SUPPORTING INFORMATION (1 of 2)

Origin of the Second-Order Proton Catalysis of Ferriin Reduction in Belousov-Zhabotinsky Reactions: Density Functional Studies of Ferroin and Ferriin Aggregates with Outer Sphere Ligands Sulfate, Bisulfate, and Sulfuric Acid

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Table S1. Total Energies and Thermochemical Data of Ferriin $[Fe(phen)_3]^{3+}$ and its Aggregates[a-d]

Compound	Total Energy	VZPE	TE	*S*	ν_1	μ	E (TC//DC)
TC4-0-000	-2977.107660	330.52	349.85	199.57	12.6	1.2332	---
TC2-0-000	-2976.690782	331.47	350.27	190.20	28.4	0.0025	-2977.132523
	-2977.132523					0.0018	
TC2-1-100	-3676.288064	342.64	364.83	215.64	22.6	50.8241	-3676.280459
TC4-1-100	-3676.264395	341.12	363.92	223.39	22.6	51.8129	---
TC2-2-110	-4375.899602	360.43	386.64	245.19	26.6	43.1464	-4375.893774
TC4-2-110	-4375.875704	358.84	385.77	255.81	24.1	40.7898	---
TC2-1-010	-3676.746393	349.96	372.67	219.92	20.6	26.7644	-3676.738817
TC4-1-010	-3676.722705	348.25	371.66	229.91	17.1	27.8008	---
TC2-1-001	-3676.718038	357.18	380.13	221.72	19.0	3.4137	-3677.15834
	-3677.162979					3.9298	
TC4-1-001	-3677.141213	356.10	379.59	230.01	13.1	5.7403	---
TC2-2-020	-4376.358621	367.92	394.54	247.94	25.7	23.5083	-4376.358621
TC4-2-020	-4376.334608	366.12	393.53	259.49	22.4	23.5372	---
TC2-2-011	-4376.777711	375.33	402.20	249.62	23.3	25.1220	-4376.771882
TC4-2-011	-4376.754637	373.97	401.43	258.50	17.9	24.4073	---
TC2-2-002	-4377.195442	382.93	410.02	250.50	21.6	1.4115	-4377.194552
TC4-2-002	-4377.172473	381.57	409.21	258.63	18.4	1.0666	---
TC2-3-030	-5075.962513	385.34	416.30	287.11	11.6	19.3035	-5075.958907
TC4-3-030	-5075.944413	383.79	415.29	292.11	18.5	16.5724	---
TC2-3-021a	-5076.382791	392.79	424.00	287.65	14.2	4.0921	-5076.379248
TC2-3-021b	-5076.385114	392.66	423.87	287.35	17.5	31.3248	-5076.378393
TC4-3-021a	-5076.364570	391.68	423.18	289.63	21.9	16.9171	---
TC2-3-012a	-5076.805951	400.27	431.62	287.09	17.2	27.2478	-5076.797256
TC2-3-012b	-5076.804522	16.68	431.73	286.86	400.4	25.2192	-5076.802496
TC4-3-012a	-5076.785513	398.64	430.58	293.26	20.8	23.7457	---
	-5076.747292					2.0946	
TC2-3-003	-5077.223158	407.93	439.47	288.50	13.5	3.3524	-5077.219705
TC4-3-003	-5076.747292	406.97	438.97	296.74	13.1	2.0946	---
	-5077.201140					2.4146	

(a) Total energies in atomic units, vibrational zero-point energies (VZPE) in kcal/mol, thermal energies (TE) in kcal/mol, molecular entropies (*S*) $kcal \cdot mol^{-1} \cdot K^{-1}$, lowest vibrational frequency (ν_1) in wave numbers (cm^{-1}), and molecular dipole moment in Debye.
(b) All data computed at SMD(APFD/6-311G*).
(c) For SMD(APFD/6-311G*)//APFD/6-311G* calculations, the first row lists the APFD/6-311G* results, and the second row shows the total energy and dipole moment obtained in the SMD single-point calculation.
(d) SMD(APFD/6-311G*)//APFD/6-311G* energy of the unrelaxed system after single-electron oxidation, that is, computed based on the optimized structure of the corresponding reduced system, E(TC//DC).

