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Theoretical Study of Deuterium Isotope Effects on Acid-Base Equilibria under Ambient and Hydrothermal Conditions

Nelaine Mora-Diez[1*], Yulia Egorova[1], Hart Plommer[1], Peter R. Tremaine[2]

[1]Department of Chemistry, Thompson Rivers University, Kamloops, BC, V2C 0C8, Canada.
[2]Department of Chemistry, University of Guelph, Guelph, ON, N1G 2W1, Canada.

Supporting Information

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Table S1.
Calculated raw data with the B3LYP functional and the IEF-PCM (uahf) solvation method.[a]

Molecule	Solvent	T(°C)	Species	TCG_{gas}	G_{gas}	E_w	ΔG_{solv}	$\Delta G_{solv\ (HF)}$	G_w	G_{1w}	G_{2w}	G_{3w}
phenol	H_2O	25	Acid	0.07489	-307.48384	-307.57159	-6.68	-6.94	-307.49801	-307.49670	-307.49449	-307.49490
			Conj base	0.06049	-306.933566	-307.096251	-62.95	-68.07	-307.03628	-307.03576	-307.03388	-307.04204
		250	Acid	0.05355	-307.50518	-307.57099	-1.46	-1.72	-307.51861	-307.51744	-307.50751	-307.50792
			Conj base	0.03952	-306.954535	-307.0932177	-56.39	-61.37	-307.05370	-307.05369	-307.04440	-307.05233
	D_2O	25	Acid	0.07132	-307.48741	-307.57159	-6.74	-7.01	-307.50139	-307.50027	-307.49815	-307.49858
			Conj base	0.06049	-306.933566	-307.0962468	-63.01	-68.13	-307.03628	-307.03575	-307.03398	-307.04214
		250	Acid	0.04963	-307.50910	-307.57099	-1.55	-1.81	-307.52233	-307.52136	-307.51157	-307.51199
			Conj base	0.03952	-306.954534	-307.0931977	-56.46	-61.45	-307.05368	-307.05367	-307.04451	-307.05246
3-methoxyphenol	H_2O	25	Acid	0.10351	-422.01195	-422.13071	-7.82	-8.11	-422.02876	-422.02720	-422.02441	-422.02488
			Conj base	0.08850	-421.46197	-421.65530	-64.28	-69.16	-421.56738	-421.56681	-421.56441	-421.57218
		250	Acid	0.07630	-422.03916	-422.13001	-1.31	-1.60	-422.05510	-422.05371	-422.04125	-422.04171
			Conj base	0.06122	-421.48925	-421.65210	-56.38	-61.14	-421.59049	-421.59088	-421.57910	-421.58669
	D_2O	25	Acid	0.09994	-422.01552	-422.13071	-7.90	-8.19	-422.03214	-422.03077	-422.02811	-422.02858
			Conj base	0.08850	-421.46197	-421.65530	-64.36	-69.23	-421.56738	-421.56680	-421.56454	-421.57230
		250	Acid	0.07237	-422.04309	-422.13001	-1.43	-1.71	-422.05883	-422.05763	-422.04537	-422.04581
			Conj base	0.06122	-421.48925	-421.65208	-56.48	-61.23	-421.59047	-421.59086	-421.57926	-421.58683
4-methoxyphenol	H_2O	25	Acid	0.10319	-422.00907	-422.12808	-8.33	-8.71	-422.02638	-422.02489	-422.02235	-422.02295
			Conj base	0.09016	-421.45392	-421.65019	-65.21	-70.17	-421.56260	-421.56003	-421.55783	-421.56574
		250	Acid	0.07575	-422.03651	-422.12729	-1.76	-2.14	-422.05296	-422.05154	-422.03932	-422.03992
			Conj base	0.06500	-421.47908	-421.64695	-57.29	-62.12	-421.58584	-421.58195	-421.57037	-421.57807
	D_2O	25	Acid	0.09963	-422.01263	-422.12801	-8.37	-8.77	-422.02974	-422.02839	-422.02597	-422.02661
			Conj base	0.09016	-421.45392	-421.65019	-65.29	-70.24	-421.56259	-421.56003	-421.55796	-421.56585
		250	Acid	0.07183	-422.04043	-422.12728	-1.87	-2.26	-422.05668	-422.05546	-422.04341	-422.04403
			Conj base	0.06500	-421.47908	-421.64693	-57.38	-62.22	-421.58582	-421.58193	-421.57052	-421.57823

4-bromophenol	H_2O	25	Acid	0.06153	-2881.03895	-2881.11483	-7.02	-7.42	-2881.0548	-2881.0533	-2881.0501	-2881.0508
			Conj base	0.04739	-2880.50114	-2880.64303	-57.51	-61.63	-2880.5965	-2880.5956	-2880.5928	-2880.5994
		250	Acid	0.03614	-2881.06435	-2881.11418	-0.77	-1.16	-2881.0794	-2881.0780	-2881.0656	-2881.0662
			Conj base	0.02220	-2880.52633	-2880.64022	-50.08	-54.09	-2880.6182	-2880.6180	-2880.6061	-2880.6125
	D_2O	25	Acid	0.05795	-2881.04254	-2881.11483	-7.10	-7.50	-2881.0582	-2881.0569	-2881.0539	-2881.0545
			Conj base	0.04739	-2880.50114	-2880.64303	-57.58	-61.70	-2880.5965	-2880.5956	-2880.5929	-2880.5995
		250	Acid	0.03218	-2881.06830	-2881.11417	-0.89	-1.27	-2881.0832	-2881.0820	-2881.0697	-2881.0703
			Conj base	0.02220	-2880.52633	-2880.64021	-50.18	-54.19	-2880.6182	-2880.6180	-2880.6063	-2880.6127
2-nitrophenol	H_2O	25	Acid	0.07442	-512.054689	-512.13880	-3.38	-3.73	-512.06564	-512.06438	-512.06008	-512.06063
			Conj base	0.06076	-511.521277	-511.67500	-55.46	-59.12	-511.61668	-511.61424	-511.60966	-511.61549
		250	Acid	0.04790	-512.081212	-512.1384083	2.90	2.56	-512.09184	-512.09051	-512.07659	-512.07713
			Conj base	0.03560	-511.546445	-511.6722588	-47.81	-51.36	-511.64072	-511.63666	-511.62264	-511.62829
	D_2O	25	Acid	0.07084	-512.05827	-512.13880	-3.47	-3.82	-512.06913	-512.06796	-512.06380	-512.06436
			Conj base	0.06076	-511.521277	-511.67500	-55.55	-59.20	-511.61668	-511.61423	-511.60980	-511.61562
		250	Acid	0.04404	-512.085073	-512.1384057	2.78	2.43	-512.09562	-512.09437	-512.08064	-512.08120
			Conj base	0.03560	-511.546444	-511.6722407	-47.92	-51.47	-511.64072	-511.63664	-511.62281	-511.62847
4-nitrophenol	H_2O	25	Acid	0.07313	-512.05104	-512.14417	-9.76	-10.02	-512.07303	-512.07104	-512.06659	-512.06700
			Conj base	0.06039	-511.53946	-511.68607	-51.51	-54.82	-511.62671	-511.62568	-511.62155	-511.62682
		250	Acid	0.04565	-512.07852	-512.14332	-3.15	-3.41	-512.09949	-512.09767	-512.08354	-512.08395
			Conj base	0.03371	-511.56614	-511.68369	-44.12	-47.33	-511.65085	-511.64998	-511.63645	-511.64157
	D_2O	25	Acid	0.06955	-512.05461	-512.14417	-9.85	-10.10	-512.07640	-512.07462	-512.07031	-512.07071
			Conj base	0.06039	-511.53946	-511.68607	-51.59	-54.90	-511.62671	-511.62568	-511.62168	-511.62695
		250	Acid	0.04172	-512.08245	-512.14331	-3.27	-3.53	-512.10320	-512.10159	-512.08766	-512.08807
			Conj base	0.03371	-511.56614	-511.68367	-44.22	-47.43	-511.65083	-511.64996	-511.63661	-511.64173
2,4-dinitrophenol	H_2O	25	Acid	0.07190	-716.61616	-716.70248	-4.85	-5.41	-716.63177	-716.63058	-716.62389	-716.62478
			Conj base	0.05847	-716.11488	-716.25329	-45.70	-48.59	-716.19563	-716.19482	-716.18771	-716.19232
		250	Acid	0.03899	-716.64908	-716.70188	2.77	2.22	-716.66413	-716.66290	-716.64467	-716.64554
			Conj base	0.02553	-716.14782	-716.25104	-37.16	-39.96	-716.22607	-716.22551	-716.20704	-716.21150
	D_2O	25	Acid	0.06833	-716.61973	-716.70248	-4.96	-5.52	-716.63524	-716.63415	-716.62764	-716.62853
			Conj base	0.05848	-716.11488	-716.25328	-45.80	-48.70	-716.19563	-716.19481	-716.18787	-716.19249
		250	Acid	0.03514	-716.65293	-716.70188	2.62	2.07	-716.66791	-716.66674	-716.64875	-716.64963

			Conj base	0.02553	-716.14782	-716.25103	-37.30	-40.10	-716.22605	-716.22549	-716.20726	-716.21173
2,5-dinitrophenol	H_2O	25	Acid	0.07141	-716.61355	-716.69843	-4.29	-4.82	-716.62837	-716.62702	-716.62038	-716.62123
			Conj base	0.05821	-716.10303	-716.24353	-47.20	-50.14	-716.18596	-716.18532	-716.17824	-716.18293
		250	Acid	0.03816	-716.64680	-716.69787	3.34	2.82	-716.66113	-716.65971	-716.64147	-716.64230
			Conj base	0.02630	-716.13493	-716.24115	-38.51	-41.37	-716.21840	-716.21485	-716.19630	-716.20086
	D_2O	25	Acid	0.06783	-716.61712	-716.69843	-4.39	-4.93	-716.63180	-716.63060	-716.62412	-716.62498
			Conj base	0.05821	-716.10303	-716.24353	-47.30	-50.24	-716.18589	-716.18532	-716.17840	-716.18309
		250	Acid	0.03430	-716.65066	-716.69787	3.19	2.67	-716.66493	-716.66357	-716.64557	-716.64640
			Conj base	0.02630	-716.13493	-716.24114	-38.65	-41.51	-716.21840	-716.21483	-716.19652	-716.20108
2,6-dinitrophenol	H_2O	25	Acid	0.07323	-716.60192	-716.69071	-5.65	-6.70	-716.62068	-716.61748	-716.61092	-716.61260
			Conj base	0.05998	-716.09544	-716.24068	-49.01	-52.18	-716.18121	-716.18071	-716.17354	-716.17859
		250	Acid	0.04235	-716.63280	-716.69005	1.96	0.94	-716.65273	-716.64770	-716.62968	-716.63131
			Conj base	0.03034	-716.12507	-716.23813	-40.26	-43.33	-716.21519	-716.20779	-716.18923	-716.19412
	D_2O	25	Acid	0.06969	-716.60547	-716.69071	-5.76	-6.81	-716.62413	-716.62102	-716.61465	-716.61632
			Conj base	0.05998	-716.09544	-716.24068	-49.12	-52.29	-716.18120	-716.18071	-716.17371	-716.17877
		250	Acid	0.03853	-716.63662	-716.69005	1.81	0.79	-716.65647	-716.65152	-716.63374	-716.63536
			Conj base	0.03034	-716.12507	-716.23812	-40.40	-43.48	-716.21518	-716.20778	-716.18945	-716.19436
3,5-dinitrophenol	H_2O	25	Acid	0.07031	-716.60780	-716.70145	-10.28	-11.06	-716.63323	-716.63114	-716.62419	-716.62543
			Conj base	0.05655	-716.10514	-716.24313	-46.95	-50.57	-716.18746	-716.18658	-716.17996	-716.18573
		250	Acid	0.03626	-716.64185	-716.70045	-2.34	-3.11	-716.66619	-716.66420	-716.64558	-716.64681
			Conj base	0.02255	-716.13914	-716.24082	-38.36	-41.87	-716.21869	-716.21827	-716.20027	-716.20586
	D_2O	25	Acid	0.06674	-716.61137	-716.70145	-10.39	-11.17	-716.63657	-716.63471	-716.62793	-716.62917
			Conj base	0.05655	-716.10514	-716.24313	-47.06	-50.68	-716.18745	-716.18658	-716.18013	-716.18590
		250	Acid	0.03234	-716.64577	-716.70045	-2.50	-3.26	-716.66989	-716.66811	-716.64976	-716.65097
			Conj base	0.02255	-716.13914	-716.24080	-38.50	-42.01	-716.21867	-716.21825	-716.20049	-716.20609
4-chloro-2,6-dinitrophenol	H_2O	25	Acid	0.06014	-1176.23295	-1176.30818	-4.14	-5.44	-1176.2492	-1176.2480	-1176.2396	-1176.2416
			Conj base	0.04808	-1175.73212	-1175.86002	-44.64	-47.22	-1175.8128	-1175.8119	-1175.8033	-1175.8074
		250	Acid	0.02423	-1176.26886	-1176.30753	4.27	3.01	-1176.2843	-1176.2833	-1176.2621	-1176.2641
			Conj base	0.01538	-1175.76482	-1175.85765	-35.22	-37.72	-1175.8423	-1175.8423	-1175.8209	-1175.8249
	D_2O	25	Acid	0.05656	-1176.23653	-1176.30818	-4.27	-5.56	-1176.2527	-1176.2516	-1176.2433	-1176.2454
			Conj base	0.04808	-1175.73213	-1175.86001	-44.76	-47.34	-1175.8128	-1175.8119	-1175.8035	-1175.8076

		250	Acid	0.02037	-1176.27272	-1176.30752	4.10	2.84	-1176.2881	-1176.2871	-1176.2662	-1176.2682
			Conj base	0.01538	-1175.76482	-1175.85764	-35.38	-37.88	-1175.8422	-1175.8423	-1175.8212	-1175.8252
β-naphthol	H_2O	25	Acid	0.11801	-461.11877	-461.25132	-6.93	-7.35	-461.13475	-461.13331	-461.12981	-461.13048
			Conj base	0.10386	-460.57764	-460.77727	-58.13	-63.62	-460.67439	-460.67341	-460.67028	-460.67903
		250	Acid	0.09045	-461.14633	-461.25063	0.18	-0.23	-461.16144	-461.16017	-461.14604	-461.14669
			Conj base	0.07671	-460.60479	-460.77429	-49.77	-55.09	-460.69809	-460.69758	-460.68410	-460.69258
	D_2O	25	Acid	0.11444	-461.12234	-461.25132	-7.02	-7.44	-461.13813	-461.13688	-461.13352	-461.13419
			Conj base	0.10386	-460.57764	-460.77727	-58.22	-63.70	-460.67438	-460.67341	-460.67042	-460.67915
		250	Acid	0.08653	-461.15025	-461.25062	0.05	-0.35	-461.16517	-461.16409	-461.15017	-461.15080
			Conj base	0.07671	-460.60479	-460.77427	-49.88	-55.21	-460.69807	-460.69756	-460.68427	-460.69277
β-naphthoic acid	H_2O	25	Acid	0.12610	-574.50006	-574.64155	-6.22	-6.85	-574.51773	-574.51545	-574.50997	-574.51097
			Conj base	0.11194	-573.96596	-574.18215	-62.45	-67.19	-574.07109	-574.07021	-574.06548	-574.07303
		250	Acid	0.09442	-574.53174	-574.64090	1.75	1.15	-574.54870	-574.54648	-574.52895	-574.52991
			Conj base	0.08045	-573.99745	-574.17905	-53.06	-57.69	-574.09915	-574.09860	-574.08200	-574.08938
	D_2O	25	Acid	0.12250	-574.50365	-574.64155	-6.33	-6.95	-574.52106	-574.51905	-574.51374	-574.51473
			Conj base	0.11194	-573.96596	-574.18214	-62.55	-67.29	-574.07108	-574.07020	-574.06564	-574.07319
		250	Acid	0.09049	-574.53566	-574.64090	1.60	1.00	-574.55237	-574.55040	-574.53311	-574.53407
			Conj base	0.08045	-573.99745	-574.17903	-53.20	-57.83	-574.09913	-574.09858	-574.08223	-574.08961
acetic acid	H_2O	25	Acid	0.03409	-229.13074	-229.17795	-6.79	-7.05	-229.14608	-229.14386	-229.14156	-229.14197
			Conj base	0.01892	-228.58357	-228.71724	-71.10	-75.62	-228.69904	-228.69833	-228.69688	-228.70408
		250	Acid	0.01592	-229.14891	-229.17743	-3.03	-3.29	-229.16389	-229.16151	-229.15374	-229.15415
			Conj base	-0.00004	-228.60253	-228.71416	-65.91	-70.33	-228.71426	-228.71421	-228.70757	-228.71461
	D_2O	25	Acid	0.03049	-229.13434	-229.17795	-6.83	-7.10	-229.14942	-229.14745	-229.14522	-229.14565
			Conj base	0.01892	-228.58357	-228.71724	-71.14	-75.66	-228.69903	-228.69832	-228.69694	-228.70414
		250	Acid	0.01200	-229.15283	-229.17743	-3.10	-3.36	-229.16757	-229.16543	-229.15777	-229.15818
			Conj base	-0.00004	-228.60253	-228.71414	-65.96	-70.38	-228.71424	-228.71419	-228.70765	-228.71469
s-collidine	H_2O	25	Acid	0.14672	-366.58292	-366.80881	-47.68	-47.47	-366.66296	-366.66209	-366.65890	-366.65857
			Conj base	0.13352	-366.20903	-366.35001	-2.54	-2.49	-366.21696	-366.21649	-366.21308	-366.21300
		250	Acid	0.11436	-366.61528	-366.80671	-39.73	-39.53	-366.69219	-366.69235	-366.67859	-366.67828
			Conj base	0.10201	-366.24054	-366.34965	4.27	4.31	-366.24786	-366.24764	-366.23374	-366.23367
	D_2O	25	Acid	0.14302	-366.58662	-366.80881	-47.77	-47.56	-366.66650	-366.66578	-366.66274	-366.66241

			Conj base	0.13352	-366.20903	-366.35001	-2.64	-2.58	-366.21696	-366.21649	-366.21324	-366.21314
		250	Acid	0.11040	-366.61924	-366.80669	-39.85	-39.65	-366.69599	-366.69629	-366.68274	-366.68242
			Conj base	0.10201	-366.24054	-366.34965	4.14	4.18	-366.24785	-366.24764	-366.23394	-366.23388
acridine	H_2O	25	Acid	0.16048	-555.93271	-556.16950	-45.17	-45.05	-556.01084	-556.00902	-556.00469	-556.00450
			Conj base	0.14723	-555.55765	-555.71495	-3.54	-4.19	-555.56915	-555.56773	-555.56330	-555.56433
		250	Acid	0.12922	-555.96397	-556.16739	-35.83	-35.71	-556.03987	-556.03817	-556.02106	-556.02087
			Conj base	0.11681	-555.58807	-555.71448	4.71	4.09	-555.59956	-555.59767	-555.58056	-555.58155
	D_2O	25	Acid	0.15682	-555.93636	-556.16950	-45.29	-45.16	-556.01433	-556.01268	-556.00854	-556.00833
			Conj base	0.14723	-555.55765	-555.71495	-3.65	-4.30	-555.56915	-555.56772	-555.56347	-555.56451
		250	Acid	0.12529	-555.96790	-556.16738	-35.98	-35.86	-556.04363	-556.04209	-556.02523	-556.02504
			Conj base	0.11681	-555.58807	-555.71448	4.55	3.93	-555.61029	-555.59766	-555.58082	-555.58181
H_2O	H_2O	25		0.00365	-76.45488	-76.47028	-6.6	-6.47	-76.467653	-76.46664	-76.46540	-76.46519
		250		-0.00466	-76.46319	-76.46981	-4.79	-4.68	-76.47545	-76.47447	-76.47082	-76.47065
H_3O^+		25		0.01513	-76.71610	-76.90213	-107.4	-106.9	-76.897566	-76.88699	-76.88717	-76.88644
		250		0.00551	-76.72573	-76.89769	-103.1	-102.7	-76.902008	-76.89218	-76.89006	-76.88936
D_2O	D_2O	25		-0.00322	-76.46175	-76.47028	-6.62	-6.5	-76.474276	-76.47350	-76.47230	-76.47210
		250		-0.01237	-76.47090	-76.46981	-4.82	-4.71	-76.482934	-76.48218	-76.47858	-76.47840
D_3O^+		25		0.00463	-76.72661	-76.90212	-107.4	-106.9	-76.906193	-76.89749	-76.89770	-76.89697
		250		-0.00610	-76.73733	-76.89766	-103.1	-102.7	-76.911832	-76.90375	-76.90166	-76.90096

[a] Calculated raw data (all in atomic units, except ΔG_{solv} and $\Delta G_{solv(HF)}$ in kcal/mol).
Symbols used: gas-phase energy (E_{gas}, B3LYP/6-311++G(d,p), uncorrected) and thermal correction (TCG_{gas}) to the standard Gibbs free energy of formation (G_{gas}, at 298.15 K); energy (E_w, B3LYP-PCM/6-311++G(d,p)//B3LYP/6-311++G(d,p), uncorrected) and standard Gibbs free energy of formation (G_w, B3LYP-PCM/6-311++G(d,p), at 298.15 K) in solution; Gibbs free energy of solvation at 298.15 K (ΔG_{solv} and $\Delta G_{solv(HF)}$ (HF-PCM/6-31G(d)//B3LYP/6-311++G(d,p)).

