	1.277593
H	-0.028919	0.853161	0.195918

$^{4}3$

Fe	-0.028547	0.070395	0.006902
O	-0.780543	1.920484	0.086914
H	-0.280530	2.733865	0.229896
H	-1.709378	2.164256	-0.011712

H_2

H	0.000000	0.000000	0.000000
H	0.000000	0.000000	0.750186

C. BHLYP/TZVPP geometries

$^{6}FeO^{+}$

Fe	0.0000000000	0.0000000000	0.0000000000
O	0.0000000000	0.0000000000	1.6541720000

$^{6}1$

Fe	0.7649085658	0.0733260427	-0.4850502089
O	-0.6045606416	-0.4683625928	-1.3934407794
H	2.4337333491	0.3291636826	0.5192356704
H	2.1377405183	1.0338797318	0.5331777398

$^{6}TS1$

Fe	-0.1587328602	-0.8630491860	-0.5379920401
O	0.8338793518	0.4063646662	0.2211470914
H	0.0258036405	1.4908032251	0.1460291679
H	-0.6520417027	1.9210058317	-0.0463927340

$^{6}2$

Fe	1.4857681122	-0.5515428309	0.4124911659
O	0.8196087676	1.0137563840	0.5063887172
H	1.1470131187	-1.9945690306	-0.1230939561
H	0.1402461287	1.6661252632	0.3544412418

$^{6}TS2$

Fe	0.2938010632	-0.3743348662	-0.2185699334
O	1.3773404791	0.8934216778	0.4827440884
H	1.6481836493	1.4195907363	1.2332392167
H	-0.2474463582	1.2984458050	0.0646010880

$^{6}3$

Fe	0.0027579683	0.0020881410	0.0076371650
O	-0.7927702499	1.9483589223	0.0870057681
H	-0.2966107811	2.7543824216	0.2316900228
H	-1.7137405844	2.1893341722	-0.0155713628

H_2O

O	-0.0377594588	-0.0757361276	0.0000000164
H	0.8951645308	0.0995483241	-0.0000000105
H	-0.4592262025	0.7748275796	-0.0000000059

$^{4}FeO^{+}$

Fe	0.0000000000	0.0000000000	0.0000000000
O	0.0000000000	0.0000000000	1.7431670000

$^{4}1$

Fe	0.4754426557	-0.0515740639	-0.2826857762
O	-0.8970125433	-0.5167490736	-1.2517540753
H	2.4068832818	0.2324516951	0.3418108849
H	2.1412724738	0.9434672178	0.3797882863

$^{4}TS1$

Fe	-0.8574042621	-1.2305704762	-0.7798844070
O	0.3336693999	-0.1163067729	-0.1417974276
H	-0.6547671492	0.6994056668	-0.5059552388
H	-1.4576871395	0.5722676723	-0.8753704964

$^{4}2$

Fe	1.8904996452	-0.5464813366	0.6012163124
O	0.9442703471	0.8839807564	0.5304721184
H	0.6947698949	-1.2935553346	-0.1419958168
H	0.0771678238	1.0502941796	0.1663207161

$^{4}TS2$

Fe	0.7399456395	-0.2879367807	-0.2450117700
O	1.7594318904	0.9077653944	0.5658442914
H	1.7750416633	1.3792839759	1.3950325291
H	0.1893987684	1.1278519914	0.3685145838

$^{4}3$

Fe	-0.0306420678	0.0798048588	0.0092049030
O	-0.7824398470	1.9249666174	0.0866273747
H	-0.2827977677	2.7270207725	0.2292955317
H	-1.7038170837	2.1595346190	-0.0136635151

H_2

H	0.0000000000	-0.0000000000	0.0000000000
H	0.0000000000	-0.0000000000	0.7370573956

D. TPSS/TZVPP geometries

$^{6}FeO^{+}$

Fe	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.634996

$^{6}1$

Fe	0.257662	-0.000353	0.000000
O	-1.384876	0.000607	0.000001
H	2.190425	-0.383811	0.000002
H	2.189376	0.388146	0.000002