Table S2. Total Energies and Thermochemical Data of Ferroin $[Fe(phen)_3]^{2+}$ and its Aggregates[a-d]

Compound	Total Energy	VZPE	TE	*S*	ν_1	μ	E (DC//TC)
DC3-0-000	-2977.250596	329.100850	348.17	195.91	4.8	10.2088	---
DC1-0-000	-2977.312196	331.160280	349.89	189.20	21.1	0.0202	-2977.310588
DC3-1-100	-3676.440315	339.815540	362.75	224.27	20.5	47.7157	---
DC1-1-100	-3676.458256	342.303680	364.44	214.53	21.1	49.1628	-3676.460076
DC3-2-110	-4376.048788	357.322910	384.35	255.25	20.5	37.8321	---
DC1-2-110	-4376.068758	359.860460	386.07	245.85	22.6	38.1699	-4376.068489
DC3-1-010	-3676.900203	346.846260	370.48	231.88	17.3	23.6528	---
DC1-1-010	-3676.918289	349.446590	372.17	219.83	20.4	24.9993	-3676.920337
DC3-1-001	-3677.320653	354.492220	378.28	231.83	15.2	1.9127	---
DC1-1-001	-3677.342898	356.461970	379.44	220.73	18.4	1.8383	-3677.33995
DC3-2-020	-4376.509321	364.526480	392.14	262.15	16.0	22.7763	---
DC1-2-020	-4376.529446	367.149530	393.86	249.70	23.0	22.7721	-4376.529036
DC3-2-011	-4376.930640	371.949450	399.85	263.76	17.6	23.1800	---
DC1-2-011	-4376.952738	374.130420	401.14	250.99	21.0	24.5675	-4376.950816
DC3-2-002	-4377.351513	379.819690	407.84	263.58	18.0	2.4193	---
DC1-2-002	-4377.373601	371.949450	399.85	263.76	17.6	23.1800	-4377.371416
DC3-3-030	-5076.115253	382.120840	413.90	297.44	10.9	9.6999	---
DC1-3-030	-5076.132528	384.697560	415.54	283.92	13.4	18.1857	-5076.131403
DC3-3-021a	-5076.537435	389.669750	421.65	296.65	14.2	14.7076	---
DC1-3-021a	-5076.554874	392.048470	423.23	286.41	18.3	5.6983	-5076.554172
DC1-3-021b	-5076.557711	391.68887	422.85	285.65	16.1	31.4301	-5076.55528
DC3-3-012a	-5076.959220	397.041680	429.42	300.57	14.3	26.6853	---
DC1-3-012a	-5076.975103	399.460940	430.96	289.94	12.2	28.3668	-5076.979121
DC1-3-012b	-5076.979298	399.11926	430.58	287.56	18.3	23.7478	-5076.977269
DC3-3-003	-5077.136934	405.58257	438.06	302.86	9.3	0.8063	---
	-5077.376543					1.7720	
DC1-3-003	-5077.399034	407.035400	438.65	287.59	21.4	2.0135	-5077.398688

(a)-(c) See Table S1.

(d) SMD(APFD/6-311G*)//APFD/6-311G* energy of the unrelaxed system after single-electron reduction, that is, computed based on the optimized structure of the corresponding oxidized system, E(DC//TC).

Table S3. Total Energies and Thermochemical Data of Sulfur and Other Species[a,b]

Compound	Total Energy	VZPE	TE	*S*	ν_1	μ
H_2SO_4	-700.008508	24.40	27.60	72.15	258.6	5.6392
HSO_4^-	-699.587286	17.14	20.03	70.31	289.8	4.2541
SO_4^{-2}	-699.125953	9.65	12.19	68.35	422.6	0.0046
H_2O	-76.387215	13.48	15.26	45.08	1699.4	2.7130
H_3O^+	-76.809944	22.63	24.43	46.04	1089.0	2.1760

(a),(b) See Table S1.