Calculated pK_a values and their errors (mean absolute error, MAE, and average error, AE) in H_2O and D_2O at 25°C/101.3 kPa and 250°C/20 MPa using the B3LYP functional and the IEF-PCM (uahf) solvation method.

Table S2.
Calculated pK_a values in H_2O at 25°C and 101.3 kPa and their errors.

		Calculated pK_a				**Error (Calc - Exp)**			
Exp. pK_a	**Molecule**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**
10.00	phenol	17.52	16.71	13.38	12.89	7.52	6.71	3.38	2.89
9.62	3-methoxyphenol	17.26	16.44	13.30	12.73	7.64	6.82	3.68	3.11
10.24	4-methoxyphenol	19.32	18.51	15.38	13.84	9.08	8.27	5.14	3.60
9.35	4-bromophenol	16.00	15.22	12.72	11.35	6.65	5.87	3.37	2.00
7.24	2-nitrophenol	12.55	12.03	9.83	7.02	7.52	6.71	3.38	2.89
7.23	4-nitrophenol	10.35	9.55	7.54	5.80	7.64	6.82	3.68	3.11
4.07	2,4-dinitrophenol	5.94	5.48	4.00	1.12	9.08	8.27	5.14	3.60
5.19	2,5-dinitrophenol	8.67	8.22	6.68	4.00	6.65	5.87	3.37	2.00
3.73	2,6-dinitrophenol	6.40	6.03	4.71	2.65	5.31	4.79	2.59	-0.22
7.00	3,5-dinitrophenol	9.98	9.18	7.33	5.55	3.12	2.32	0.31	-1.43
2.97	4-chloro-2,6-dinitrophenol	6.09	5.53	4.82	1.24	1.87	1.41	-0.07	-2.95
9.55	β-naphthol	17.04	16.22	12.73	12.26	7.49	6.67	3.18	2.71
4.21	β-naphthoic acid	10.30	9.30	6.51	5.95	6.09	5.09	2.30	1.74
4.75	acetic acid	10.43	9.39	6.49	6.13	5.68	4.64	1.74	1.38
7.43	s-collidine	10.46	9.92	10.03	5.66	3.03	2.49	2.60	-1.77
5.58	acridine	8.48	7.88	7.54	3.67	2.90	2.30	1.96	-1.91
					MAE	4.91	4.21	2.18	1.95
					AE	4.91	4.21	2.18	0.23

Table S3.
Calculated pK_a values in D_2O at 25°C and 101.3 kPa and their errors.

		Calculated pK_a				Error (Calc - Exp)			
Exp. pK_a	**Molecule**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**
10.62	phenol	17.49	16.68	13.36	13.52	6.87	6.06	2.74	2.90
10.20	3-methoxyphenol	17.23	16.41	13.29	13.36	7.03	6.21	3.09	3.16
10.85	4-methoxyphenol	19.26	18.45	15.35	14.46	8.41	7.60	4.50	3.61
9.94	4-bromophenol	15.98	15.21	12.71	11.99	6.04	5.27	2.77	2.05
7.79	2-nitrophenol	12.52	12.00	9.82	7.70	4.73	4.21	2.03	-0.09
7.76	4-nitrophenol	10.32	9.54	7.53	6.43	2.56	1.78	-0.23	-1.33
4.57	2,4-dinitrophenol	5.91	5.46	3.98	1.80	1.34	0.89	-0.59	-2.77
5.69	2,5-dinitrophenol	8.64	8.19	6.67	4.69	2.95	2.50	0.98	-1.00
4.22	2,6-dinitrophenol	6.36	5.99	4.67	3.32	2.14	1.77	0.45	-0.90
7.57	3,5-dinitrophenol	9.95	9.15	7.30	6.17	2.38	1.58	-0.27	-1.40
3.44	4-chloro-2,6-dinitrophenol	6.06	5.51	4.80	1.91	2.62	2.07	1.36	-1.53
10.09	β-naphthol	17.00	16.19	12.72	12.90	6.91	6.10	2.63	2.81
4.63	β-naphthoic acid	10.28	9.29	6.51	6.56	5.65	4.66	1.88	1.93
5.25	acetic acid	10.41	9.37	6.49	6.75	5.16	4.12	1.24	1.50
	s-collidine	10.48	9.94	10.06	6.36				
	acridine	8.49	7.90	7.56	4.35				
					MAE	4.63	3.92	1.77	1.93
					AE	4.63	3.92	1.61	0.64

Table S4.
Calculated pK_a values in H_2O at 250°C and 20.0 MPa and their errors.

		Calculated pK_a				Error (Calc - Exp)			
Exp. pK_a	**Molecule**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**
	phenol	10.87	10.30	8.46	8.31				
	3-methoxyphenol	10.62	10.05	8.31	8.23				
	4-methoxyphenol	12.40	11.83	10.10	8.89				
	4-bromophenol	9.89	9.33	7.96	7.33				
6.85	2-nitrophenol	8.27	7.90	6.69	4.69	1.42	1.05	-0.16	-2.16
6.57	4-nitrophenol	6.66	6.10	5.00	4.04	0.09	-0.47	-1.57	-2.53
	2,4-dinitrophenol	3.95	3.62	2.81	1.27				
	2,5-dinitrophenol	5.91	5.59	4.75	2.50				
	2,6-dinitrophenol	4.62	4.36	3.63	1.13				
	3,5-dinitrophenol	6.19	5.63	4.62	3.75				
	4-chloro-2,6-dinitrophenol	4.91	4.53	4.14	2.30				
8.97	β-naphthol	10.56	9.99	8.07	7.90	1.59	1.02	-0.90	-1.07
5.98	β-naphthoic acid	6.71	6.06	4.51	4.28	0.73	0.08	-1.47	-1.70
6.00	acetic acid	6.55	5.86	4.25	4.30	0.55	-0.14	-1.75	-1.70
4.26	s-collidine	5.87	5.51	5.58	2.91	1.61	1.25	1.32	-1.35
3.41	acridine	4.77	4.37	4.19	1.86	1.36	0.96	0.78	-1.55
					MAE	1.05	0.71	1.14	1.72
					AE	1.05	0.53	-0.54	-1.72

Table S5.
Calculated pK_a values in D_2O at 250°C and 20.0 MPa and their errors.

		Calculated pK_a				Error (Calc - Exp)			
Exp. pK_a	**Molecule**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**
	phenol	10.88	10.33	8.48	8.68				
	3-methoxyphenol	10.64	10.07	8.34	8.60				
	4-methoxyphenol	12.41	11.85	10.13	9.26				
	4-bromophenol	9.91	9.37	7.99	7.71				
	2-nitrophenol	8.27	7.91	6.70	5.07				
	4-nitrophenol	6.67	6.13	5.03	4.41				
	2,4-dinitrophenol	3.95	3.62	2.81	1.65				
	2,5-dinitrophenol	5.92	5.60	4.76	2.88				
	2,6-dinitrophenol	4.61	4.35	3.63	1.51				
	3,5-dinitrophenol	6.21	5.66	4.64	4.11				
	4-chloro-2,6-dinitrophenol	4.91	4.54	4.15	2.70				
9.36	β-naphthol	10.58	10.02	8.09	8.27	1.22	0.66	-1.27	-1.09
	β-naphthoic acid	6.73	6.08	4.53	4.64				
6.44	acetic acid	6.57	5.88	4.28	4.66	0.13	-0.56	-2.16	-1.78
	s-collidine	5.89	5.54	5.60	3.30				
	acridine	4.79	4.39	4.21	2.24				
					MAE	0.68	0.61	1.71	1.44
					AE	0.68	0.05	-1.71	-1.44

Calculated pK_a differences and their errors (mean absolute error, MAE, and average error, AE) in H_2O and D_2O at 25°C/101.3 kPa and 250°C/20 MPa using the B3LYP functional and the IEF-PCM (uahf) solvation method.

Table S6.
Calculated temperature-dependence of pK_a in H_2O (pK_a (25°C) - pK_a (250°C)) and errors.

		Calculated pK_a Difference				**Error (Calc - Exp)**			
Exp.	**Molecule**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**
	phenol	6.65	6.42	4.92	4.58				
	3-methoxyphenol	6.64	6.39	4.99	4.50				
	4-methoxyphenol	6.92	6.68	5.28	4.95				
	4-bromophenol	6.12	5.88	4.76	4.01				
0.39	2-nitrophenol	4.28	4.13	3.14	2.32	3.89	3.74	2.75	1.93
0.66	4-nitrophenol	3.69	3.46	2.55	1.76	3.03	2.80	1.89	1.10
	2,4-dinitrophenol	1.98	1.86	1.19	-0.15				
	2,5-dinitrophenol	2.75	2.62	1.93	1.51				
	2,6-dinitrophenol	1.78	1.68	1.07	1.52				
	3,5-dinitrophenol	3.79	3.55	2.70	1.81				
	4-chloro-2,6-dinitrophenol	1.18	1.00	0.67	-1.07				
0.58	β-naphthol	6.47	6.23	4.66	4.36	5.89	5.65	4.08	3.78
-1.77	β-naphthoic acid	3.59	3.24	2.00	1.67	5.36	5.01	3.77	3.44
-1.25	acetic acid	3.87	3.53	2.24	1.83	5.12	4.78	3.49	3.08
3.17	s-collidine	4.59	4.40	4.45	2.74	1.42	1.23	1.28	-0.43
2.17	acridine	3.71	3.51	3.34	1.81	1.54	1.34	1.17	-0.36
					MAE	3.75	3.51	2.63	2.02
					AE	3.75	3.51	2.63	1.79

Table S7.
Calculated temperature-dependence of pK_a in D_2O (pK_a (25°C) - pK_a (250°C)) and errors.

		Calculated pK_a Difference				Error (Calc - Exp)			
Exp.	**Molecule**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**
	phenol	6.60	6.36	4.88	4.85				
	3-methoxyphenol	6.59	6.34	4.95	4.76				
	4-methoxyphenol	6.84	6.60	5.22	5.21				
	4-bromophenol	6.07	5.83	4.72	4.28				
	2-nitrophenol	4.25	4.10	3.12	2.63				
	4-nitrophenol	3.65	3.41	2.50	2.02				
	2,4-dinitrophenol	1.95	1.84	1.16	0.14				
	2,5-dinitrophenol	2.72	2.59	1.91	1.81				
	2,6-dinitrophenol	1.75	1.64	1.05	1.82				
	3,5-dinitrophenol	3.74	3.49	2.66	2.06				
	4-chloro-2,6-dinitrophenol	1.15	0.97	0.65	-0.79				
0.73	β-naphthol	6.42	6.17	4.63	4.62	5.69	5.44	3.90	3.89
	β-naphthoic acid	3.55	3.21	1.97	1.93				
-1.19	acetic acid	3.84	3.49	2.21	2.09	5.03	4.68	3.40	3.28
	s-collidine	4.59	4.40	4.46	3.06				
	acridine	3.70	3.51	3.35	2.12				
					MAE	5.36	5.06	3.65	3.59
					AE	5.36	5.06	3.65	3.59

Table S8.
Calculated DIE on pK_a values (ΔpK_a = pK_a (D_2O) - pK_a (H_2O)) under ambient conditions (25°C/101.3 kPa) and their errors.

		Calculated ΔpK_a				Error (Calc - Exp)			
Exp.	**Molecule**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**
0.62	phenol	-0.03	-0.03	-0.01	0.63	-0.65	-0.65	-0.63	0.01
0.58	3-methoxyphenol	-0.03	-0.03	-0.01	0.63	-0.61	-0.61	-0.59	0.05
0.61	4-methoxyphenol	-0.06	-0.06	-0.03	0.62	-0.67	-0.67	-0.64	0.01
0.59	4-bromophenol	-0.02	-0.01	0.00	0.64	-0.61	-0.60	-0.59	0.05
0.55	2-nitrophenol	-0.03	-0.02	-0.01	0.68	-0.58	-0.57	-0.56	0.13
0.53	4-nitrophenol	-0.03	-0.02	-0.02	0.63	-0.56	-0.55	-0.55	0.10
0.50	2,4-dinitrophenol	-0.03	-0.02	-0.02	0.67	-0.53	-0.52	-0.52	0.17
0.50	2,5-dinitrophenol	-0.03	-0.02	-0.01	0.69	-0.53	-0.52	-0.51	0.19
0.49	2,6-dinitrophenol	-0.04	-0.04	-0.03	0.67	-0.53	-0.53	-0.52	0.18
0.57	3,5-dinitrophenol	-0.03	-0.03	-0.02	0.62	-0.60	-0.60	-0.59	0.05
0.47	4-chloro-2,6-dinitrophenol	-0.03	-0.02	-0.02	0.67	-0.50	-0.49	-0.49	0.20
0.54	β-naphthol	-0.03	-0.03	-0.01	0.63	-0.57	-0.57	-0.55	0.09
0.42	β-naphthoic acid	-0.02	-0.01	-0.01	0.61	-0.44	-0.43	-0.43	0.19
0.50	acetic acid	-0.02	-0.01	0.00	0.62	-0.52	-0.51	-0.50	0.12
	s-collidine	0.02	0.02	0.04	0.71				
	acridine	0.01	0.02	0.02	0.68				
					MAE	0.56	0.56	0.55	0.11
					AE	-0.56	-0.56	-0.55	0.11

Table S9.
Calculated DIE on pK_a values (ΔpK_a = pK_a (D_2O) - pK_a (H_2O)) under hydrothermal conditions (250°C/20 MPa) and their errors.

		Calculated ΔpK_a				Error (Calc - Exp)			
Exp.	**Molecule**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**	**G_{1w}**	**G_{2w}**	**G_{3w}**	**G_w**
	phenol	0.02	0.03	0.02	0.37				
	3-methoxyphenol	0.02	0.03	0.03	0.37				
	4-methoxyphenol	0.02	0.03	0.03	0.37				
	4-bromophenol	0.03	0.04	0.03	0.38				
	2-nitrophenol	0.00	0.01	0.01	0.38				
	4-nitrophenol	0.02	0.03	0.03	0.36				
	2,4-dinitrophenol	0.00	0.01	0.01	0.38				
	2,5-dinitrophenol	0.00	0.01	0.01	0.38				
	2,6-dinitrophenol	-0.01	0.00	-0.01	0.37				
	3,5-dinitrophenol	0.02	0.03	0.02	0.36				
	4-chloro-2,6-dinitrophenol	0.00	0.01	0.01	0.40				
0.39	β-naphthol	0.02	0.03	0.02	0.37	-0.37	-0.36	-0.37	-0.02
	β-naphthoic acid	0.02	0.02	0.02	0.36				
0.44	acetic acid	0.02	0.03	0.03	0.35	-0.42	-0.41	-0.41	-0.09
	s-collidine	0.02	0.02	0.02	0.38				
	acridine	0.01	0.02	0.02	0.38				
					MAE	0.40	0.39	0.39	0.05
					AE	-0.40	-0.39	-0.39	-0.05

Table S10.
Predicted pK_a values in D_2O using experimental pK_a values in H_2O (from Table 3) and calculated DIE values (ΔpK_a value, from Table 4 using eq. 11) under ambient and hydrothermal conditions.

	25°C, 1 atm				250°C, 20.0 Mpa			
Acids	**Exp $pK_a(H_2O)$**	**Calc ΔpK_a**	**Predicted [a] $pK_a(D_2O)$**	**Exp $pK_a(D_2O)$**	**Exp $pK_a(H_2O)$**	**Calc ΔpK_a**	**Predicted [a] $pK_a(D_2O)$**	**Exp $pK_a(D_2O)$**
phenol	10.00	0.63	10.63	10.62		0.37		
3-methoxyphenol	9.62	0.63	10.25	10.20		0.37		
4-methoxyphenol	10.24	0.62	10.86	10.85		0.37		
4-bromophenol	9.35	0.64	9.99	9.94		0.38		
2-nitrophenol	7.24	0.68	7.92	7.79	6.85	0.38	7.23	
4-nitrophenol	7.23	0.63	7.86	7.76	6.57	0.36	6.93	
2,4-dinitrophenol	4.07	0.67	4.74	4.57		0.38		
2,5-dinitrophenol	5.19	0.69	5.88	5.69		0.38		
2,6-dinitrophenol	3.73	0.67	4.40	4.22		0.37		
3,5-dinitrophenol	7.00	0.62	7.62	7.57		0.36		
4-chloro-2,6-dinitrophenol	2.97	0.67	3.64	3.44		0.40		
β-naphthol	9.55	0.63	10.18	10.09	8.97	0.37	9.34	9.36
β-naphthoic acid	4.21	0.61	4.82	4.63	5.98	0.36	6.34	
acetic acid	4.75	0.62	5.37	5.25	6.00	0.35	6.35	6.44
s-collidine	7.43	0.71	8.14		4.26	0.38	4.64	
acridine	5.58	0.68	6.26		3.41	0.38	3.79	
MAE			0.11				0.06	

[a] Predicted $pK_a(D_2O)$ = Exp $pK_a(H_2O)$ + Calc ΔpK_a

Figure S1. Experimental and calculated pK_a values in H_2O under ambient conditions

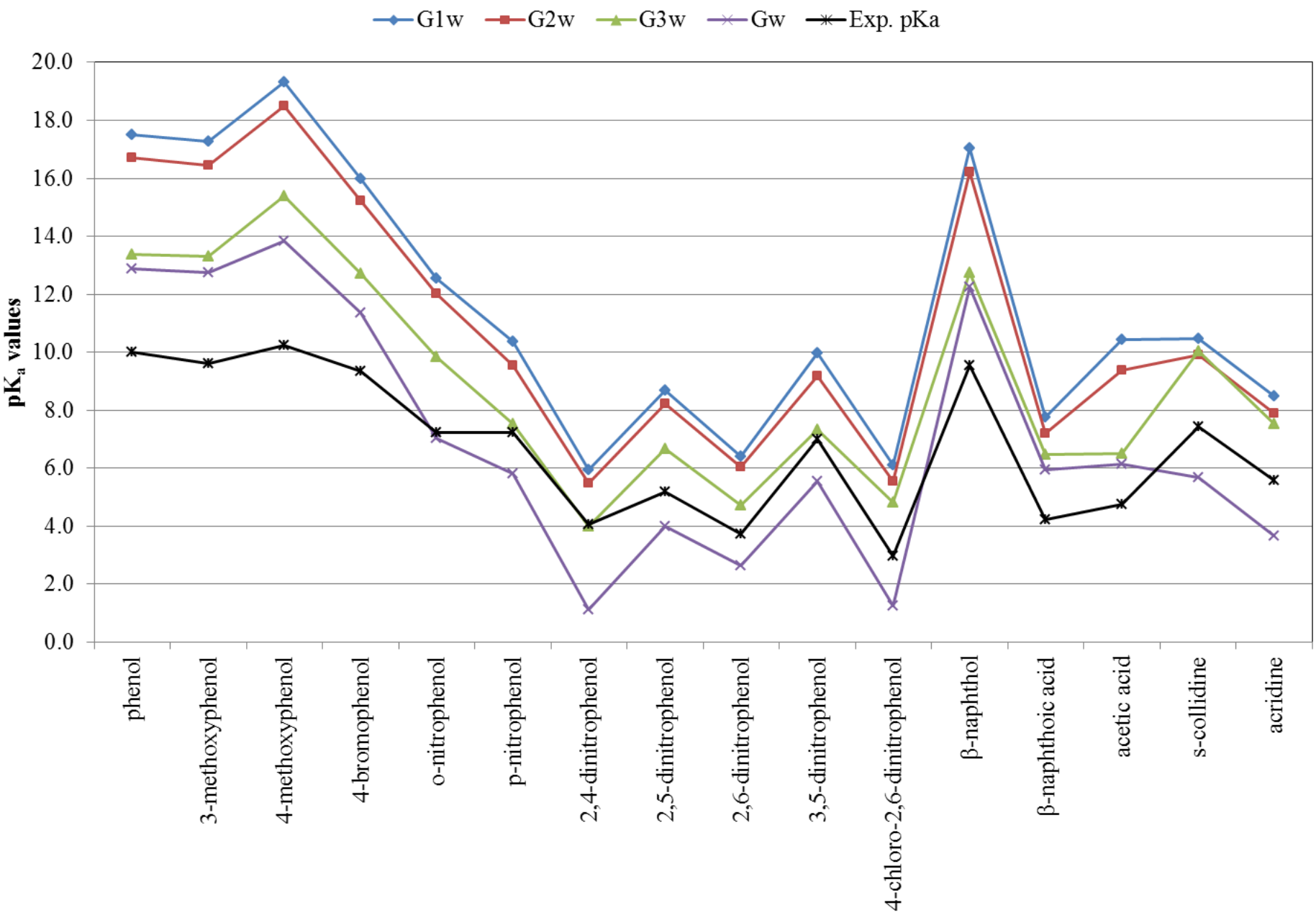


Figure S2. Experimental and calculated pK_a values in D_2O under ambient conditions