$^{6}TS1$

Fe	-0.437630	-0.053964	0.000002
O	1.297561	-0.166691	-0.000013
H	0.933684	1.081826	0.000183
H	0.064199	1.654762	-0.000128

$^{6}2$

Fe	-0.421589	-0.051571	0.000001
O	1.322105	-0.027522	-0.000004
H	-1.663693	0.935225	-0.000010
H	2.048156	0.625802	0.000015

$^{6}TS2$

Fe	0.510587	-0.018339	0.000038
O	-1.299357	-0.095299	-0.000313
H	-2.276013	-0.001083	0.001697
H	-0.604405	1.240278	-0.000176

$^{6}3$

Fe	-0.611087	0.000000	0.000093
O	1.473752	0.000000	-0.000342
H	2.049118	0.788031	0.000154
H	2.049120	-0.788030	0.000154

H_2O

O	0.000000	0.119088	0.000000
H	0.763016	-0.476351	0.000000
H	-0.763016	-0.476351	0.000000

$^{4}FeO^{+}$

Fe	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.621085

$^{4}1$

Fe	0.317947	-0.144542	0.000000
O	-1.227292	0.107384	0.000000
H	0.775853	1.449505	-0.407628
H	0.775853	1.449504	0.407628

$^{4}TS1$

Fe	-0.404849	-0.058106	0.000002
O	1.216975	-0.154395	-0.000013
H	0.832706	1.151870	0.000173
H	-0.042430	1.594037	-0.000133

$^{4}2$

Fe	0.440006	-0.044498	0.000027
O	-1.240284	-0.115811	-0.000138
H	0.363781	1.460859	-0.000411
H	-1.881655	0.622579	0.000811

$^{4}TS2$

Fe	-0.487301	-0.013981	0.009384
O	1.266392	-0.136753	-0.063688
H	1.995716	0.286992	0.426750
H	0.542972	1.170544	-0.161240

$^{4}3$

Fe	-0.575463	-0.000003	0.000011
O	1.381231	-0.000014	-0.000159
H	1.955948	0.783986	0.000493
H	1.956249	-0.783805	0.000493

H_2

H	0.000000	0.000000	0.000000
H	0.000000	0.000000	0.743200

E. CASSCF/TZVPP geometries

$^{6}FeO^{+}$

Fe	0.0000000000	0.0000000000	0.000000000
O	0.0000000000	0.0000000000	1.698078052

$^{6}1$

Fe	-0.9175236053	1.5748853238	0.0174024410
O	-0.2882501644	0.0011387124	-0.0773466217
H	-1.3450841744	3.6650467312	0.2006570366
H	-2.0549178502	3.3883300970	0.0683520950

$^{6}3$

Fe	-0.0189430557	0.0004130577	-0.0000648224
O	2.1334053908	-0.0004320564	0.0003492751
H	2.6939430055	0.7635009955	-0.0001430793
H	2.6950783306	-0.7634829969	-0.0001433736

H_2O

O	-0.0458103941	-0.0918810352	0.0000000000
H	0.8956001176	0.1094019197	0.0000000000
H	-0.4516124353	0.7810986478	0.0000000000

$^{4}FeO^{+}$

Fe	0.0000000000	0.0000000000	0.0000000000
O	0.0000000000	0.0000000000	1.7549457290

$^{4}1$

Fe	0.0229656742	-0.0162604558	0.0399926517
O	-0.4492490448	-0.0205975365	-1.4844202278
H	2.0331747438	0.0931246787	-0.0893543289
H	1.8550255753	0.8248092490	-0.0362276862

$^{4}2$

Fe	1.9606415051	-0.5544644407	0.6138821996
O	0.9344672464	0.8600111545	0.5065520185
H	0.6548519857	-1.1075754219	-0.1225044687
H	0.0529694807	0.9400250350	0.1120487522

H_2

H	0.0000000000	0.0000000000	0.0000000000
H	0.0000000000	0.0000000000	0.7552740010