Table S4. Coordination Modes of Trication Doublets

Compound	Sulfate	Bisulfate	Sulfuric Acid
TC2-1-100	C3-C4a		
TC2-1-010		C3($E_{3\text{-}4}$)-C4a(N)	
TC2-1-001			C3($E_{3\text{-}4}$,N)-C4a(N,E)
TC2-2-110	^{1}C4a-^{2}C3	^{2}C6a(N)-^{3}C3($E_{3\text{-}4}$)	
TC2-2-020		^{1}C4a(N)-^{2}C3($E_{3\text{-}4}$) ^{2}C6a(N)-^{3}C3($E_{3\text{-}4}$)	
TC2-2-011		^{1}C3($E_{3\text{-}4}$)-^{2}C4a(N)	^{2}C8($E_{3\text{-}4}$,N)-^{3}C4a(N,E)
TC2-2-002			^{1}C4a(N,E)-^{2}C3($E_{3\text{-}4}$,N) ^{2}C6a(N,E)-^{3}C3($E_{3\text{-}4}$,N)
TC2-3-030		^{1}H_{C9H}(N)-^{2}C6a(N) ^{2}C6a(N)-^{3}C3($E_{3\text{-}4}$) ^{3}C4a(N)-^{1}H_{C2H}(N)	
TC2-3-021a		^{1}H_{C9H}(N)-^{2}C6a(N) ^{3}C4a(E)-^{1}H_{C2H}(E)	^{2}C8(N,$E_{3\text{-}4}$)-^{3}C4a(N,E)
TC2-3-021b		^{1}C3(N)-^{2}C4a(E) ^{2}C6a(N)-^{3}C3($E_{3\text{-}4}$)	^{3}C4a(N,E)-^{1}H_{C8H}(N,E)
TC2-3-012a		^{1}H_{C9H}(N)-^{2}C6a(N)	^{2}C8(N,E_3)-^{3}C4a(N,E) ^{3}C6a(N,E)-^{1}C3(N,$E_{3\text{-}4}$)
TC2-3-012b		^{1}C3($E_{3\text{-}4}$)-^{2}C4a(N)	^{2}C6a(N,E)-^{3}C3(N,$E_{3\text{-}4}$) ^{3}H_{C8H}(N,E)-^{1}C4a(N,E)
TC2-3-003			^{1}H_{C9H}(N,E)-^{2}C6a(N,E) ^{2}C8(N,$E_{7\text{-}8}$)-^{3}C4a(N,E) ^{3}C6a(N,E)-^{1}C3(N,$E_{3\text{-}4}$)

Table S5. Coordination Modes of Dication Singlets

Compound	Sulfate	Bisulfate	Sulfuric Acid
DC1-1-100	C3-C4a		
DC1-1-010		C3($E_{3\text{-}4}$)-C4a(N)	
DC1-1-001			C3($E_{3\text{-}4}$,N)-C4a(N,E)
DC1-2-110	^{1}C3-^{2}C4a	^{2}C8($E_{3\text{-}4}$)-^{3}C4a(N)	
DC1-2-020		^{1}C4a(N)-^{2}C3($E_{3\text{-}4}$) ^{2}C6a(N)-^{3}C3($E_{3\text{-}4}$)	
DC1-2-011		^{1}C3($E_{3\text{-}4}$)-^{2}C4a(N)	^{2}C8($E_{3\text{-}4}$,N)-^{3}C4a(N,E)
DC1-2-002			^{1}C4a(N,E)-^{2}C3($E_{3\text{-}4}$,N) ^{2}C6a(N,E)-^{3}C3($E_{3\text{-}4}$,N)
DC1-3-030		^{1}U(E_{N})-^{2}C6a(N) ^{2}C6a(N)-^{3}C3($E_{3\text{-}4}$) ^{3}C4a(N)-^{1}U(E_{N})	
DC1-3-021a		^{1}U(N)-^{2}C6a(N) ^{3}C4a(E)-^{1}U(E)	^{2}C8(N,$E_{3\text{-}4}$)-^{3}C4a(N,E)
DC1-3-021b		^{1}C3(N)-^{2}C4a(E) ^{2}C6a(N)-^{3}C3($E_{3\text{-}4}$)	^{3}C4a(N,E)-^{1}H_{C8H}(N,E)
DC1-3-012a		^{1}U(E)-^{2}C6a(E)	^{2}C6a(N,E)-^{3}C3(N,$E_{3\text{-}4}$) ^{3}C6a(N,E)-^{1}U(N,E)
DC1-3-012b		^{1}C3($E_{3\text{-}4}$)-^{2}C4a(N)	^{2}C6a(N,E)-^{3}C3(N,$E_{3\text{-}4}$) ^{3}H_{C8H}(N,E)-^{1}C4a(N,E)
DC1-3-003			^{1}U(N,E)-^{2}C6a(N,E) ^{2}C8(N,$E_{7\text{-}8}$)-^{3}C4a(N,E) ^{3}C6a(N,E)-^{1}C3(N,$E_{3\text{-}4}$)