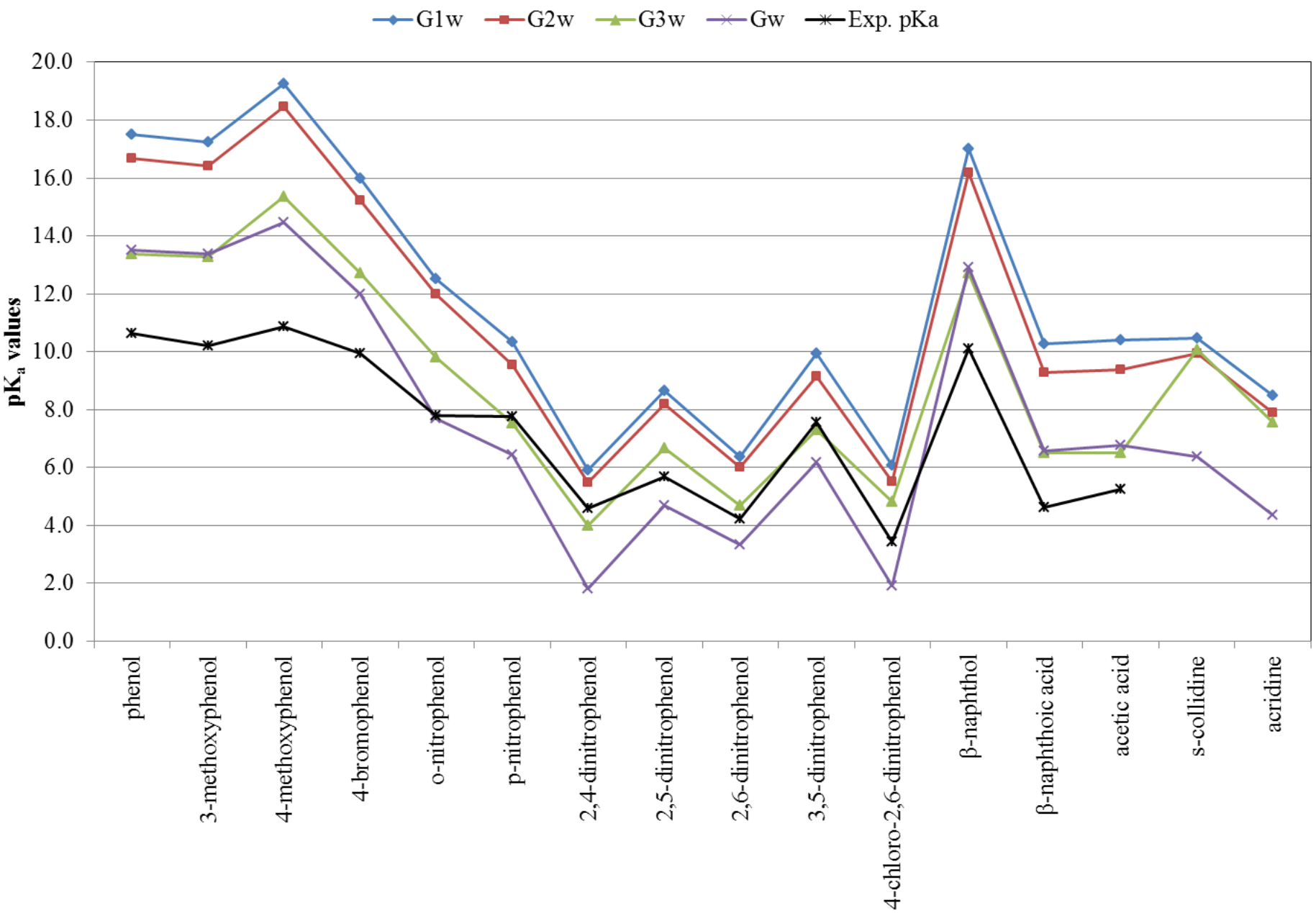


Figure S3. Experimental and calculated pK_a values in H_2O under hydrothermal conditions

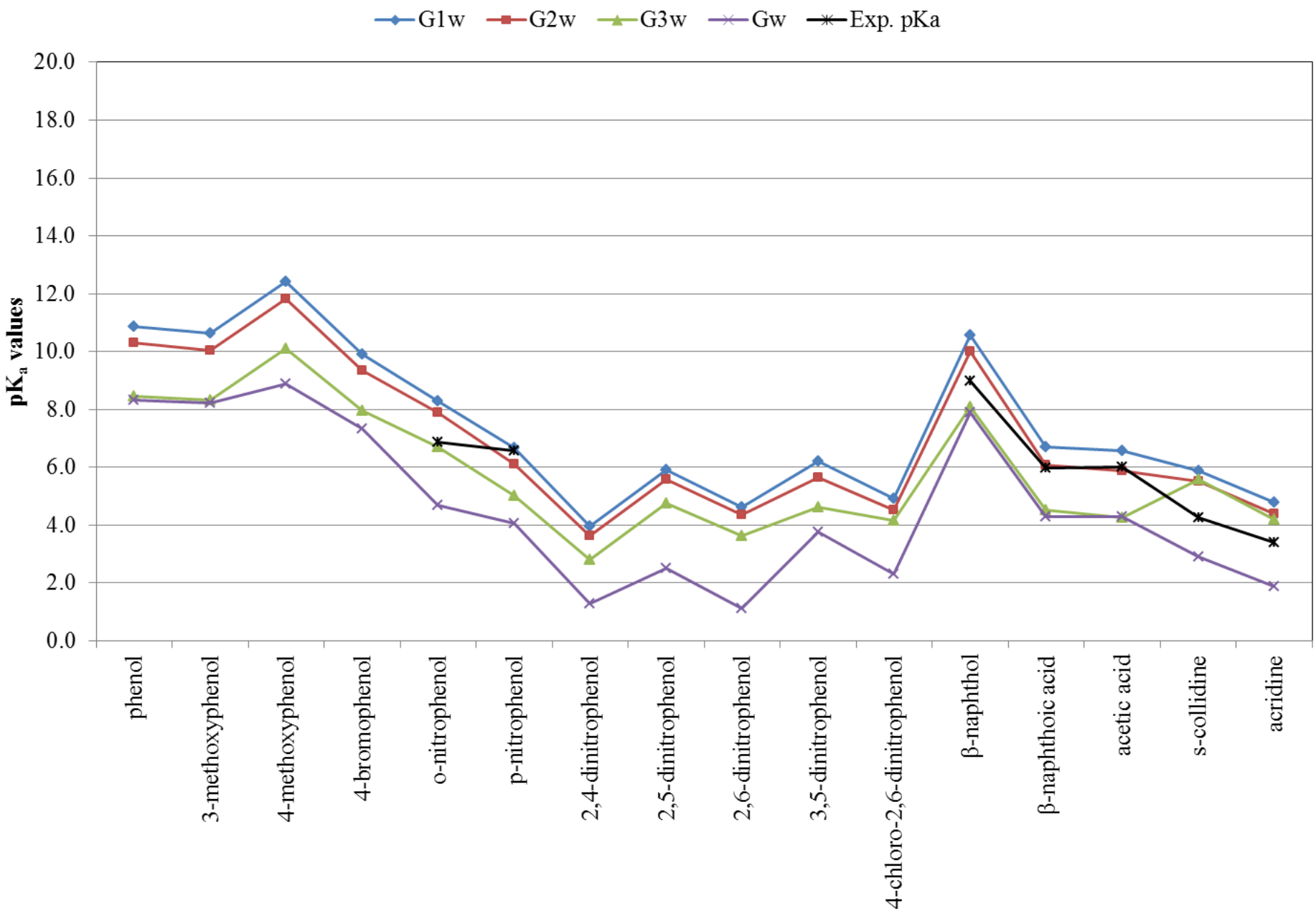


Figure S4. Experimental and calculated pK_a values in D_2O under hydrothermal conditions

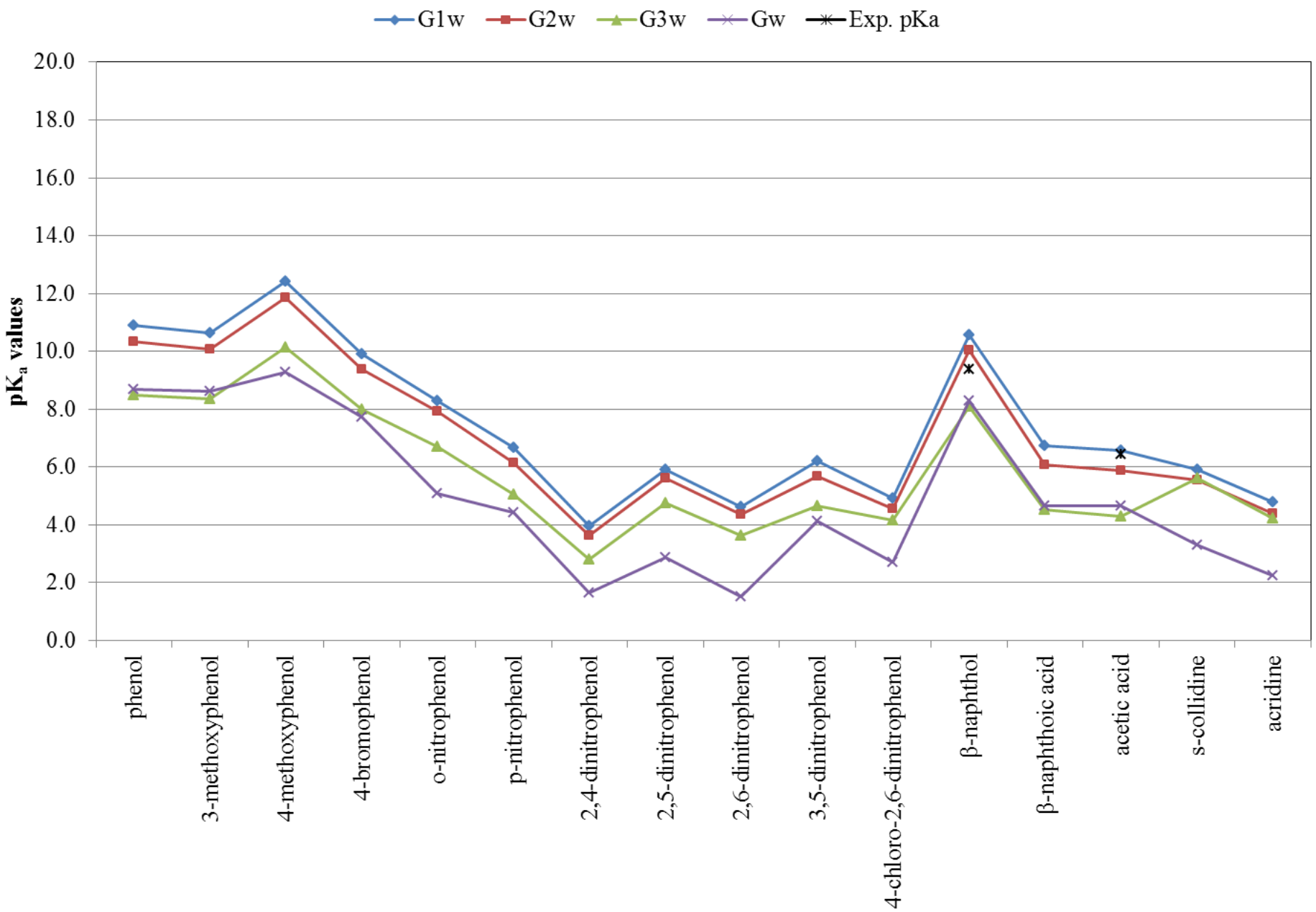
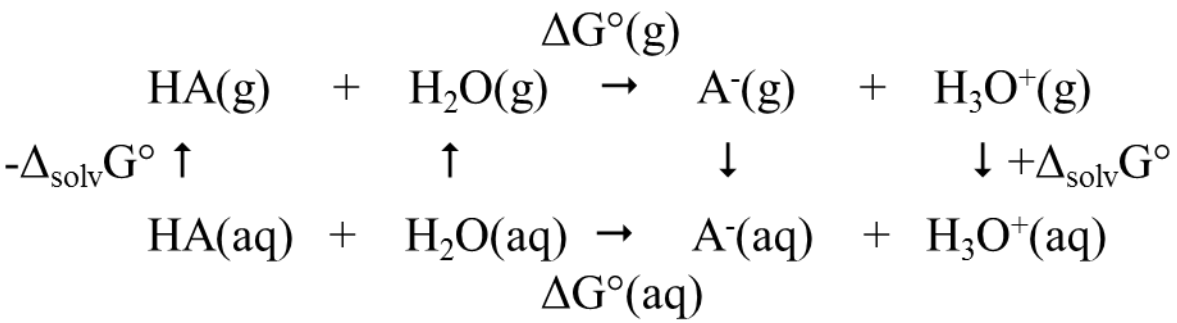


Figure S5. A Born-Haber cycle for the ionization of an acid in light and heavy water.



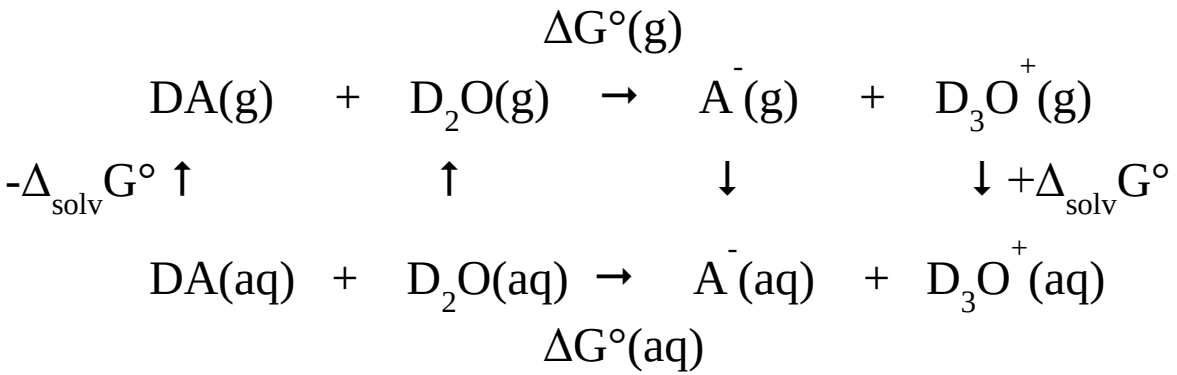


Figure S6. Experimental and calculated temperature-dependence of pK_a values in H_2O

$pK_a(25°C) - pK_a(250°C)$

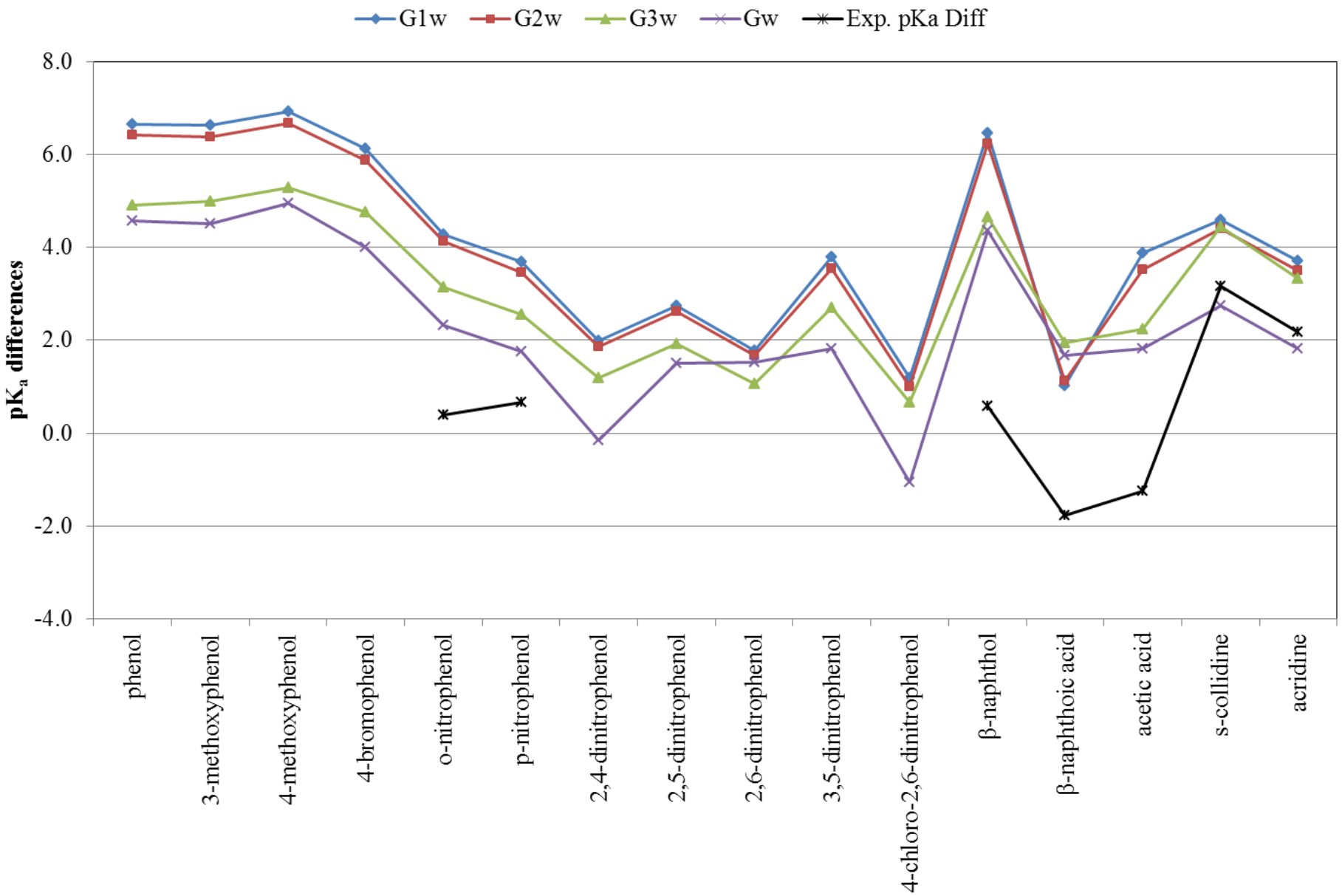


Figure S7. Experimental and calculated temperature-dependence of pK_a values in D_2O