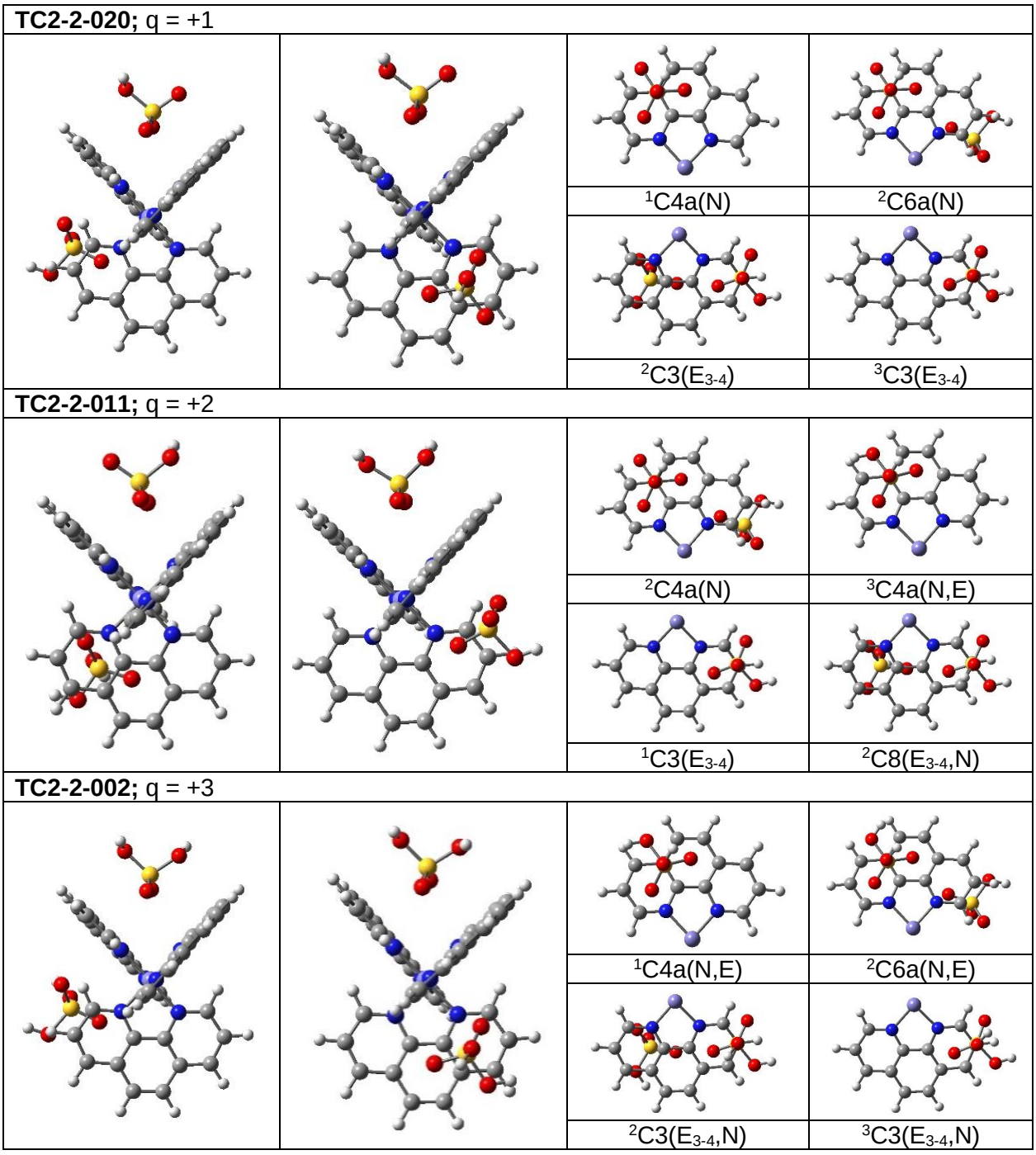

Figure S1. Molecular models of **TC2-2-020, TC2-2-011,** and **TC2-2-002** computed at the SMD(APFD/6-311G*) level of ferriin doublet in its aggregate with two OSLs of sulfate, bisulfate, and sulfuric acid. The cavity views emphasize the placement of one OSL between two phen ligands, and the four images on the right emphasize the placement of the two OSLs relative to one phen ligand.