$pK_a(25^oC) - pK_a(250^oC)$

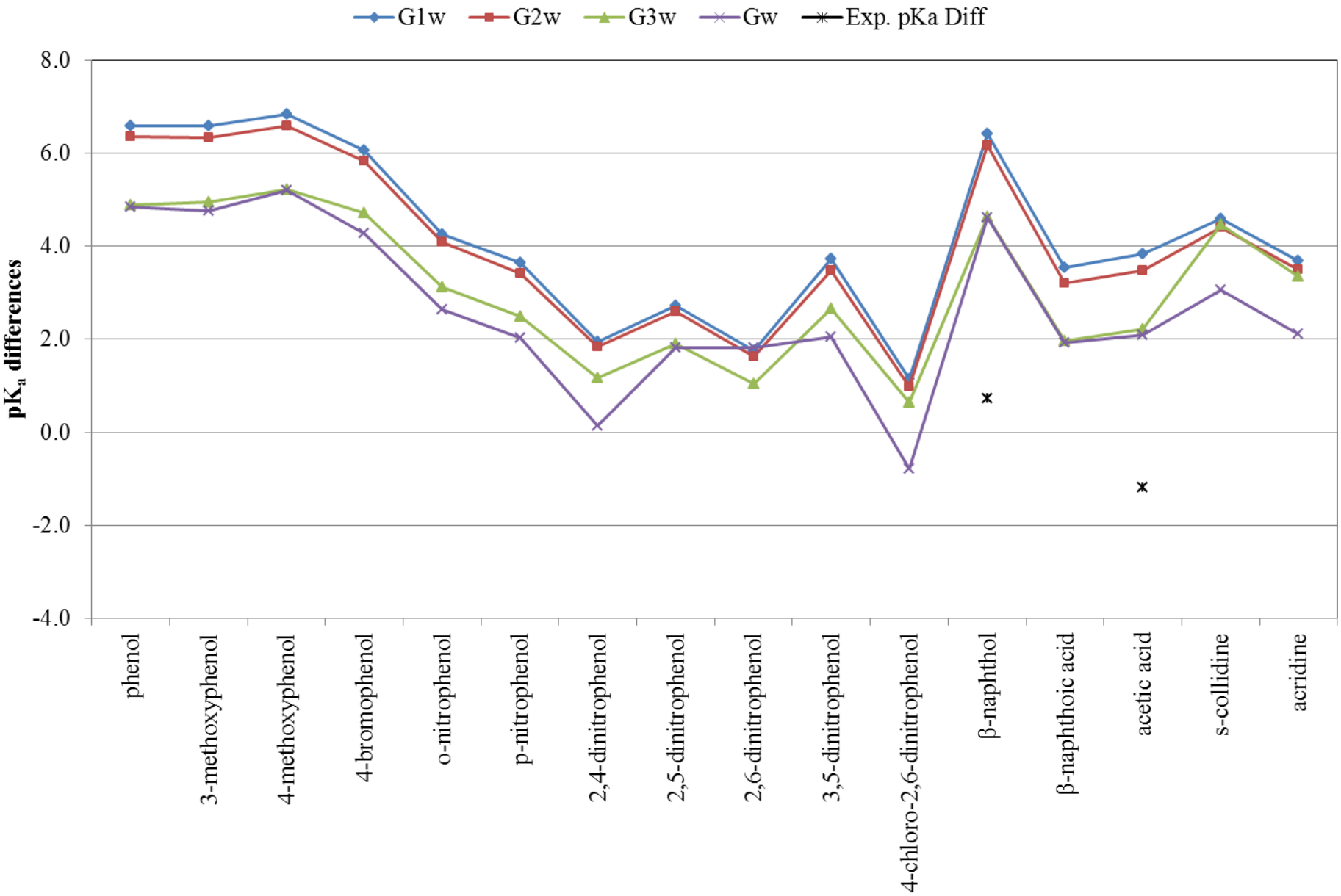
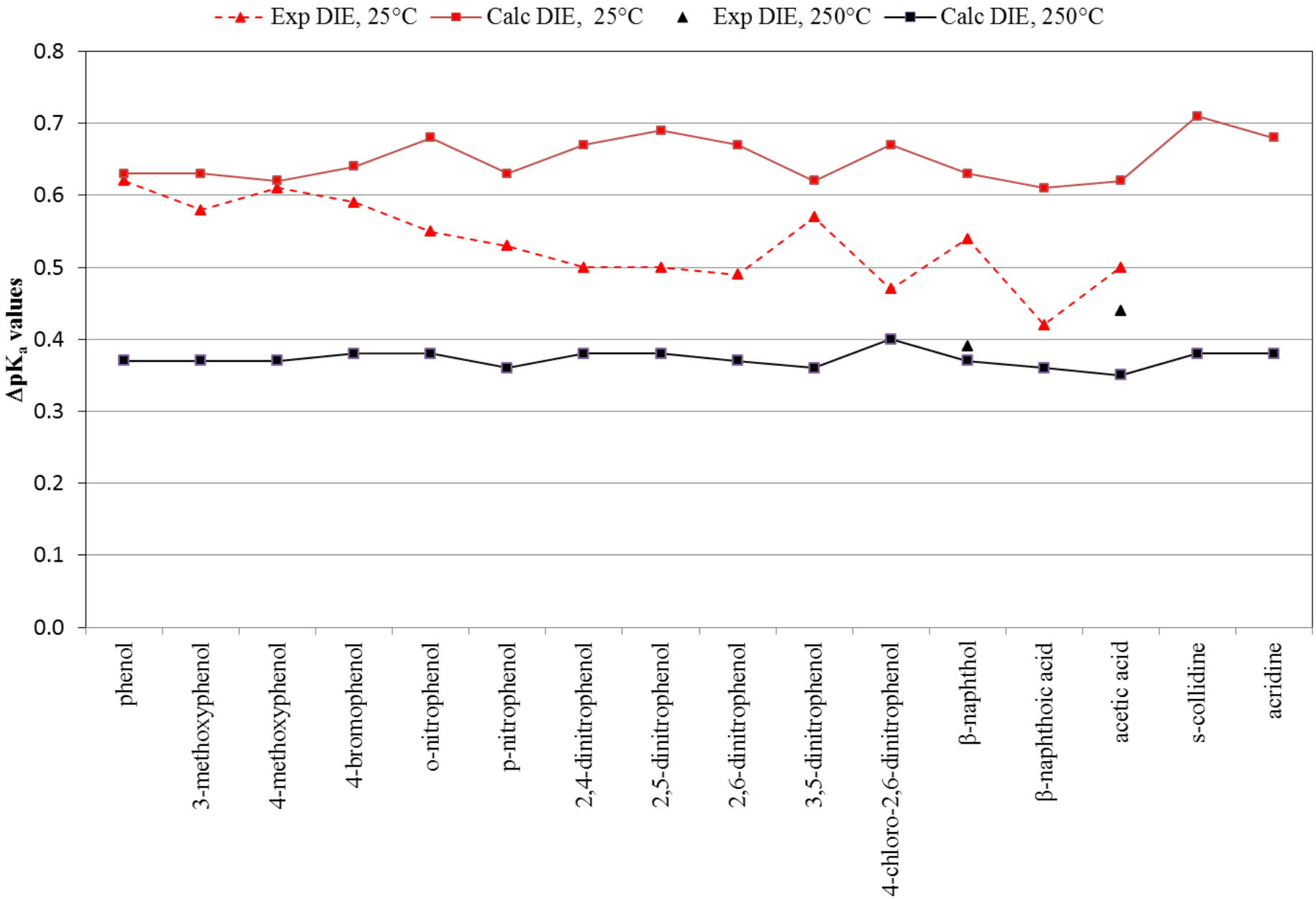


Figure S8. Experimental and calculated (G_w) DIE: $\Delta pK_a = pK_a(D_2O) - pK_a(H_2O)$



Appendix A

(42 pages)

Preliminary initial calculations working with a subset of acids at different levels of theory.

Calculated raw data with the two functionals (BLYP and B3LYP) and several solvation methods (IEF-PCM, CPCM, Onsager and SMD)
(Tables A1 to A3)

Calculated pK_a values and their errors in H_2O and D_2O at 25°C/101.3 kPa and 250°C/20 MPa.
(Tables A4 to A11)

Calculated pK_a differences and their errors in H_2O and D_2O at 25°C/101.3 kPa and 250°C/20 MPa.
(Tables A12 to A19)

Preliminary initial calculations working with a subset of acids at different levels of theory.

The calculations reported in this section were performed by Dr. Elena Formoso at Euskal Herriko Univertsitatea, in Donostia, Spain. Earlier calculations were performed by a former TRU undergraduate student, Tiffany S. Fransbergen.

The following discussion focuses on results obtained for acetic acid, β-naphthol, protonated s-collidine, protonated acridine, and β-naphthoic acid applying different levels of theory. The raw data for these calculations appear in Tables A1 to A3.

Comparison of the calculated pK_a values with experiment

The calculated pK_a values and their errors, expressed as mean absolute errors (MAE) and average errors (AE), using the B3LYP (Tables A4 to A7) and BLYP (Tables A8 to A11) functionals and four solvation methods (IEF-PCM, CPCM, Onsager and SMD) in H_2O and D_2O at 25°C, 101.3 kPa and at 250°C, 20.0 MPa, are displayed in Tables A4(a,b) to A11(a,b).

The errors when using the Onsager solvation method (Tables A6 and A10) are very large (52.3–119.0 pK_a units), which is to be expected since this is the simplest method for accounting for solvent effects. The SMD calculations (Tables A7 and A11) were only performed on the two systems for which the complete set of experimental data is available, β-naphthol and acetic acid. The SMD errors (4.7–15.2 pK_a units) are much larger than when applying IEF-PCM or CPCM with both functionals. These errors are very similar independent of how these solvent methods are accounted for (energies or geometries/frequencies). They tend to be slightly smaller when considered during geometry optimizations and frequency calculations.

The best results (which are in general very similar) are obtained when using the IEF-PCM (Tables A4 and A8) and CPCM (see Tables A5 and A9) solvation models. The calculated errors are always larger on the pK_a values at 25ºC/101.3 kPa in both H_2O and D_2O. The best results overall when calculating the pK_a values for the five systems in the four situations considered are obtained with BLYP and the IEF-PCM method when solvent effects are accounted for only on the energies. CPCM leads to slightly better results except when the calculations are done in D_2O at 250°C and 20.0 MPa. Table 1 displays the method combination and type of equation for calculating the G values in solution for which the lowest errors (MAE and AE) are obtained.

TABLE 1. Best results in the calculation of pK_a values.

Solvent, T, P	Level of theory	Best G equation	MAE	AE
H_2O 25ºC, 101.3 kPa	BLYP-IEF-PCM	G_{3w}	1.09	1.09
	CPCM		1.06	1.06
	B3LYP-CPCM	G_w	1.98	0.97
D_2O 25ºC, 101.3 kPa	BLYP-IEF-PCM	G_{3w}	0.17	0.17
	CPCM		0.15	0.08
	B3LYP-CPCM		1.81	1.81
H_2O 250ºC, 20.0 MPa	BLYP-IEF-PCM	G_{2w}	0.33	0.23
	CPCM		0.28	0.12
	B3LYP-CPCM		0.52	0.37
D_2O 250ºC, 20.0 MPa	BLYP-IEF-PCM	G_{2w}	0.16	-0.16
	CPCM		0.29	-0.29
	B3LYP-CPCM	G_{1w}	0.55	0.55

TABLE 2. Best results in the calculation of pK_a differences.

pK_a (25ºC) - pK_a (250ºC)

Solvent	Level of theory	Best G equation	MAE	AE
H_2O	BLYP-IEF-PCM	G_w	2.28	2.00
	CPCM		2.65	2.39
	B3LYP-IEF-PCM		2.59	2.46
D_2O	BLYP-IEF-PCM	G_{3w}	3.17	3.17
	CPCM		3.15	3.15
	B3LYP-IEF-PCM	G_w	3.43	3.43

pK_a (D_2O) - pK_a (H_2O)

T, P	Level of theory	Best G equation	MAE	AE
25ºC, 101.3 kPa	B3LYP-IEF-PCM	G_w	0.09	0.09
	CPCM		0.09	0.09
	BLYP-IEF-PCM		0.07	0.07
250ºC, 20.0 MPa	B3LYP-IEF-PCM	G_w	0.06	-0.06
	CPCM		0.17	-0.17

In all cases the best approach at the BLYP-IEF-PCM level of theory is to combine G_{gas} with $\Delta G_{solv(HF)}$ for calculating the pK_a values at 25°C (G_{3w}), or with ΔG_{solv} for calculating the pK_a values at 250°C (G_{2w}). This methodology seems useful for prediction purposes except when dealing with pK_a values in H_2O at 25°C and 101.3 kPa for which the errors are too high (MAE=1.09), showing the largest discrepancies with experiment in the cases of the two N acids for which the acid form is protonated (s-collidine and acridine, errors of 2.02 and 1.11 pK_a units, respectively). This error is smaller for acridine (0.62) in H_2O at 250°C and 20.0 MPa. With the exception of the calculations in H_2O at 25°C and 101.3 kPa, the errors for the other systems (C-acids with anionic and neutral forms) are smaller than 0.33 pK_a units. It is important to notice that pK_a errors of 0.5 units are equivalent to errors of 0.65 kcal/mol in the calculated ΔG values.

Comparison of the calculated differences of pK_a values

It is of interest to explore the accuracy of the calculation of four differences of pK_a values, in a given solvent at the two sets of temperature/pressure conditions (represented here by pK_a(25°C) – pK_a(250°C), in both H_2O and D_2O), and at a given set of temperature/pressure conditions between the two solvents (represented here by $pK_a(D_2O) – pK_a(H_2O)$, at 25ºC/101.3 kPa and at 250ºC/20.0 MPa). The calculated values and their errors (MAE and AE) are shown in Tables A12 to A19. Tables A12 to A15 report the results using B3LYP and Tables A16 to A19 display the BLYP results. Unfortunately, with the exception of the pK_a(25°C) – pK_a(250°C) values in H_2O for which there are four experimental values available, there are only two for the other three pK_a differences considered. The best results obtained are shown in Table A4 and are discussed in the two sections that follow.

The temperature-dependence of pK_a (pK_a(25°C) – pK_a(250°C))

The Onsager and SMD calculations (see Tables A14, A15, A18 and A19) have errors (MAE) that are much larger (45.3–55.4 and 8.8–9.2 pK_a units for Onsager and SMD, respectively) than when using IEF-PCM (2.3–3.4 pK_a units) and CPCM (2.7–3.8 pK_a units) with both B3LYP and BLYP. The calculated pK_a difference has larger errors in D_2O, except when using the SMD method. For a given functional, the IEF-PCM results are slightly better than the CPCM ones, and the BLYP results are better than the B3LYP ones. Nonetheless, the errors are large enough not to make possible the prediction of this quantity using the methodologies considered. This is related to the fact that the calculated errors are always larger (and most of the time positive, the calculated values tend to be larger than the experimental ones) on the pK_a values at 25ºC/101.3 kPa in both H_2O and D_2O. As a result, the calculated differences are always positive values (the calculated pK_a values are always smaller at the greater temperature and pressure considered), which is as if

the dissociation process of all these acids were predicted to be endothermic. This is certainly not the case for acetic and β-naphthoic acids. Thus, we conclude that procedure, with the methods considered, cannot be used to predict the standard change in enthalpy and entropy of the acid dissociation process.

The Deuterium Isotope Effect, $\Delta pK_a = pK_a(D_2O) - pK_a(H_2O)$

The difference in pK_a between the two solvents at a given set of conditions is the quantity that is best calculated with the methods applied. The Onsager method is unable to detect the difference in pK_a; with the other three solvation methods, this difference is only detected when solvent effects are included in the geometry optimization and frequency calculation (using G_w values).

The best predictions and most consistent results are obtained with the B3LYP functional and the IEF-PCM solvation method. The MAE values, taking into account the two available experimental data, are of 0.09 and 0.06 pK_a units at 25ºC/101.3 kPa and 250ºC/20.0 MPa, respectively. These low errors indicate the predictive potential of this approach. The experimental and calculated values are displayed in Table A5. It is of importance to notice that in spite of the significant structural differences between the compounds considered, the calculated values are very similar for a given set of conditions. An average pK_a difference between D_2O and H_2O of 0.63 and 0.36 pK_a units is predicted at 25ºC/101.3 kPa and 250ºC/20.0 MPa, respectively. The well-known reduction in pK_a values when going from H_2O to D_2O becomes smaller under hydrothermal conditions, and the methodology chosen is able to reproduce the experimental trend.

To increase the statistical relevance of these calculations a larger set of acids was considered and calculations were performed at the B3LYP-IEF-PCM/6-311++G(d,p) level of theory.

Calculated raw data (all in atomic units, except ΔG_{solv} and $\Delta G_{solv(HF)}$ in kcal/mol).
Symbols used: gas-phase energy (E_{gas}) and thermal correction (TCG_{gas}) to the Gibbs free energy (G_{gas}), Functional/6-311++G(d,p); energy (E_w, Functional-Solvent Method/6-311++G(d,p)//Functional/6-311++G(d,p)) and Gibbs free energy (G_w, Functional-Solvent Method/6-311++G(d,p)) in solution, Gibbs free energy of solvation (ΔG_{solv} and $\Delta G_{solv(HF)}$ (HF-Solvent Method/6-31G(d)//Functional/6-311++G(d,p)).

Table A1.
Calculated raw data with the B3LYP functional and the CPCM and Onsager solvation methods.

				CPCM (uahf)				Onsager	
Molecule	**Solvent**	**T(°C)**	**Species**	**E_w**	**ΔG_{solv}**	**$\Delta G_{solv\ (HF)}$**	**G_w**	**E_w**	**G_w**
β-naphthol	H_2O	25	Acid	-461.25149	-7.04	-7.46	-461.13495	-461.23701	-461.11906
			Conj base	-460.77751	-58.28	-63.79	-460.67466	-460.69022	-460.58633
		250	Acid	-461.25110	-0.11	-0.53	-461.16198	-461.23699	-461.14662
			Conj base	-460.77494	-50.18	-55.55	-460.69879	-460.68977	-460.61284
	D_2O	25	Acid	-461.25149	-7.13	-7.55	-461.13833	-461.23701	-461.12263
			Conj base	-460.77751	-58.37	-63.87	-460.67465	-460.69022	-460.58633
		250	Acid	-461.25109	-0.24	-0.66	-461.16570	-461.23699	-461.15055
			Conj base	-460.77493	-50.29	-55.67	-460.69874	-460.68977	-460.61283
s-collidine	H_2O	25	Acid	-366.80893	-47.76	-47.54	-366.66317	-366.73021	-366.58283
			Conj base	-366.35010	-2.60	-2.54	-366.21711	-366.34326	-366.21025
		250	Acid	-366.80702	-39.93	-39.72	-366.69283	-366.73018	-366.61465
			Conj base	-366.34989	4.12	4.17	-366.24841	-366.34323	-366.24149
	D_2O	25	Acid	-366.80892	-47.85	-47.63	-366.66671	-366.73021	-366.58656
			Conj base	-366.35010	-2.69	-2.63	-366.21711	-366.34326	-366.21025
		250	Acid	-366.80701	-40.05	-39.85	-366.69663	-366.73018	-366.61891
			Conj base	-366.34989	3.99	4.04	-366.24841	-366.34323	-366.24208
acridine	H_2O	25	Acid	-556.16965	-45.27	-45.15	-556.01101	-556.09338	-555.93295
			Conj base	-555.71506	-3.61	-4.27	-555.56928	-555.70542	-555.55883
		250	Acid	-556.16779	-36.08	-35.97	-556.04033	-556.09337	-555.96420
			Conj base	-555.71477	4.52	3.88	-555.59988	-555.70540	-555.58972
	D_2O	25	Acid	-556.16964	-45.38	-45.26	-556.01450	-556.09338	-555.93661

			Conj base	-555.71506	-3.72	-4.38	-555.56928	-555.70542	-555.55883
		250	Acid	-556.16777	-36.23	-36.12	-556.05484	-556.09337	-555.96813
			Conj base	-555.71477	4.37	3.72	-555.61062	-555.70540	-555.58972
β-naphthoic acid	H_2O	25	Acid	-574.64169	-6.31	-6.94	-574.51789	-574.62691	-574.50094
			Conj base	-574.18235	-62.58	-67.33	-574.07149	-574.10674	-573.99500
		250	Acid	-574.64128	1.52	0.90	-574.54914	-574.62688	-574.53260
			Conj base	-574.17960	-53.41	-58.07	-574.09973	-574.10528	-574.02461
	D_2O	25	Acid	-574.64169	-6.42	-7.05	-574.52122	-574.62691	-574.50453
			Conj base	-574.18235	-62.68	-67.43	-574.07148	-574.10674	-573.99500
		250	Acid	-574.64127	1.37	0.75	-574.55281	-574.62688	-574.53652
			Conj base	-574.17959	-53.55	-58.21	-574.09959	-574.10528	-574.02460
acetic acid	H_2O	25	Acid	-229.17805	-6.85	-7.11	-229.14624	-229.16588	-229.13185
			Conj base	-228.71738	-71.19	-75.71	-228.69917	-228.60668	-228.58738
		250	Acid	-229.17770	-3.20	-3.46	-229.16439	-229.16584	-229.14992
			Conj base	-228.71454	-66.14	-70.58	-228.71382	-228.60651	-228.60593
	D_2O	25	Acid	-229.17805	-6.90	-7.16	-229.14957	-229.16588	-229.13543
			Conj base	-228.71738	-71.23	-75.75	-228.69918	-228.60668	-228.58734
		250	Acid	-229.17769	-3.26	-3.53	-229.16806	-229.16584	-229.15384
			Conj base	-228.71452	-66.19	-70.63	-228.71471	-228.60651	-228.60593
H_2O	H_2O	25		-76.47038	-6.66	-6.53	-76.46776	-76.46174	-76.45814
		250		-76.47007	-4.95	-4.83	-76.47573	-76.46162	-76.46633
H_3O^+		25		-76.90209	-107.33	-106.88	-76.89645	-76.73335	-76.71768
		250		-76.89803	-103.33	-102.9	-76.90076	-76.73327	-76.72634
D_2O	D_2O	25		-76.47038	-6.68	-6.55	-76.47438	-76.46174	-76.46500
		250		-76.47006	-4.98	-4.86	-76.48321	-76.46162	-76.47403
D_3O^+		25		-76.90209	-107.34	-106.89	-76.90510	-76.73335	-76.72819
		250		-76.89800	-103.34	-102.91	-76.91057	-76.73327	-76.73791

Table A2.
Calculated raw data with the BLYP functional and the CPCM and Onsager solvation methods.

				IEF-PCM (uahf)					CPCM (uahf)				Onsager		
Molecule	**Solvent**	**T(°C)**	**Species**	**TCG_{gas}**	**G_{gas}**	**E_w**	**ΔG_{solv}**	**$\Delta G_{solv\ (HF)}$**	**G_w**	**E_w**	**ΔG_{solv}**	**$\Delta G_{solv\ (HF)}$**	**G_w**	**E_w**	**G_w**
β-naphthol	H_2O	25	Acid	0.11312	-460.94613	-461.07345	-6.53	-7.56	-460.96180	-461.07362	-6.64	-7.68	-460.96200	-461.05945	-460.94639
			Conj base	0.09904	-460.41160	-460.60333	-56.02	-63.92	-460.50482	-460.60355	-56.17	-64.09	-460.50507	-460.51856	-460.41932
		250	Acid	0.08506	-460.97419	-461.07277	0.59	-0.40	-460.98900	-461.07323	0.30	-0.73	-460.98952	-461.05944	-460.97447
			Conj base	0.07129	-460.43934	-460.60045	-47.71	-55.35	-460.52916	-460.60106	-48.09	-55.82	-460.52983	-460.51815	-460.44645
	D_2O	25	Acid	0.10966	-460.94959	-461.07345	-6.62	-7.66	-460.96505	-461.07362	-6.73	-7.78	-460.96525	-461.05945	-460.94985
			Conj base	0.09904	-460.41160	-460.60332	-56.11	-64.01	-460.50481	-460.60355	-56.25	-64.18	-460.50506	-460.51856	-460.41932
		250	Acid	0.08124	-460.97801	-461.07276	0.46	-0.53	-460.99261	-461.07322	0.17	-0.86	-460.99313	-461.05944	-460.97828
			Conj base	0.07129	-460.43934	-460.60043	-47.82	-55.47	-460.52914	-460.60105	-48.21	-55.94	-460.52981	-460.51814	-460.44644
s-collidine	H_2O	25	Acid	0.14155	-366.40693	-366.62759	-47.50	-47.28	-366.48726	-366.62770	-47.57	-47.36	-366.48747	-366.54909	-366.40742
			Conj base	0.12819	-366.03521	-366.17066	-2.27	-2.56	-366.04291	-366.17074	-2.33	-2.62	-366.04307	-366.16403	-366.03653
		250	Acid	0.10887	-366.43961	-366.62549	-39.53	-39.32	-366.51719	-366.62580	-39.73	-39.52	-366.51791	-366.54906	-366.43997
			Conj base	0.09603	-366.06736	-366.17030	4.55	4.27	-366.07445	-366.17053	4.41	4.12	-366.07505	-366.16400	-366.06913
	D_2O	25	Acid	0.13796	-366.41052	-366.62758	-47.59	-47.37	-366.49069	-366.62770	-47.66	-47.45	-366.49090	-366.54909	-366.41101
			Conj base	0.12819	-366.03521	-366.17066	-2.37	-2.66	-366.04291	-366.17074	-2.42	-2.71	-366.04307	-366.16403	-366.03653
		250	Acid	0.10501	-366.44347	-366.62547	-39.66	-39.44	-366.52089	-366.62578	-39.85	-39.64	-366.52161	-366.54906	-366.44383
			Conj base	0.09603	-366.06736	-366.17030	4.42	4.14	-366.07444	-366.17053	4.28	3.99	-366.07505	-366.16400	-366.06913
acridine	H_2O	25	Acid	0.15443	-555.71481	-555.94526	-44.78	-44.67	-555.79263	-555.94540	-44.86	-45.06	-555.79280	-555.86943	-555.71504
			Conj base	0.14070	-555.34207	-555.49238	-3.05	-4.35	-555.35242	-555.49249	-3.11	-4.43	-555.35252	-555.48331	-555.34258
		250	Acid	0.12256	-555.74668	-555.94316	-35.41	-35.31	-555.82219	-555.94355	-35.65	-35.86	-555.82274	-555.86943	-555.74691
			Conj base	0.10916	-555.37361	-555.49193	5.21	3.27	-555.38347	-555.49221	5.03	3.75	-555.38377	-555.48329	-555.37410
	D_2O	25	Acid	0.15087	-555.71837	-555.94526	-44.89	-44.78	-555.79592	-555.94540	-44.98	-45.18	-555.79619	-555.86943	-555.71859
			Conj base	0.14070	-555.34207	-555.49238	-3.16	-4.46	-555.35000	-555.49249	-3.23	-4.54	-555.35253	-555.48331	-555.34258
		250	Acid	0.11872	-555.75052	-555.94315	-35.56	-35.46	-555.82595	-555.94353	-35.81	-36.01	-555.82640	-555.86943	-555.75074
			Conj base	0.10916	-555.37361	-555.49193	5.05	3.81	-555.38347	-555.49221	4.88	3.60	-555.38379	-555.48329	-555.37410
β-naphthoic	H_2O	25	Acid	0.12059	-574.31290	-574.44842	-5.71	-6.96	-574.33008	-574.44855	-5.79	-7.05	-574.33025	-574.43436	-574.31391
			Conj base	0.10650	-573.78337	-573.99131	-60.47	-67.30	-573.88517	-573.99150	-60.59	-67.44	-573.88548	-573.91630	-573.80953
		250	Acid	0.08828	-574.34521	-574.44779	2.29	1.08	-574.36170	-574.44815	2.06	0.82	-574.36213	-574.43432	-574.34620

acid			Conj base	0.07421	-573.81566	-573.98828	-51.10	-57.76	-573.91397	-573.98881	-51.43	-58.15	-573.91457	-573.91495	-573.83993
		25	Acid	0.11711	-574.31638	-574.44842	-5.82	-7.07	-574.33329	-574.44855	-5.90	-7.16	-574.33345	-574.43436	-574.31738
	D_2O		Conj base	0.10650	-573.78337	-573.99130	-60.57	-67.40	-573.88517	-573.99150	-60.70	-67.55	-573.88547	-573.91630	-573.80952
		250	Acid	0.08447	-574.34902	-574.44779	2.13	0.93	-574.36526	-574.44815	1.90	0.67	-574.36568	-574.43432	-574.35001
			Conj base	0.07421	-573.81566	-573.98826	-51.24	-57.89	-573.91395	-573.98879	-51.57	-58.28	-573.91454	-573.91494	-573.83992
acetic acid		25	Acid	0.03164	-229.07590	-229.12038	-6.52	-7.18	-229.09133	-229.12048	-6.58	-7.24	-229.09164	-229.10835	-229.07665
	H_2O		Conj base	0.01797	-228.53233	-228.66227	-69.28	-75.57	-228.64530	-228.66240	-69.36	-75.66	-228.64479	-228.55412	-228.53607
		250	Acid	0.01303	-229.09451	-229.11987	-2.76	-3.40	-229.11138	-229.12014	-2.93	-3.58	-229.10902	-229.10832	-229.09521
			Conj base	-0.00055	-228.55085	-228.65926	-64.12	-70.27	-228.66000	-228.65962	-64.34	-70.52	-228.66122	-228.55396	-228.55440
		25	Acid	0.02816	-229.07938	-229.12038	-6.57	-7.23	-229.09454	-229.12048	-6.63	-7.29	-229.09484	-229.10835	-229.08012
	D_2O		Conj base	0.01797	-228.53233	-228.66227	-69.32	-75.61	-228.64568	-228.66240	-69.40	-75.70	-228.64501	-228.55412	-228.53609
		250	Acid	0.00922	-229.09832	-229.11987	-2.83	-3.47	-229.11489	-229.12013	-3.00	-3.64	-229.11447	-229.10832	-229.09901
			Conj base	-0.00055	-228.55085	-228.65924	-64.17	-70.32	-228.66296	-228.65960	-64.39	-70.57	-228.66002	-228.55396	-228.55706
H_2O		25		0.00289	-76.43888	-76.45353	-6.59	-6.65	-76.45166	-76.45362	-6.65	-6.71	-76.45176	-76.44502	-76.44217
	H_2O	250		-0.00544	-76.44721	-76.45305	-4.78	-4.85	-76.45948	-76.45331	-4.94	-5.01	-76.45975	-76.44490	-76.45038
H_3O^+		25		0.01523	-76.69654	-76.88364	-107.89	-107.67	-76.88005	-76.88386	-108.03	-107.81	-76.88041	-76.71379	-76.69897
		250		0.00637	-76.70540	-76.87916	-103.65	-103.44	-76.88358	-76.87977	-104.03	-103.82	-76.88462	-76.71372	-76.70767
D_2O		25		-0.00378	-76.44554	-76.45353	-6.61	-6.67	-76.45808	-76.45362	-6.67	-6.73	-76.45818	-76.44502	-76.44883
	D_2O	250		-0.01296	-76.45472	-76.45305	-4.81	-4.88	-76.46677	-76.45331	-4.97	-5.04	-76.46704	-76.44490	-76.45789
D_3O^+		25		0.00497	-76.70680	-76.88363	-107.90	-107.68	-76.88824	-76.88386	-108.04	-107.82	-76.88858	-76.71379	-76.70922
		250		-0.00499	-76.71676	-76.87913	-103.65	-103.44	-76.89300	-76.87974	-104.04	-103.83	-76.89398	-76.71372	-76.71899

Table A3.
Calculated raw data with the B3LYP and BLYP functionals and the SMD solvation method.

				B3LYP			BLYP		
Molecule	**Solvent**	**T(°C)**	**Species**	**E_{gas}**	**E_w**	**G_w**	**E_{gas}**	**E_w**	**G_w**
β-naphthol	H_2O	25	Acid	-461.23678	-461.25304	-461.13518	-461.05925	-461.07471	-460.96153
			Conj base	-460.68150	-460.77473	-460.67176	-460.51063	-460.60033	-460.50204
		250	Acid	-461.23678	-461.25230	-461.16182	-461.05925	-461.07401	-460.98871
			Conj base	-460.68150	-460.77178	-460.69559	-460.51063	-460.59748	-460.52666
	D_2O	25	Acid	-461.23678	-461.25304	-461.13875	-461.05925	-461.07471	-460.96498
			Conj base	-460.68150	-460.77472	-460.67176	-460.51063	-460.60033	-460.50204
		250	Acid	-461.23678	-461.25230	-461.16573	-461.05925	-461.07400	-460.99252
			Conj base	-460.68150	-460.77176	-460.69557	-460.51063	-460.59747	-460.52664
acetic acid	H_2O	25	Acid	-229.16483	-229.17127	-229.13761	-229.10755	-229.11324	-229.08149
			Conj base	-228.60249	-228.70831	-228.68863	-228.55030	-228.65272	-228.63451
		250	Acid	-229.16483	-229.17068	-229.15472	-229.10755	-229.11268	-229.09874
			Conj base	-228.60249	-228.70515	-228.70280	-228.55030	-228.64964	-228.64878
	D_2O	25	Acid	-229.16483	-229.17127	-229.14116	-229.10755	-229.11324	-229.08493
			Conj base	-228.60249	-228.70831	-228.68862	-228.55030	-228.65272	-228.63451
		250	Acid	-229.16483	-229.17067	-229.15859	-229.10755	-229.11268	-229.10252
			Conj base	-228.60249	-228.70513	-228.70278	-228.55030	-228.64962	-228.64876
H_2O	H_2O	25		-76.45853	-76.47022	-76.46686	-76.44176	-76.45303	-76.45035
		250		-76.45853	-76.46962	-76.47455	-76.44176	-76.45245	-76.45807
H_3O^+		25		-76.73124	-76.88635	-76.87152	-76.71177	-76.86713	-76.85314
		250		-76.73124	-76.88259	-76.87715	-76.71177	-76.86336	-76.85889
D_2O	D_2O	25		-76.45853	-76.47022	-76.47545	-76.44176	-76.45303	-76.45697
		250		-76.45853	-76.46962	-76.48462	-76.44176	-76.45244	-76.46554
D_3O^+		25		-76.73124	-76.88635	-76.88225	-76.71177	-76.86713	-76.86366
		250		-76.73124	-76.88257	-76.88890	-76.71177	-76.86333	-76.87042

Calculated pK_a values and their errors (mean absolute deviations, MAE, and average deviations, AE) using two functionals (B3LYP and BLYP) and several solvation methods (IEF-PCM, CPCM, Onsager and SMD) in H_2O and D_2O at 25°C, 101.3 kPa and at 250°C, 20.0 MPa.

Table A4(a).
Calculated pK_a values at the B3LYP-IEF-PCM (uahf) level of theory.

H_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
9.63	β-naphthol	17.04	16.22	12.73	12.93
7.43	s-collidine	10.46	9.92	10.03	6.32
5.58	acridine	8.48	7.88	7.54	4.34
4.16	β-naphthoic acid	10.30	9.30	6.51	6.61
4.74	acetic acid	10.43	9.39	6.49	6.83

H_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
8.97	β-naphthol	10.56	9.99	8.07	8.48
	s-collidine	5.87	5.51	5.58	3.49
3.41	acridine	4.77	4.37	4.19	2.44
5.98	β-naphthoic acid	6.71	6.06	4.51	4.89
6.00	acetic acid	6.55	5.86	4.25	5.32

D_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
10.17	β-naphthol	17.00	16.19	12.72	13.54
	s-collidine	10.48	9.94	10.06	7.01
	acridine	8.49	7.90	7.56	5.01
	β-naphthoic acid	10.28	9.29	6.51	7.21
5.23	acetic acid	10.41	9.37	6.49	7.42

D_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
9.36	β-naphthol	10.58	10.02	8.09	8.84
	s-collidine	5.89	5.54	5.60	3.86
	acridine	4.79	4.39	4.21	2.81
	β-naphthoic acid	6.73	6.08	4.53	5.22
6.44	acetic acid	6.57	5.88	4.28	5.66

Table A4(b).
Errors in the calculated pK_a values at the B3LYP-IEF-PCM (uahf) level of theory.

H_2O, 25°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	7.41	6.59	3.10	3.30
s-collidine	3.03	2.49	2.60	-1.11
acridine	2.90	2.30	1.96	-1.24
β-naphthoic acid	6.14	5.14	2.35	2.45
acetic acid	5.69	4.65	1.75	2.09
MAE	5.03	4.23	2.35	2.04
AE	5.03	4.23	2.35	1.09

H_2O, 250°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	1.59	1.02	-0.90	-0.49
s-collidine				
acridine	1.36	0.96	0.78	-0.97
β-naphthoic acid	0.73	0.08	-1.47	-1.09
acetic acid	0.55	-0.14	-1.75	-0.68
MAE	1.06	0.55	1.23	0.81
AE	1.06	0.48	-0.83	-0.81

D_2O, 25°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	6.83	6.02	2.55	3.37
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	5.18	4.14	1.26	2.19
MAE	6.01	5.08	1.91	2.78
AE	6.01	5.08	1.91	2.78

D_2O, 250°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	1.22	0.66	-1.27	-0.52
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	0.13	-0.56	-2.16	-0.78
MAE	0.68	0.61	1.71	0.65
AE	0.68	0.05	-1.71	-0.65

Table A5(a).
Calculated pK_a values at the B3LYP-CPCM (uahf) level of theory.

H_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
9.63	β-naphthol	16.95	16.13	12.64	12.80
7.43	s-collidine	10.42	9.87	9.99	6.24
5.58	acridine	8.44	7.84	7.50	4.25
4.16	β-naphthoic acid	10.21	9.21	6.43	6.41
4.74	acetic acid	10.35	9.31	6.42	6.71

H_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
8.97	β-naphthol	10.43	9.86	7.92	8.26
	s-collidine	5.81	5.45	5.51	3.34
3.41	acridine	4.71	4.31	4.13	2.30
5.98	β-naphthoic acid	6.57	5.93	4.37	4.64
6.00	acetic acid	6.44	5.75	4.13	4.95

D_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
10.17	β-naphthol	16.92	16.10	12.62	13.41
	s-collidine	10.44	9.90	10.02	6.93
	acridine	8.45	7.85	7.51	4.93
	β-naphthoic acid	10.19	9.20	6.42	7.00
5.23	acetic acid	10.34	9.30	6.41	7.30

D_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
9.36	β-naphthol	10.45	9.88	7.94	8.63
	s-collidine	5.83	5.47	5.54	3.72
	acridine	4.73	4.33	4.14	2.68
	β-naphthoic acid	6.59	5.95	4.39	5.03
6.44	acetic acid	6.46	5.77	4.15	5.07

Table A5(b).
Errors in the calculated pK_a values at the B3LYP-CPCM (uahf) level of theory.

H_2O, 25°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	7.32	6.50	3.01	3.17
s-collidine	2.99	2.44	2.56	-1.19
acridine	2.86	2.26	1.92	-1.33
β-naphthoic acid	6.05	5.05	2.27	2.25
acetic acid	5.61	4.57	1.68	1.97
MAE	4.97	4.16	2.29	1.98
AE	4.97	4.16	2.29	0.97

H_2O, 250°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	1.46	0.89	-1.05	-0.71
s-collidine				
acridine	1.30	0.90	0.72	-1.11
β-naphthoic acid	0.59	-0.05	-1.61	-1.34
acetic acid	0.44	-0.25	-1.87	-1.05
MAE	0.95	0.52	1.31	1.05
AE	0.95	0.37	-0.95	-1.05

D_2O, 25°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	6.75	5.93	2.45	3.24
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	5.11	4.07	1.18	2.07
MAE	5.93	5.00	1.81	2.66
AE	5.93	5.00	1.81	2.66

D_2O, 250°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	1.09	0.52	-1.42	-0.73
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	0.02	-0.67	-2.29	-1.37
MAE	0.55	0.60	1.85	1.05
AE	0.55	-0.08	-1.85	-1.05

Table A6(a).
Calculated pK_a values at the B3LYP-Onsager level of theory.

H_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_w
9.63	β-naphthol	124.09	123.92
7.43	s-collidine	51.00	50.25
5.58	acridine	51.44	50.96
4.16	β-naphthoic acid	111.84	111.60
4.74	acetic acid	129.33	129.32

H_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_w
8.97	β-naphthol	70.04	70.03
	s-collidine	28.39	27.92
3.41	acridine	28.64	28.27
5.98	β-naphthoic acid	63.26	63.27
6.00	acetic acid	72.63	72.70

D_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_w
10.17	β-naphthol	124.05	123.88
	s-collidine	51.02	50.29
	acridine	51.45	50.96
	β-naphthoic acid	111.82	111.57
5.23	acetic acid	129.31	129.31

D_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_w
9.36	β-naphthol	70.05	70.04
	s-collidine	28.40	27.87
	acridine	28.65	28.28
	β-naphthoic acid	63.27	63.28
6.44	acetic acid	72.64	72.71

Table A6(b).
Errors in the calculated pK_a values at the B3LYP-Onsager level of theory.

H_2O, 25°C

Molecule	G_{1w}	G_w
β-naphthol	114.46	114.29
s-collidine	43.57	42.82
acridine	45.86	45.38
β-naphthoic acid	107.68	107.44
acetic acid	124.59	124.58
MAE	87.23	86.90
AE	87.23	86.90

H_2O, 250°C

Molecule	G_{1w}	G_w
β-naphthol	61.07	61.06
s-collidine		
acridine	25.23	24.86
β-naphthoic acid	57.28	57.29
acetic acid	66.63	66.70
MAE	52.55	52.48
AE	52.55	52.48

D_2O, 25°C

Molecule	G_{1w}	G_w
β-naphthol	113.88	113.71
s-collidine		
acridine		
β-naphthoic acid		
acetic acid	124.08	124.08
MAE	118.98	118.89
AE	118.98	118.89

D_2O, 250°C

Molecule	G_{1w}	G_w
β-naphthol	60.69	60.68
s-collidine		
acridine		
β-naphthoic acid		
acetic acid	66.20	66.27
MAE	63.44	63.48
AE	63.44	63.48

Table A7(a).
Calculated pK_a values at the B3LYP-SMD level of theory.

H_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_w
9.63	β-naphthol	26.11	25.28
4.74	acetic acid	18.58	18.64

H_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_w
8.97	β-naphthol	15.51	14.94
6.00	acetic acid	10.99	11.19

D_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_w
10.17	β-naphthol	26.08	25.94
5.23	acetic acid	18.56	19.29

D_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_w
9.36	β-naphthol	15.52	15.52
6.44	acetic acid	11.01	11.76

Table A7(b).
Errors in the calculated pK_a values at the B3LYP-SMD level of theory.

H_2O, 25°C

Molecule	G_{1w}	G_w
β-naphthol	16.48	15.65
acetic acid	13.84	13.90
MAE	15.16	14.78
AE	15.16	14.78

H_2O, 250°C

Molecule	G_{1w}	G_w
β-naphthol	6.54	5.97
acetic acid	4.99	5.19
MAE	5.76	5.58
AE	5.76	5.58

D_2O, 25°C

Molecule	G_{1w}	G_w
β-naphthol	15.91	15.77
acetic acid	13.33	14.06
MAE	14.62	14.92
AE	14.62	14.92

D_2O, 250°C

Molecule	G_{1w}	G_w
β-naphthol	6.16	6.16
acetic acid	4.57	5.32
MAE	5.37	5.74
AE	5.37	5.74

Table A8(a).
Calculated pK_a values at the BLYP-IEF-PCM (uahf) level of theory.

H_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
9.63	β-naphthol	15.85	15.07	10.24	11.40
7.43	s-collidine	10.12	9.62	9.45	5.59
5.58	acridine	8.09	7.52	6.69	3.69
4.16	β-naphthoic acid	9.87	8.91	5.03	5.85
4.74	acetic acid	10.52	9.51	5.59	6.37

H_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
8.97	β-naphthol	9.86	9.30	6.64	7.62
	s-collidine	5.61	5.26	5.18	3.14
3.41	acridine	4.42	4.03	3.30	2.09
5.98	β-naphthoic acid	6.42	5.78	3.62	4.45
6.00	acetic acid	6.84	6.15	3.97	5.41

D_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
10.17	β-naphthol	15.80	15.02	10.20	12.09
	s-collidine	10.12	9.62	9.45	6.36
	acridine	8.07	7.51	6.68	4.37
	β-naphthoic acid	9.82	8.87	4.99	6.52
5.23	acetic acid	10.47	9.47	5.55	6.86

D_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
9.36	β-naphthol	9.86	9.31	6.65	8.02
	s-collidine	5.62	5.28	5.19	3.55
	acridine	4.43	4.04	3.60	2.51
	β-naphthoic acid	6.42	5.80	3.64	4.83
6.44	acetic acid	6.84	6.17	3.98	4.99

Table A8(b).
Errors in the calculated pK_a values at the BLYP-IEF-PCM (uahf) level of theory.