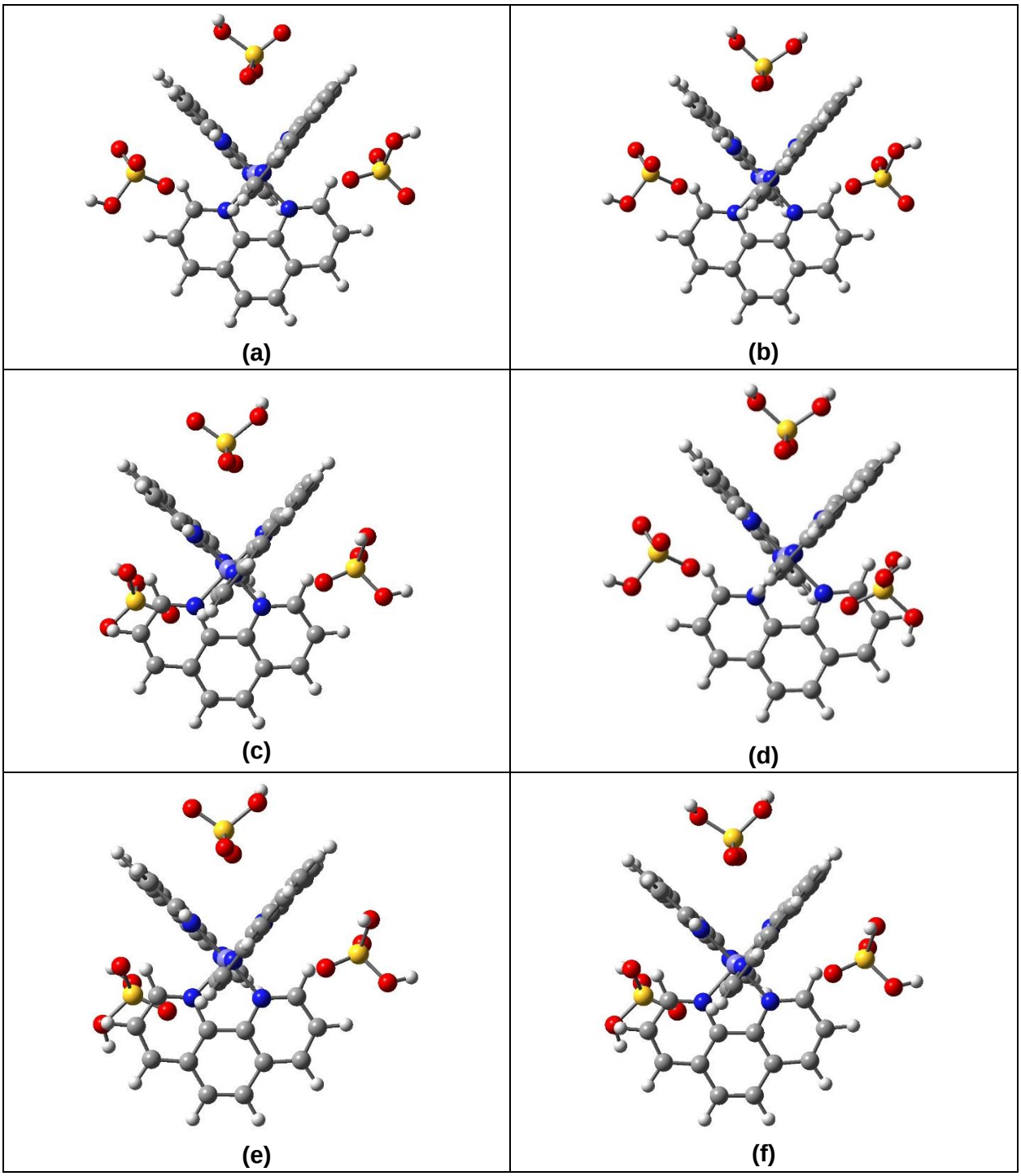

Figure S2. Cavity views of **TC2-3** aggregates computed at the SMD(APFD/6-311G*) level of ferriin doublet in its aggregates with three OSLs. (a) **TC2-3-030**, (b) **TC2-3-021a**, (c) **TC2-3-021b**, (d) **TC2-3-012a**, (e) **TC2-3-012b**, and (f) **TC2-3-003.**

Table S6. Summary of Literature Contributions to the Proton Affinity of Water

Authors	Year	PA(H_2O) (kcal/mol)	Method
Jursic	1999	162.4	*Ab initio* and DFT
Hunter & Lias	1998	165.2 ± 0.7	Summary of theoretical and proton transfer equilibrium data
Peterson *et al.*	1998	165.1 ± 0.3	Perturbation theory, coupled cluster theory
Ng *et al.*	1977	165.8 ± 1.8	Photoionization experiment
Chong *et al.*	1971	168	Ionization experiment with quadrupole mass filter
Chupka *et al.*	1968	165	Photoionization experiment
Munson & Franklin	1964	167	Appearance potentials of hydronium from organic compounds