H_2O, 25°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	6.22	5.44	0.61	1.77
s-collidine	2.69	2.19	2.02	-1.84
acridine	2.51	1.94	1.11	-1.89
β-naphthoic acid	5.71	4.75	0.87	1.69
acetic acid	5.78	4.77	0.85	1.63
MAE	4.58	3.82	1.09	1.77
AE	4.58	3.82	1.09	0.27

H_2O, 250°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	0.89	0.33	-2.33	-1.35
s-collidine				
acridine	1.01	0.62	-0.11	-1.32
β-naphthoic acid	0.44	-0.20	-2.36	-1.53
acetic acid	0.84	0.15	-2.03	-0.59
MAE	0.79	0.33	1.71	1.20
AE	0.79	0.23	-1.71	-1.20

D_2O, 25°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	5.63	4.85	0.03	1.92
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	5.24	4.24	0.32	1.63
MAE	5.44	4.55	0.17	1.77
AE	5.44	4.55	0.17	1.77

D_2O, 250°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	0.50	-0.05	-2.71	-1.34
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	0.40	-0.27	-2.46	-1.45
MAE	0.45	0.16	2.59	1.40
AE	0.45	-0.16	-2.59	-1.40

Table A9(a).
Calculated pK_a values at the BLYP-CPCM (uahf) level of theory.

H_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
9.63	β-naphthol	15.77	14.99	10.15	11.26
7.43	s-collidine	10.08	9.57	9.41	5.50
5.58	acridine	8.05	7.48	6.86	3.60
4.16	β-naphthoic acid	9.78	8.83	4.93	5.67
4.74	acetic acid	10.45	9.43	5.50	6.63

H_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
8.97	β-naphthol	9.72	9.17	6.49	7.39
	s-collidine	5.54	5.20	5.11	2.97
3.41	acridine	4.36	3.97	3.64	1.95
5.98	β-naphthoic acid	6.28	5.65	3.48	4.20
6.00	acetic acid	6.72	6.04	3.85	4.31

D_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
10.17	β-naphthol	15.71	14.94	10.10	11.95
	s-collidine	10.08	9.57	9.41	6.27
	acridine	8.03	7.47	6.86	4.35
	β-naphthoic acid	9.73	8.78	4.89	6.34
5.23	acetic acid	10.40	9.40	5.47	7.19

D_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
9.36	β-naphthol	9.73	9.17	6.49	7.79
	s-collidine	5.55	5.21	5.11	3.40
	acridine	4.36	3.98	3.65	2.36
	β-naphthoic acid	6.29	5.66	3.48	4.60
6.44	acetic acid	6.72	6.05	3.85	5.46

Table A9(b).
Errors in the calculated pK_a values at the BLYP-CPCM (uahf) level of theory.

H_2O, 25°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	6.14	5.36	0.52	1.63
s-collidine	2.65	2.14	1.98	-1.93
acridine	2.47	1.90	1.28	-1.98
β-naphthoic acid	5.62	4.67	0.77	1.51
acetic acid	5.71	4.69	0.76	1.89
MAE	4.52	3.75	1.06	1.79
AE	4.52	3.75	1.06	0.23

H_2O, 250°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	0.75	0.20	-2.48	-1.58
s-collidine				
acridine	0.95	0.56	0.23	-1.46
β-naphthoic acid	0.30	-0.33	-2.50	-1.78
acetic acid	0.72	0.04	-2.15	-1.69
MAE	0.68	0.28	1.84	1.63
AE	0.68	0.12	-1.73	-1.63

D_2O, 25°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	5.54	4.77	-0.07	1.78
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	5.17	4.17	0.24	1.96
MAE	5.36	4.47	0.15	1.87
AE	5.36	4.47	0.08	1.87

D_2O, 250°C

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	0.37	-0.19	-2.87	-1.57
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	0.28	-0.39	-2.59	-0.98
MAE	0.33	0.29	2.73	1.27
AE	0.33	-0.29	-2.73	-1.27

Table A10(a).
Calculated pK_a values at the BLYP-Onsager level of theory.

H_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_w
9.63	β-naphthol	122.62	122.58
7.43	s-collidine	51.28	50.74
5.58	acridine	51.60	51.45
4.16	β-naphthoic acid	112.12	112.14
4.74	acetic acid	128.95	128.79

H_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_w
8.97	β-naphthol	69.17	69.23
	s-collidine	28.46	28.02
3.41	acridine	28.60	28.54
5.98	β-naphthoic acid	63.35	63.53
6.00	acetic acid	72.65	72.58

D_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_w
10.17	β-naphthol	122.56	122.52
	s-collidine	51.27	50.74
	acridine	51.58	51.44
	β-naphthoic acid	112.07	112.09
5.23	acetic acid	128.90	128.73

D_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_w
9.36	β-naphthol	69.17	69.23
	s-collidine	28.46	28.04
	acridine	28.59	28.54
	β-naphthoic acid	63.34	63.53
6.44	acetic acid	72.64	71.88

Table A10(b).
Errors in the calculated pK_a values at the BLYP-Onsager level of theory.

H_2O, 25°C

Molecule	G_{1w}	G_w
β-naphthol	112.99	112.95
s-collidine	43.85	43.31
acridine	46.02	45.87
β-naphthoic acid	107.96	107.98
acetic acid	124.21	124.05
MAE	87.01	86.83
AE	87.01	86.83

H_2O, 250°C

Molecule	G_{1w}	G_w
β-naphthol	60.20	60.26
s-collidine		
acridine	25.19	25.13
β-naphthoic acid	57.37	57.55
acetic acid	66.65	66.58
MAE	52.35	52.38
AE	52.35	52.38

D_2O, 25°C

Molecule	G_{1w}	G_w
β-naphthol	112.39	112.35
s-collidine		
acridine		
β-naphthoic acid		
acetic acid	123.67	123.50
MAE	118.03	117.92
AE	118.03	117.92

D_2O, 250°C

Molecule	G_{1w}	G_w
β-naphthol	59.81	59.87
s-collidine		
acridine		
β-naphthoic acid		
acetic acid	66.20	65.44
MAE	63.00	62.66
AE	63.00	62.66

Table A11(a).
Calculated pK_a values at the BLYP-SMD level of theory.

H_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_w
9.63	β-naphthol	25.18	24.34
4.74	acetic acid	18.99	18.58

H_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_w
8.97	β-naphthol	14.94	14.31
6.00	acetic acid	11.46	11.14

D_2O, 25°C

Exp. pK_a	Molecule	G_{1w}	G_w
10.17	β-naphthol	25.12	24.13
5.23	acetic acid	18.95	18.37

D_2O, 250°C

Exp. pK_a	Molecule	G_{1w}	G_w
9.36	β-naphthol	14.94	14.24
6.44	acetic acid	11.46	11.07

Table A11(b).
Errors in the calculated pK_a values at the BLYP-SMD level of theory.

H_2O, 25°C

Molecule	G_{1w}	G_w
β-naphthol	15.55	14.71
acetic acid	14.25	13.84
MAE	14.90	14.28
AE	14.90	14.28

H_2O, 250°C

Molecule	G_{1w}	G_w
β-naphthol	5.97	5.34
acetic acid	5.46	5.14
MAE	5.71	5.24
AE	5.71	5.24

D_2O, 25°C

Molecule	G_{1w}	G_w
β-naphthol	14.95	13.96
acetic acid	13.72	13.14
MAE	14.33	13.55
AE	14.33	13.55

D_2O, 250°C

Molecule	G_{1w}	G_w
β-naphthol	5.58	4.88
acetic acid	5.02	4.63
MAE	5.30	4.76
AE	5.30	4.76

Calculated pK_a differences (pK_a(25°C) - pK_a(250°C) in H_2O and D_2O, and $pK_a(D_2O)$ - $pK_a(H_2O)$ at 25°C, 101.3 kPa and at 250°C, 20.0 MPa) and their errors (mean absolute deviations, MAE, and average deviations, AE) using two functionals (B3LYP and BLYP) and several solvation methods (IEF-PCM, CPCM, Onsager and SMD).

Table A12(a).
Calculated pK_a differences at the B3LYP-IEF-PCM (uahf) level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.66	β-naphthol	6.47	6.23	4.66	4.45
	s-collidine	4.59	4.40	4.45	2.83
2.17	acridine	3.71	3.51	3.34	1.89
-1.82	β-naphthoic acid	3.59	3.24	2.00	1.73
-1.26	acetic acid	3.87	3.53	2.24	1.51

D_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.81	β-naphthol	6.42	6.17	4.63	4.70
	s-collidine	4.59	4.40	4.46	3.15
	acridine	3.70	3.51	3.35	2.20
	β-naphthoic acid	3.55	3.21	1.97	1.99
-1.21	acetic acid	3.84	3.49	2.21	1.76

25°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.54	β-naphthol	-0.03	-0.03	-0.01	0.61
	s-collidine	0.02	0.02	0.04	0.69
	acridine	0.01	0.02	0.02	0.67
	β-naphthoic acid	-0.02	-0.01	-0.01	0.60
0.49	acetic acid	-0.02	-0.01	0.00	0.60

250°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.39	β-naphthol	0.02	0.03	0.02	0.36
	s-collidine	0.02	0.02	0.02	0.37
	acridine	0.01	0.02	0.02	0.37
	β-naphthoic acid	0.02	0.02	0.02	0.33
0.44	acetic acid	0.02	0.03	0.03	0.35

Table A12(b).
Errors in the calculated pK_a differences at the B3LYP-IEF-PCM (uahf) level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	5.81	5.57	4.00	3.79
s-collidine				
acridine	1.54	1.34	1.17	-0.28
β-naphthoic acid	5.41	5.06	3.82	3.55
acetic acid	5.13	4.79	3.50	2.77
MAE	4.47	4.19	3.12	2.59
AE	4.47	4.19	3.12	2.46

D_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	5.61	5.36	3.82	3.89
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	5.05	4.70	3.42	2.97
MAE	5.33	5.03	3.62	3.43
AE	5.33	5.03	3.62	3.43

25°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	-0.57	-0.57	-0.55	0.07
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	-0.51	-0.50	-0.49	0.11
MAE	0.54	0.54	0.52	0.09
AE	-0.54	-0.54	-0.52	0.09

250°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	-0.37	-0.36	-0.37	-0.03
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	-0.42	-0.41	-0.41	-0.09
MAE	0.40	0.39	0.39	0.06
AE	-0.40	-0.39	-0.39	-0.06

Table A13(a).
Calculated pK_a differences at the B3LYP-CPCM (uahf) level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.66	β-naphthol	6.52	6.28	4.72	4.54
	s-collidine	4.61	4.42	4.48	2.91
2.17	acridine	3.73	3.53	3.37	1.96
-1.82	β-naphthoic acid	3.64	3.29	2.06	1.76
-1.26	acetic acid	3.91	3.56	2.29	1.76

D_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.81	β-naphthol	6.47	6.22	4.68	4.78
	s-collidine	4.61	4.43	4.48	3.21
	acridine	3.72	3.52	3.37	2.25
	β-naphthoic acid	3.60	3.26	2.03	1.97
-1.21	acetic acid	3.88	3.53	2.26	2.23

25°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.54	β-naphthol	-0.03	-0.03	-0.02	0.62
	s-collidine	0.02	0.03	0.03	0.69
	acridine	0.01	0.01	0.01	0.67
	β-naphthoic acid	-0.02	-0.01	-0.01	0.60
0.49	acetic acid	-0.02	-0.01	-0.01	0.59

250°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.39	β-naphthol	0.02	0.02	0.02	0.38
	s-collidine	0.02	0.02	0.02	0.38
	acridine	0.01	0.02	0.01	0.38
	β-naphthoic acid	0.02	0.02	0.02	0.39
0.44	acetic acid	0.02	0.02	0.02	0.12

Table A13(b).
Errors in the calculated pK_a differences at the B3LYP-CPCM (uahf) level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	5.86	5.62	4.06	3.88
s-collidine				
acridine	1.56	1.36	1.20	-0.21
β-naphthoic acid	5.46	5.11	3.88	3.58
acetic acid	5.17	4.82	3.55	3.02
MAE	4.51	4.22	3.17	2.67
AE	4.51	4.22	3.17	2.57

D_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	5.66	5.41	3.87	3.97
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	5.09	4.74	3.47	3.44
MAE	5.37	5.08	3.67	3.71
AE	5.37	5.08	3.67	3.71

25°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	-0.57	-0.57	-0.56	0.08
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	-0.51	-0.50	-0.50	0.10
MAE	0.54	0.53	0.53	0.09
AE	-0.54	-0.53	-0.53	0.09

250°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	-0.37	-0.37	-0.37	-0.01
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	-0.42	-0.42	-0.42	-0.32
MAE	0.40	0.39	0.39	0.17
AE	-0.40	-0.39	-0.39	-0.17

Table A14(a).
Calculated pK_a differences at the B3LYP-Onsager level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_w
0.66	β-naphthol	54.05	53.89
	s-collidine	22.61	22.33
2.17	acridine	22.80	22.69
-1.82	β-naphthoic acid	48.58	48.33
-1.26	acetic acid	56.70	56.62

D_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_w
0.81	β-naphthol	54.00	53.84
	s-collidine	22.62	22.42
	acridine	22.80	22.68
	β-naphthoic acid	48.55	48.29
-1.21	acetic acid	56.67	56.6

25°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_w
0.54	β-naphthol	-0.03	-0.04
	s-collidine	0.02	0.04
	acridine	0.00	0.00
	β-naphthoic acid	-0.02	-0.03
0.49	acetic acid	-0.02	-0.01

250°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_w
0.39	β-naphthol	0.01	0.01
	s-collidine	0.02	-0.05
	acridine	0.01	0.01
	β-naphthoic acid	0.01	0.01
0.44	acetic acid	0.01	0.01

Table A14(b).
Errors in the calculated pK_a differences at the B3LYP-Onsager level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Molecule		G_{1w}	G_w
β-naphthol		53.39	53.23
s-collidine			
acridine		20.63	20.52
β-naphthoic acid		50.40	50.15
acetic acid		57.96	57.88
	MAE	45.59	45.45
	AE	45.59	45.45

D_2O, pK_a (25°C) - pK_a (250°C)

Molecule		G_{1w}	G_w
β-naphthol		53.19	53.03
s-collidine			
acridine			
β-naphthoic acid			
acetic acid		57.88	57.81
	MAE	55.54	55.42
	AE	55.54	55.42

25°C, pK_a (D_2O) - pK_a (H_2O)

Molecule		G_{1w}	G_w
β-naphthol		-0.57	-0.58
s-collidine			
acridine			
β-naphthoic acid			
acetic acid		-0.51	-0.50
	MAE	0.54	0.54
	AE	-0.54	-0.54

250°C, pK_a (D_2O) - pK_a (H_2O)

Molecule		G_{1w}	G_w
β-naphthol		-0.38	-0.38
s-collidine			
acridine			
β-naphthoic acid			
acetic acid		-0.43	-0.43
	MAE	0.41	0.40
	AE	-0.41	-0.40

Table A15(a).
Calculated pK_a differences at the B3LYP-SMD level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_w
0.66	β-naphthol	10.60	10.34
-1.26	acetic acid	7.58	7.46

D_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_w
0.81	β-naphthol	10.56	10.42
-1.21	acetic acid	7.55	7.53

25°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_w
0.54	β-naphthol	-0.03	0.66
0.49	acetic acid	-0.02	0.65

250°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_w
0.39	β-naphthol	0.02	0.59
0.44	acetic acid	0.02	0.58

Table A15(b).
Errors in the calculated pK_a differences at the B3LYP-SMD level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_w
β-naphthol	9.94	9.68
acetic acid	8.84	8.72
MAE	9.39	9.20
AE	9.39	9.20

D_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_w
β-naphthol	9.75	9.61
acetic acid	8.76	8.74
MAE	9.25	9.17
AE	9.25	9.17

25°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_w
β-naphthol	-0.57	0.12
acetic acid	-0.51	0.16
MAE	0.54	0.14
AE	-0.54	0.14

250°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_w
β-naphthol	-0.37	0.20
acetic acid	-0.42	0.14
MAE	0.40	0.17
AE	-0.40	0.17

Table A16(a).
Calculated pK_a differences at the BLYP-IEF-PCM (uahf) level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.66	β-naphthol	6.00	5.78	3.61	3.78
	s-collidine	4.51	4.35	4.27	2.45
2.17	acridine	3.66	3.49	3.39	1.60
-1.82	β-naphthoic acid	3.45	3.13	1.41	1.40
-1.26	acetic acid	3.68	3.35	1.62	0.96

D_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.81	β-naphthol	5.94	5.71	3.55	4.08
	s-collidine	4.50	4.33	4.26	2.81
	acridine	3.65	3.47	3.08	1.86
	β-naphthoic acid	3.40	3.08	1.35	1.69
-1.21	acetic acid	3.63	3.30	1.57	1.87

25°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.54	β-naphthol	-0.06	-0.05	-0.05	0.69
	s-collidine	0.00	0.00	0.00	0.77
	acridine	-0.02	-0.01	-0.01	0.68
	β-naphthoic acid	-0.05	-0.04	-0.04	0.67
0.49	acetic acid	-0.05	-0.04	-0.04	0.49

250°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.39	β-naphthol	0.00	0.01	0.01	0.39
	s-collidine	0.01	0.02	0.01	0.41
	acridine	0.00	0.01	0.30	0.43
	β-naphthoic acid	0.00	0.01	0.01	0.38
0.44	acetic acid	0.00	0.01	0.01	-0.42

Table A16(b).
Errors in the calculated pK_a differences at the BLYP-IEF-PCM (uahf) level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	5.34	5.12	2.95	3.12
s-collidine				
acridine	1.49	1.32	1.22	-0.57
β-naphthoic acid	5.27	4.95	3.23	3.22
acetic acid	4.94	4.61	2.88	2.22
MAE	4.26	4.00	2.57	2.28
AE	4.26	4.00	2.57	2.00

D_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	5.13	4.90	2.74	3.27
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	4.84	4.51	2.78	3.08
MAE	4.99	4.71	2.76	3.17
AE	4.99	4.71	2.76	3.17

25°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	-0.60	-0.59	-0.59	0.15
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	-0.54	-0.53	-0.53	0.00
MAE	0.57	0.56	0.56	0.07
AE	-0.57	-0.56	-0.56	0.07

250°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	-0.39	-0.38	-0.38	0.00
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	-0.44	-0.43	-0.43	-0.86
MAE	0.41	0.40	0.40	0.43
AE	-0.41	-0.40	-0.40	-0.43

Table A17(a).
Calculated pK_a differences at the BLYP-CPCM (uahf) level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.66	β-naphthol	6.05	5.82	3.66	3.88
	s-collidine	4.54	4.37	4.30	2.53
2.17	acridine	3.69	3.51	3.22	1.65
-1.82	β-naphthoic acid	3.50	3.18	1.46	1.47
-1.26	acetic acid	3.73	3.39	1.66	2.32

D_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.81	β-naphthol	5.98	5.77	3.61	4.17
	s-collidine	4.53	4.37	4.30	2.87
	acridine	3.67	3.49	3.21	1.99
	β-naphthoic acid	3.45	3.12	1.40	1.74
-1.21	acetic acid	3.68	3.35	1.62	1.73

25°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.54	β-naphthol	-0.06	-0.05	-0.05	0.69
	s-collidine	0.00	0.00	0.00	0.77
	acridine	-0.02	-0.01	0.00	0.75
	β-naphthoic acid	-0.05	-0.05	-0.05	0.67
0.49	acetic acid	-0.05	-0.04	-0.04	0.57

250°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
0.39	β-naphthol	0.00	0.01	0.01	0.40
	s-collidine	0.01	0.01	0.01	0.42
	acridine	0.00	0.01	0.01	0.41
	β-naphthoic acid	0.00	0.01	0.01	0.39
0.44	acetic acid	0.00	0.01	0.00	1.16

Table A17(b).
Errors in the calculated pK_a differences at the BLYP-CPCM (uahf) level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	5.39	5.16	3.00	3.22
s-collidine				
acridine	1.52	1.34	1.05	-0.52
β-naphthoic acid	5.32	5.00	3.28	3.29
acetic acid	4.99	4.65	2.92	3.58
MAE	4.30	4.04	2.56	2.65
AE	4.30	4.04	2.56	2.39

D_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	5.17	4.96	2.80	3.36
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	4.89	4.56	2.83	2.94
MAE	5.03	4.76	2.81	3.15
AE	5.03	4.76	2.81	3.15

25°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	-0.60	-0.59	-0.59	0.15
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	-0.54	-0.53	-0.53	0.08
MAE	0.57	0.56	0.56	0.11
AE	-0.57	-0.56	-0.56	0.11

250°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_{2w}	G_{3w}	G_w
β-naphthol	-0.39	-0.38	-0.38	0.01
s-collidine				
acridine				
β-naphthoic acid				
acetic acid	-0.44	-0.43	-0.44	0.72
MAE	0.41	0.41	0.41	0.37
AE	-0.41	-0.41	-0.41	0.37

Table A18(a).
Calculated pK_a differences at the BLYP-Onsager level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_w
0.66	β-naphthol	53.45	53.35
	s-collidine	22.82	22.71
2.17	acridine	23.00	22.91
-1.82	β-naphthoic acid	48.77	48.61
-1.26	acetic acid	56.30	56.21

D_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_w
0.81	β-naphthol	53.40	53.29
	s-collidine	22.81	22.70
	acridine	22.99	22.89
	β-naphthoic acid	48.73	48.56
-1.21	acetic acid	56.26	56.85

25°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_w
0.54	β-naphthol	-0.06	-0.06
	s-collidine	0.00	0.00
	acridine	-0.02	-0.02
	β-naphthoic acid	-0.05	-0.05
0.49	acetic acid	-0.05	-0.07

250°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_w
0.39	β-naphthol	-0.01	0.00
	s-collidine	0.01	0.01
	acridine	0.00	0.01
	β-naphthoic acid	-0.01	0.00
0.44	acetic acid	-0.01	-0.70

Table A18(b).
Errors in the calculated pK_a differences at the BLYP-Onsager level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Molecule		G_{1w}	G_w
β-naphthol		52.79	52.69
s-collidine			
acridine		20.83	20.74
β-naphthoic acid		50.59	50.43
acetic acid		57.56	57.47
	MAE	45.45	45.33
	AE	45.45	45.33

D_2O, pK_a (25°C) - pK_a (250°C)

Molecule		G_{1w}	G_w
β-naphthol		52.59	52.48
s-collidine			
acridine			
β-naphthoic acid			
acetic acid		57.47	58.07
	MAE	55.03	55.27
	AE	55.03	55.27

25°C, pK_a (D_2O) - pK_a (H_2O)

Molecule		G_{1w}	G_w
β-naphthol		-0.60	-0.60
s-collidine			
acridine			
β-naphthoic acid			
acetic acid		-0.54	-0.54
	MAE	0.57	0.57
	AE	-0.57	-0.57

250°C, pK_a (D_2O) - pK_a (H_2O)

Molecule		G_{1w}	G_w
β-naphthol		-0.40	-0.39
s-collidine			
acridine			
β-naphthoic acid			
acetic acid		-0.45	-1.14
	MAE	0.42	0.76
	AE	-0.42	-0.76

Table A19(a).
Calculated pK_a differences at the BLYP-SMD level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_w
0.66	β-naphthol	10.24	10.03
-1.26	acetic acid	7.54	7.44

D_2O, pK_a (25°C) - pK_a (250°C)

Exp.	Molecule	G_{1w}	G_w
0.81	β-naphthol	10.18	9.89
-1.21	acetic acid	7.49	7.30

25°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_w
0.54	β-naphthol	-0.06	-0.21
0.49	acetic acid	-0.05	-0.21

250°C, pK_a (D_2O) - pK_a (H_2O)

Exp.	Molecule	G_{1w}	G_w
0.39	β-naphthol	0.00	-0.06
0.44	acetic acid	0.00	-0.07

Table A19(b).
Errors in the calculated pK_a differences at the BLYP-SMD level of theory.

H_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_w
β-naphthol	9.58	9.37
acetic acid	8.80	8.70
MAE	9.19	9.04
AE	9.19	9.04

D_2O, pK_a (25°C) - pK_a (250°C)

Molecule	G_{1w}	G_w
β-naphthol	9.37	9.08
acetic acid	8.70	8.51
MAE	9.03	8.80
AE	9.03	8.80

25°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_w
β-naphthol	-0.60	-0.75
acetic acid	-0.54	-0.70
MAE	0.57	0.73
AE	-0.57	-0.73

250°C, pK_a (D_2O) - pK_a (H_2O)

Molecule	G_{1w}	G_w
β-naphthol	-0.39	-0.45
acetic acid	-0.44	-0.51
MAE	0.41	0.48
AE	-0.41	-0.48

Appendix B

(7 pages)

Data obtained while investigating the numeric source of the DIE on pK_a values.

Linear dependence of constant Q2 with respect to temperature.
$Q_2 = [\Delta_f G^\circ_{D_2O}(D_3O^+) - \Delta_f G^\circ_{H_2O}(H_3O^+) + \Delta_f G^\circ_{H_2O}(H_2O) - \Delta_f G^\circ_{D_2O}(D_2O)]$
(Figure B1)

Differences in Gibbs free energies of formation (in au) in heavy and light water for the conjugate bases (A^-) and the acids (HA/DA) under ambient and hydrothermal conditions.
(Table B1)

Uncorrected energy values for the acids in H_2O and D_2O and their differences (in au) under ambient and hydrothermal conditions.
(Table B2)

Various corrections for the acids in H_2O and D_2O (in au) under ambient conditions.
(Table B3)

Various corrections for the acids in H_2O and D_2O (in au) under ambient conditions.
(Table B4)

Differences between various corrections for the acids in H_2O and D_2O (in au) under ambient and hydrothermal conditions.
(Table B5)

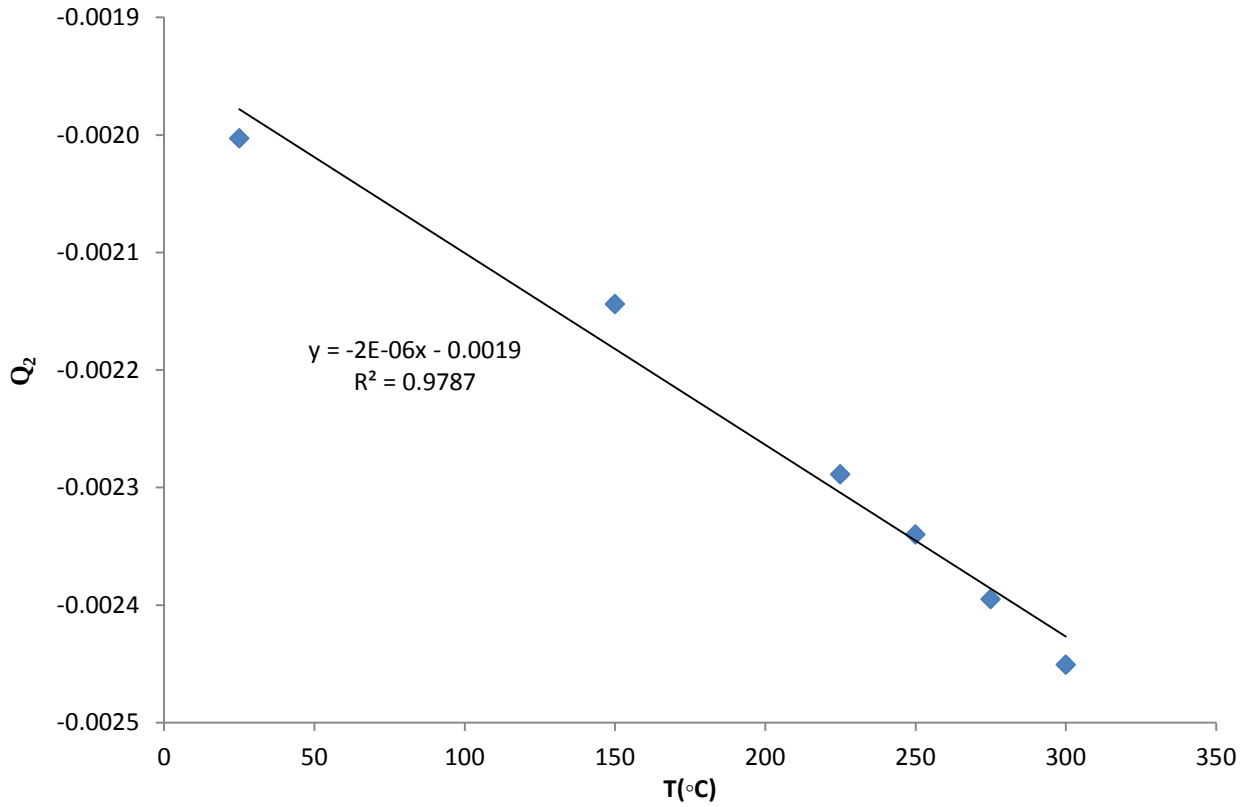


Figure B1. Linear dependence of constant Q_2 with respect to temperature.

$$Q_2 = [\Delta_f G^{\circ}_{D_2O}(D_3O^+) - \Delta_f G^{\circ}_{H_2O}(H_3O^+) + \Delta_f G^{\circ}_{H_2O}(H_2O) - \Delta_f G^{\circ}_{D_2O}(D_2O)]$$

Table B1. Differences in Gibbs free energies of formation (in au) in heavy and light water for the conjugate bases (A^-) and the acids (HA/DA) under ambient and hydrothermal conditions.[a]

	$\Delta_f G^\circ_{D_2O}(A^-) - \Delta_f G^\circ_{H_2O}(A^-)$		$\Delta_f G^\circ_{H_2O}(HA) - \Delta_f G^\circ_{D_2O}(DA)$	
	25ºC	250ºC	25ºC	250ºC
phenol	0.00001	0.00002	0.00337	0.00373
3-methoxyphenol	0.00000	0.00002	0.00338	0.00373
4-methoxyphenol	0.00001	0.00002	0.00337	0.00373
4-bromophenol	0.00000	0.00002	0.00339	0.00376
2-nitrophenol	0.00000	0.00000	0.00349	0.00378
4-nitrophenol	0.00000	0.00002	0.00336	0.00371
2,4-dinitrophenol	0.00000	0.00001	0.00347	0.00378
2,5-dinitrophenol	0.00007	0.00000	0.00344	0.00380
2,6-dinitrophenol	0.00000	0.00001	0.00345	0.00374
3,5-dinitrophenol	0.00000	0.00002	0.00334	0.00370
4-chloro-2,6-dinitrophenol	0.00000	0.00006	0.00346	0.00379
β-naphthol	0.00000	0.00002	0.00337	0.00373
β-naphthoic acid	0.00000	0.00002	0.00333	0.00368
acetic acid	0.00001	0.00002	0.00334	0.00368
s-collidine	0.00000	0.00000	0.00354	0.00380
acridine	0.00000	0.00001	0.00349	0.00376
Average	**0.00001**	**0.00002**	**0.00341**	**0.00374**
Std dev	**0.00002**	**0.00001**	**6.2E-05**	**3.9E-05**

[a] At the B3LYP-IEF-PCM/6-311++G(d,p) level of theory.

Table B2. Uncorrected energy values for the acids in H_2O and D_2O and their differences (in au) under ambient and hydrothermal conditions.[a]

	25°C, 101.3 kPa			250°C, 20.0 MPa		
Acid	$E_{H_2O}(HA)$	$E_{D_2O}(DA)$	$E_{H_2O}(HA) - E_{D_2O}(DA)$	$E_{H_2O}(HA)$	$E_{D_2O}(DA)$	$E_{H_2O}(HA) - E_{D_2O}(DA)$
phenol	-307.57185	-307.57185	0.00000	-307.57122	-307.57122	0.00000
3-methoxyphenol	-422.13103	-422.13103	0.00000	-422.13030	-422.13030	0.00000
4-methoxyphenol	-422.12828	-422.12828	0.00000	-422.12752	-422.12752	0.00000
4-bromophenol	-2881.11514	-2881.11514	0.00000	-2881.11446	-2881.11445	0.00000
2-nitrophenol	-512.13900	-512.13900	0.00000	-512.13859	-512.13859	0.00000
4-nitrophenol	-512.14483	-512.14483	0.00000	-512.14392	-512.14391	-0.00001
2,4-dinitrophenol	-716.70283	-716.70283	0.00000	-716.70219	-716.70219	0.00000
2,5-dinitrophenol	-716.69868	-716.69868	0.00000	-716.69809	-716.69809	0.00000
2,6-dinitrophenol	-716.69211	-716.69211	0.00000	-716.69145	-716.69144	0.00000
3,5-dinitrophenol	-716.70207	-716.70207	0.00000	-716.70101	-716.70101	-0.00001
4-chloro-2,6-dinitrophenol	-1176.30848	-1176.30848	0.00000	-1176.30780	-1176.30780	0.00000
β-naphthol	-461.25160	-461.25160	0.00000	-461.25088	-461.25087	0.00000
β-naphthoic acid	-574.64217	-574.64217	0.00000	-574.64148	-574.64147	0.00000
acetic acid	-229.17843	-229.17843	0.00000	-229.17787	-229.17787	0.00000
s-collidine	-366.80911	-366.80911	0.00000	-366.80698	-366.80697	-0.00001
acridine	-556.16983	-556.16983	0.00000	-556.16769	-556.16768	-0.00001

[a] Obtained from geometry optimizations at the B3LYP-IEF-PCM/6-311++G(d,p) level of theory.

Table B3. Various corrections for the acids in H_2O and D_2O (in au) under ambient conditions.[a]

	H_2O					D_2O				
25°C, 101.3 kPa	**ZPE**	**TCE**	**ATC**	**T S**	**TCG**	**ZPE**	**TCE**	**ATC**	**T S**	**TCG**
phenol	0.10285	0.10842	0.00557	0.03553	0.07383	0.09969	0.10543	0.00574	0.03592	0.07046
3-methoxyphenol	0.13494	0.14311	0.00817	0.04179	0.10227	0.13177	0.14012	0.00835	0.04218	0.09889
4-methoxyphenol	0.13479	0.14306	0.00827	0.04210	0.10190	0.13165	0.14009	0.00844	0.04250	0.09854
4-bromophenol	0.09270	0.09968	0.00698	0.04033	0.06029	0.08953	0.09669	0.00716	0.04073	0.05690
2-nitrophenol	0.10613	0.11382	0.00770	0.04141	0.07336	0.10277	0.11065	0.00787	0.04172	0.06987
4-nitrophenol	0.10520	0.11321	0.00800	0.04235	0.07180	0.10203	0.11022	0.00818	0.04272	0.06844
2,4-dinitrophenol	0.10805	0.11838	0.01034	0.04837	0.07095	0.10471	0.11523	0.01051	0.04868	0.06749
2,5-dinitrophenol	0.10793	0.11832	0.01040	0.04896	0.07031	0.10459	0.11517	0.01058	0.04925	0.06687
2,6-dinitrophenol	0.10834	0.11861	0.01027	0.04813	0.07143	0.10501	0.11546	0.01045	0.04843	0.06798
3,5-dinitrophenol	0.10695	0.11769	0.01073	0.04979	0.06884	0.10381	0.11473	0.01091	0.05017	0.06549
4-chloro-2,6-dinitrophenol	0.09839	0.10999	0.01160	0.05166	0.05928	0.09506	0.10685	0.01179	0.05198	0.05581
β-naphthol	0.14951	0.15756	0.00805	0.04166	0.11685	0.14634	0.15457	0.00823	0.04204	0.11347
β-naphthoic acid	0.16018	0.16991	0.00973	0.04641	0.12445	0.15701	0.16693	0.00992	0.04676	0.12111
acetic acid	0.06012	0.06477	0.00465	0.03325	0.03246	0.05696	0.06178	0.00482	0.03360	0.02913
s-collidine	0.18247	0.19234	0.00987	0.04718	0.14611	0.17901	0.18904	0.01002	0.04742	0.14257
acridine	0.19382	0.20332	0.00950	0.04528	0.15899	0.19043	0.20008	0.00965	0.04553	0.15550

[a] At the B3LYP-IEF-PCM/6-311++G(d,p) level of theory.

Table B4. Various corrections for the acids in H_2O and D_2O (in au) under hydrothermal conditions.[a]

	H_2O					D_2O				
250°C, 20.0 MPa	**ZPE**	**TCE**	**ATC**	**T S**	**TCG**	**ZPE**	**TCE**	**ATC**	**T S**	**TCG**
phenol	0.10292	0.11933	0.01641	0.06837	0.05262	0.09974	0.11652	0.01677	0.06929	0.04888
3-methoxyphenol	0.13501	0.15808	0.02307	0.08456	0.07518	0.13183	0.15527	0.02344	0.08548	0.07144
4-methoxyphenol	0.13486	0.15804	0.02318	0.08513	0.07457	0.13171	0.15523	0.02352	0.08605	0.07084
4-bromophenol	0.09277	0.11199	0.01922	0.07862	0.03502	0.08960	0.10918	0.01958	0.07957	0.03126
2-nitrophenol	0.10618	0.12802	0.02184	0.08292	0.04675	0.10283	0.12508	0.02226	0.08377	0.04297
4-nitrophenol	0.10528	0.12761	0.02233	0.08483	0.04443	0.10210	0.12481	0.02271	0.08574	0.04072
2,4-dinitrophenol	0.10811	0.13613	0.02802	0.09967	0.03811	0.10476	0.13320	0.02844	0.10053	0.03433
2,5-dinitrophenol	0.10798	0.13612	0.02815	0.10083	0.03696	0.10464	0.13320	0.02857	0.10170	0.03316
2,6-dinitrophenol	0.10839	0.13627	0.02788	0.09921	0.03872	0.10506	0.13336	0.02831	0.10005	0.03497
3,5-dinitrophenol	0.10703	0.13569	0.02866	0.10252	0.03482	0.10388	0.13291	0.02903	0.10345	0.03112
4-chloro-2,6-dinitrophenol	0.09844	0.12897	0.03053	0.10713	0.02349	0.09511	0.12607	0.03096	0.10803	0.01969
β-naphthol	0.14958	0.17421	0.02463	0.08643	0.08943	0.14639	0.17140	0.02500	0.08735	0.08570
β-naphthoic acid	0.16027	0.18902	0.02875	0.09788	0.09279	0.15708	0.18624	0.02916	0.09879	0.08911
acetic acid	0.06020	0.07141	0.01121	0.05890	0.01415	0.05702	0.06863	0.01161	0.05980	0.01047
s-collidine	0.18254	0.20932	0.02677	0.09618	0.11479	0.17909	0.20628	0.02718	0.09695	0.11098
acridine	0.19390	0.22387	0.02996	0.09770	0.12783	0.19049	0.22087	0.03038	0.09848	0.12405

[a] At the B3LYP-IEF-PCM/6-311++G(d,p) level of theory.

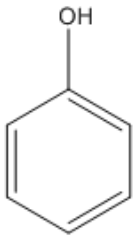
Table B5. Differences between various corrections for the acids in H_2O and D_2O (in au) under ambient and hydrothermal conditions.[a]

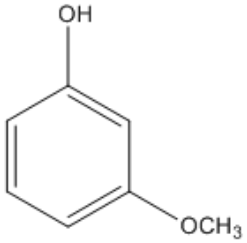
	25°C, 101.3 kPa					250°C, 20.0 MPa				
Acids	**ΔZPE**	**ΔTCE**	**T ΔS**	**ΔTCG –ΔZPE[b]**	**ΔTCG**	**ΔZPE**	**ΔTCE**	**TΔS**	**ΔTCG –ΔZPE[b]**	**ΔTCG**
phenol	0.00316	0.00299	-0.00039	0.00021	0.00337	0.00317	0.00281	-0.00092	0.00056	0.00373
3-methoxyphenol	0.00317	0.00299	-0.00039	0.00021	0.00338	0.00318	0.00282	-0.00092	0.00056	0.00374
4-methoxyphenol	0.00314	0.00297	-0.00040	0.00023	0.00337	0.00315	0.00281	-0.00093	0.00059	0.00373
4-bromophenol	0.00317	0.00299	-0.00040	0.00022	0.00339	0.00318	0.00281	-0.00095	0.00058	0.00376
2-nitrophenol	0.00335	0.00318	-0.00031	0.00014	0.00349	0.00335	0.00293	-0.00085	0.00043	0.00378
4-nitrophenol	0.00317	0.00299	-0.00037	0.00019	0.00336	0.00318	0.00281	-0.00091	0.00053	0.00371
2,4-dinitrophenol	0.00334	0.00316	-0.00031	0.00013	0.00347	0.00335	0.00292	-0.00086	0.00044	0.00378
2,5-dinitrophenol	0.00333	0.00315	-0.00029	0.00011	0.00344	0.00334	0.00292	-0.00087	0.00046	0.00380
2,6-dinitrophenol	0.00333	0.00315	-0.00030	0.00012	0.00345	0.00333	0.00290	-0.00084	0.00041	0.00374
3,5-dinitrophenol	0.00314	0.00296	-0.00038	0.00020	0.00334	0.00315	0.00278	-0.00092	0.00055	0.00371
4-chloro-2,6-dinitrophenol	0.00332	0.00314	-0.00032	0.00014	0.00346	0.00333	0.00290	-0.00090	0.00047	0.00380
β-naphthol	0.00317	0.00299	-0.00038	0.00020	0.00337	0.00318	0.00282	-0.00092	0.00055	0.00373
β-naphthoic acid	0.00317	0.00299	-0.00035	0.00016	0.00333	0.00319	0.00278	-0.00091	0.00049	0.00368
acetic acid	0.00316	0.00299	-0.00034	0.00017	0.00334	0.00318	0.00278	-0.00090	0.00050	0.00368
s-collidine	0.00346	0.00330	-0.00024	0.00008	0.00354	0.00345	0.00304	-0.00077	0.00036	0.00381
acridine	0.00339	0.00324	-0.00025	0.00010	0.00350	0.00341	0.00300	-0.00078	0.00037	0.00378
Average	**0.00325**	**0.00307**	**-0.00034**	**0.00016**	**0.00341**	**0.00326**	**0.00286**	**-0.00088**	**0.00049**	**0.00375**
Standard deviation	**1.0E-04**	**1.1E-04**	**5.0E-05**	**4.6E-05**	**6.3E-05**	**1.0E-04**	**8.0E-05**	**5.1E-05**	**7.2E-05**	**4.0E-05**

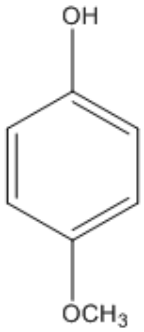
[a] At the B3LYP-IEF-PCM/6-311++G(d,p) level of theory; $\Delta X = X_{H_2O}(HA) - X_{D_2O}(DA)$.

[b] Equivalent to ΔATC - T ΔS, the error made when simplifying eq. 16 into eq 20; T ΔS is the error made when simplifying eq. 16 into eq 19.

Cartesian coordinates of the acids and conjugate bases studied calculated at the B3LYP-IEF-PCM/ 6-311++G(d,p) level of theory in H_2O at 25°C, 101.3 kPa.

phenol	**Acid**	**Conjugate base**
	C,0,0.0062891972,0.0000908636,-0.0135959256	C,0,-0.0780011203,0.0001422653,-0.0449579384
	C,0,-0.0041048976,0.000524136,1.3818721416	C,0,0.0006934363,0.0004750869,1.3996704732
	C,0,1.2014136001,-0.0000561108,2.0769123344	C,0,1.2082282304,-0.0000549443,2.0834764412
	C,0,2.4187429246,-0.0010563394,1.3944937252	C,0,2.4384719657,-0.0010942708,1.4080960228
	C,0,2.4191146001,-0.00148238,0.0013029265	C,0,2.4083741641,-0.0014752033,0.0049977735
	C,0,1.2182740284,-0.0009173965,-0.7067440778	C,0,1.2124721318,-0.0009473031,-0.6989818139
	H,0,-0.9549476434,0.0012960063,1.9006100737	H,0,-0.9408617377,0.0013151679,1.9436515066
	H,0,1.1881220925,0.0002778112,3.1611530858	H,0,1.1989364676,0.0002656066,3.1732772582
	H,0,3.3537464506,-0.0015014685,1.9415897495	H,0,3.3784867025,-0.0014193997,1.9508893292
	H,0,3.3568723488,-0.0022592113,-0.542976708	H,0,3.3475623538,-0.0022715596,-0.5478827485
	H,0,1.223371382,-0.0012510223,-1.7928462924	H,0,1.2129464026,-0.0012860142,-1.7863834417
	O,0,-1.206656446,0.0006862801,-0.6504315565	O,0,-1.1772478504,0.0005748534,-0.6796528371
	H,0,-1.073727037,0.0002922967,-1.6040126159	

3-methoxyphenol	**Acid**	**Conjugate base**
	C,0,0.1447502633,0.000147777,-0.0793070967	C,0,0.1462485256,0.0000564557,-0.0658631206
	C,0,0.0514310743,0.0006111466,1.3187055461	C,0,0.0440626735,0.0004822302,1.31634956
	C,0,1.2035247493,-0.0000390967,2.0961289648	C,0,1.1962235246,-0.0001976464,2.1849077073
	C,0,2.4670394434,-0.0010490309,1.4974163893	C,0,2.4659354236,-0.0011022265,1.4853097076
	C,0,2.5436290476,-0.0014512247,0.1127205993	C,0,2.5357616004,-0.0015433233,0.1066150837
	C,0,1.4003436173,-0.0008974344,-0.6918326332	C,0,1.3909993261,-0.0010359622,-0.7146786604
	H,0,-0.934801418,0.0013540789,1.7711644426	H,0,-0.9407117322,0.0013363996,1.771991734
	H,0,3.3526458974,-0.0015422731,2.1196158968	H,0,3.3681637081,-0.001461908,2.0905820252
	H,0,3.5176113325,-0.0022227197,-0.3640701233	H,0,3.5123406266,-0.0023218194,-0.3758520879
	H,0,1.5140275567,-0.0012475667,-1.7660424438	H,0,1.5045836355,-0.0014471617,-1.7895398685
	O,0,-1.0606779105,0.0008307998,-0.7208664202	O,0,-1.0852104476,0.0006778305,-0.7356055268
	C,0,-1.1639620175,0.0003548136,-2.1423728703	C,0,-1.1572183252,0.0004432529,-2.1424791235
	H,0,-1.7203394497,-0.89017933,-2.4431755503	H,0,-1.7069409988,-0.8895708796,-2.4753128249
	H,0,-1.7187218855,0.8916502495,-2.4439101323	H,0,-1.7060830342,0.890870625,-2.4756196205
	H,0,-0.1979415048,-0.0007331083,-2.6437524754	H,0,-0.1819025894,-0.0001042069,-2.6294717728
	O,0,1.1572221946,0.000296704,3.464401032	O,0,1.1070853288,0.0005000705,3.4490659311
	H,0,0.2404988165,0.0010085102,3.7587939649	

4-methoxyphenol	**Acid**	**Conjugate base**
	C,0,1.8468740447,-0.1006446811,0.0000145317	C,0,-0.1458167958,0.1191221808,-0.042012917
	C,0,1.3136553464,1.1916471867,0.0000500261	C,0,-0.1065780766,0.0990133934,1.3970145274
	C,0,-0.0592301499,1.3774114075,-0.0000033464	C,0,1.0810632791,0.0651860313,2.1313867743
	C,0,-0.9284154018,0.2788803593,-0.000111005	C,0,2.3180680068,0.0479739563,1.4840004198
	C,0,-0.3980741308,-1.0101817804,-0.0001578857	C,0,2.3419358383,0.0648506797,0.0862676596
	C,0,0.9894207025,-1.1941306036,-0.0000749744	C,0,1.1662167045,0.099457206,-0.649896033
	H,0,1.9883602131,2.0392026373,0.0001444953	H,0,-1.0594870675,0.1109898963,1.9194468666
	H,0,-0.483351848,2.3742717496,-0.0000089055	H,0,1.02148609,0.0526895158,3.2155850813
	H,0,-1.0395161783,-1.8809829574,-0.0003846259	H,0,3.3076056064,0.0509121415,-0.4139167426
	H,0,1.3911622271,-2.2032124733,-0.000032694	H,0,1.2070614711,0.1120488057,-1.7360208129
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	H,0,3.4614515756,-1.1494482568,-0.0000528941	O,0,3.5680645159,0.0180774054,2.1313081837
	O,0,-2.2662331623,0.574805373,-0.0002519856	C,0,3.5595951707,-0.047748367,3.5313366692
	C,0,-3.1926774985,-0.4993089653,0.0002826869	H,0,3.0449172773,-0.9478195553,3.9010150551
	H,0,-3.083460767,-1.1237742332,0.8945521228	H,0,4.6046735256,-0.0808624882,3.8500865053

H,0,-4.1811137537,-0.0422908075,0.000591225
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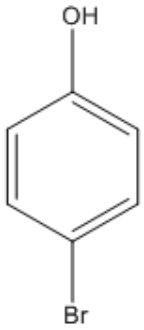
H,0,3.0775042809,0.8309716033,3.9865997577

4-bromophenol



Acid

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C,0,2.4020816429,-0.015934849,1.3939932166
C,0,2.3433298047,0.0719744543,0.0082357672
C,0,1.1035010974,0.1751576723,-0.6204584325
H,0,-0.91460134,0.1138653945,2.1052454051
H,0,1.2910538877,-0.0708977863,3.237046703
H,0,3.2505850689,0.0606930968,-0.5818560031
H,0,1.0557242099,0.243842021,-1.7030771486
O,0,-1.3115445134,0.2892012027,-0.4234275896
H,0,-1.2368498437,0.3455986603,-1.3816999425
Br,0,4.1064261145,-0.1581317411,2.2640675147

Conjugate base

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C,0,1.2292172978,0.0087038293,2.140546589
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C,0,2.3829900397,0.0541749331,0.0120507952
C,0,1.1644786376,0.1194574973,-0.6487042474
H,0,-0.9136472237,0.0813762613,2.0552321822
H,0,1.2614379806,-0.0347861721,3.2248759971
H,0,3.3096261869,0.0459220349,-0.553641112
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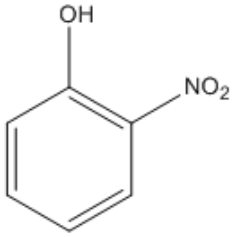
2-nitrophenol



Acid

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H,0,1.1911005303,0.0011044584,3.1531370323
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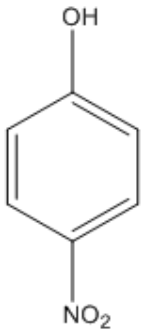
H,0,3.3451224708,-0.0033291317,-0.5647752316
O,0,-1.2376840774,0.0004376889,-0.6085643317
H,0,-1.1072785914,-0.0005936362,-1.5804275695
N,0,1.2529485575,-0.0006848289,-2.1463677421
O,0,2.3377894307,-0.0001123344,-2.7151329612
O,0,0.1756764609,-0.0005393059,-2.7773370433

Conjugate base

C,0,-0.1144944574,-0.0106777714,-0.0225557573
C,0,0.0002633396,-0.0111043505,1.4194676415
C,0,1.2013772812,0.0014500536,2.0803019794
C,0,2.4244351834,0.0113915682,1.3662822512
C,0,2.3911780773,0.0070567806,-0.0063705869
C,0,1.1652171922,0.0031777555,-0.7145469011
H,0,-0.9365055961,-0.0215002317,1.9703734099
H,0,1.214936867,0.0043627457,3.1671006789
H,0,3.3718052791,0.0257589743,1.8930564814
H,0,3.3083114733,0.0152924653,-0.5802096239
O,0,-1.2612242275,-0.033739657,-0.5670865412
N,0,1.2533791576,0.000372401,-2.138911334
O,0,2.3763477492,-0.1315905501,-2.6755662953
O,0,0.2317230584,0.1318803288,-2.8309086866

4-nitrophenol



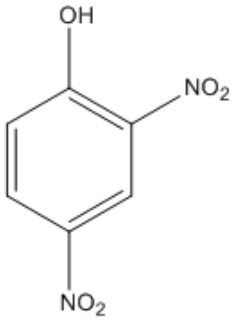
Acid

C,0,0.0175979282,0.0000322068,0.0059922673
C,0,0.0091120523,0.0005732504,1.4046471092
C,0,1.2103985271,0.0000778625,2.0892970509
C,0,2.421831037,-0.0009701913,1.3791723543
C,0,2.4176564455,-0.0014792359,-0.0244472982
C,0,1.2158232811,-0.0009712554,-0.7118102149
H,0,-0.9313124295,0.00142962,1.9408074081
H,0,1.231262743,0.0005113545,3.1747720514
H,0,3.3601841671,-0.0023203764,-0.5668405775
H,0,1.2007391642,-0.0013695486,-1.7942586616
O,0,3.5597498481,-0.0015624484,2.1032842827
H,0,4.3536345189,-0.0018299086,1.5255294622
N,0,-1.2439436961,0.0005061073,-0.714567628
O,0,-2.2922718315,0.0004572404,-0.0656822578
O,0,-1.2184200205,0.0011282028,-1.9472461018

Conjugate base

C,0,-0.0005272059,0.0006815386,-0.0002052612
C,0,0.0011803361,0.0008474907,1.4116791682
C,0,1.1889953376,0.0001589277,2.0993806939
C,0,2.4615171114,-0.0009884553,1.4214429244
C,0,2.4124799159,-0.002118273,-0.0195660816
C,0,1.2231073109,-0.0000011894,-0.7045873518
H,0,-0.9439756215,0.0014456519,1.9407142338
H,0,1.1926889565,0.0004607005,3.1859804853
H,0,3.3554111527,-0.0029876179,-0.5595624265
H,0,1.2088007559,-0.0001684727,-1.7876357929
O,0,3.5673643722,-0.0019924437,2.0599119413
N,0,-1.2257860818,0.0003745894,-0.7076309257
O,0,-2.3009550315,0.0004078139,-0.0720471639
O,0,-1.2128908242,-0.0002274741,-1.9565431777

2,4-dinitrophenol



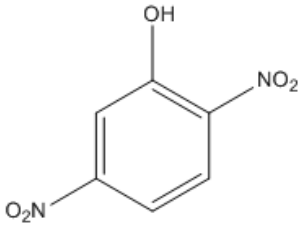
Acid

C,0,-0.0307703108,0.0002744926,-0.0134489195
C,0,-0.0036703775,0.0009737963,1.394367629
C,0,1.1883379565,0.0000218233,2.0819640165
C,0,2.3968422144,-0.0015447973,1.3684926923
C,0,2.4211407124,-0.0019668976,-0.0111568779
C,0,1.2107452888,-0.0008357383,-0.7017654262
H,0,-0.9533011638,0.0022145096,1.9211957819
H,0,1.1997536418,0.0005126368,3.1650511351
H,0,3.3557291758,-0.0028105512,-0.5557321845
O,0,-1.223071901,0.0012151076,-0.5970196863
H,0,-1.1083824754,-0.0005417714,-1.5721829095
N,0,1.2643895844,-0.0008962666,-2.1533702942
O,0,2.3499344607,0.0026158425,-2.7107838525
O,0,0.1881967175,-0.0038854216,-2.7750616028
N,0,3.6652241417,-0.0016876555,2.0991474123
O,0,4.7089974837,-0.0033433469,1.4528401053
O,0,3.6194027618,-0.0004017031,3.3260311304

Conjugate base

C,0,-0.1116400797,0.001280986,-0.0139696317
C,0,-0.0030481581,0.0003224405,1.4365380147
C,0,1.1830316426,-0.000784631,2.1057702259
C,0,2.3979084193,-0.0012600957,1.3734116019
C,0,2.3855910865,-0.0016784946,-0.0107167029
C,0,1.1796792407,-0.0010195033,-0.7048801842
H,0,-0.9426874665,0.0011513391,1.9814532488
H,0,1.2126861195,-0.0010326605,3.1884397579
H,0,3.3150373498,-0.0025054098,-0.5612141106
O,0,-1.2391574329,0.0045388824,-0.5613436494
N,0,1.2775172037,-0.0019205647,-2.1473206365
O,0,2.4060800188,-0.0004726921,-2.6663190996
O,0,0.2493746957,-0.0043662683,-2.8271155806
N,0,3.6537373106,-0.0010685625,2.066317513
O,0,4.7065057712,0.0006282282,1.4127523311
O,0,3.6424327357,-0.0023181924,3.3056382164

2,5-dinitrophenol



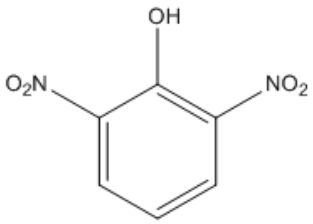
Acid

C,0,5.3146561685,1.2806511347,1.1608091944
C,0,4.6537507024,0.509758749,0.200066176
C,0,4.3097432673,1.1216335387,-0.987191583
C,0,4.6203000257,2.4699703949,-1.2051882762
C,0,5.2893905577,3.2415344184,-0.2260898975
C,0,5.6348447439,2.6093147621,0.978225478
H,0,4.4217623525,-0.5301683577,0.3846700215
H,0,3.7966651872,0.5695995098,-1.7643235995
H,0,6.1482255071,3.1812551873,1.7426417661
N,0,4.2317296365,3.0582423009,-2.4770968068
O,0,4.5062941507,4.2539768912,-2.6759095561
O,0,3.6545588192,2.3671925421,-3.3012505547
N,0,5.6937783538,0.6409896893,2.4450911595
O,0,5.4049146452,-0.5386319783,2.5977276933
O,0,6.2717898903,1.3242669396,3.2795583772
O,0,5.6232811601,4.5272753869,-0.3483919323
H,0,5.3317745719,4.852921761,-1.2259578698

Conjugate base

C,0,-0.0139138469,-0.0013819899,0.0223602201
C,0,0.0314863336,-0.0007318786,1.3949399218
C,0,1.2519510435,-0.0001800951,2.1023151092
C,0,2.5367374073,-0.001857863,1.423665139
C,0,2.4305808859,-0.0035439512,-0.021492538
C,0,1.2197943419,-0.0026310943,-0.6587592033
H,0,-0.9504212666,-0.0005597092,-0.5159874505
H,0,-0.8878244984,-0.0000072881,1.9647072836
H,0,3.3566196668,-0.0041158782,-0.5836077287
O,0,3.6786132066,0.0011598291,1.961984062
N,0,1.1574708529,0.0014776065,3.5367913812
O,0,0.0270744874,0.0031940025,4.0609531199
O,0,2.1859210233,0.0014039559,4.2223987562
N,0,1.2041830297,0.0001217984,-2.1406494903
O,0,0.1124532338,0.0052665644,-2.7017841251
O,0,2.2739976391,-0.0030692391,-2.740630177

2,6-dinitrophenol



Acid

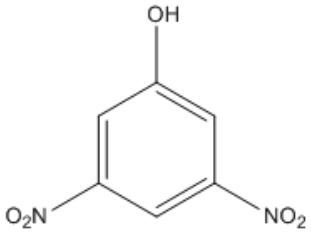
C,0,0.1590124402,-0.7750570967,0.2604511496
C,0,0.0055882072,0.0270412841,1.3770240845
C,0,1.0557407619,0.8412728079,1.8099569858
C,0,2.3110478367,0.8686090597,1.146725996
C,0,2.4204985417,0.0275762547,0.0168653931
C,0,1.3696014004,-0.7611077678,-0.4283797999
H,0,-0.6538261682,-1.4068219919,-0.0770580833
H,0,-0.9257640567,0.0430462345,1.9295442295
H,0,1.5134170807,-1.3735502572,-1.3115023666
O,0,3.3280057755,1.6401010074,1.4981229519
H,0,3.0532925781,2.1779894705,2.2760173298
N,0,0.8238756558,1.6779316303,2.9742473249
O,0,1.7418948859,2.429153427,3.3539121344

Conjugate base

C,0,0.1760544907,-0.7813695818,0.2731579536
C,0,0.0319369451,0.0383808494,1.3864559156
C,0,1.0753240629,0.8470612489,1.8233247768
C,0,2.3669078135,0.9435408536,1.1436155594
C,0,2.439858079,0.0333681027,0.000919774
C,0,1.3824287719,-0.7665357632,-0.4174576721
H,0,-0.63003627,-1.4335796203,-0.0392965091
H,0,-0.8941638161,0.0431595376,1.9492276963
H,0,1.5269555602,-1.3998782052,-1.284903291
O,0,3.2617360155,1.7581291381,1.4497277897
N,0,0.8224911457,1.6425114981,3.0025469225
O,0,1.7616346168,1.9526053088,3.7371609653
O,0,-0.3486494309,1.972448956,3.2486059157

O,0,-0.2541568921,1.6223064868,3.5426787212
N,0,3.6754713867,-0.0317777133,-0.7438053987
O,0,3.586040192,-0.1736427693,-1.9601447151
O,0,4.7336315243,0.0328027034,-0.1334333673
N,0,3.6540834704,-0.0460587247,-0.7780545477
O,0,3.5637791211,-0.3552780976,-1.9768018892
O,0,4.7378595942,0.1720361796,-0.2344030097
*in H_2O at 250°C and 20.0 MPa

3,5-dinitrophenol



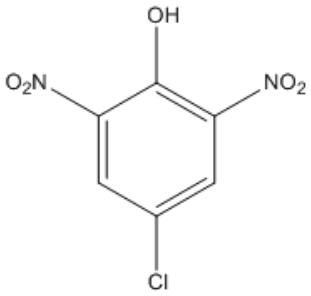
Acid

C,0,0.0339162293,0.0001149621,0.0220531069
C,0,-0.0187251734,0.0006718035,1.4104588869
C,0,1.2000196009,0.0000881402,2.0702942576
C,0,2.4222652077,-0.0010235445,1.4070672859
C,0,2.4277274459,-0.0015457778,0.0119726218
C,0,1.2215581603,-0.0009775348,-0.6934885106
H,0,-0.956343413,0.0015182331,1.9451290951
H,0,3.3389399473,-0.0014520304,1.9836013178
H,0,1.2154817217,-0.0013820252,-1.7745116436
O,0,3.5697153428,-0.0026173137,-0.7220153105
H,0,4.3446392357,-0.0029027061,-0.1491861982
N,0,1.2073958331,0.0006296489,3.5554790798
O,0,2.2980060877,0.0000374153,4.1110667252
O,0,0.127094388,0.0017071584,4.1242902694
N,0,-1.2459413921,0.0007114969,-0.7350491473
O,0,-2.2810162375,0.0014083029,-0.0862481442
O,0,-1.1769857304,-0.0000836229,-1.9555241008

Conjugate base

C,0,0.0311290957,0.0000564497,0.0187655236
C,0,-0.0321178964,0.0006356297,1.4135667692
C,0,1.2073989747,0.0000952743,2.0562621371
C,0,2.4254971762,-0.0009158415,1.3967377784
C,0,2.5014883675,-0.001531587,-0.0491116677
C,0,1.2113828356,-0.0009607701,-0.7063024081
H,0,-0.9638737968,0.0014156723,1.9514794699
H,0,3.3482567087,-0.0012863843,1.9598345468
H,0,1.1851786575,-0.0013538821,-1.7869853382
O,0,3.5889783894,-0.0025193125,-0.6769399397
N,0,1.2056723315,0.0006676481,3.5369374498
O,0,2.2845604991,0.0000860653,4.1250147828
O,0,0.1218730496,0.0016257733,4.1195360678
N,0,-1.2519931803,0.0005886161,-0.7201495842
O,0,-2.298477216,0.0014893472,-0.0729145301
O,0,-1.2217708563,0.0000988343,-1.9485313672

4-chloro-2,6-dinitrophenol



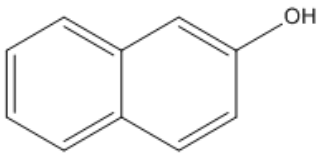
Acid

C,0,-1.7314009324,-1.8049021128,-0.1572900576
C,0,-0.3807421553,-2.1902570962,-0.0191256499
C,0,0.5439944659,-1.124391918,0.1168641872
C,0,0.1511644834,0.2155865197,0.1063061693
C,0,-1.1881321348,0.5304673022,-0.0197054351
C,0,-2.1381426125,-0.4835315365,-0.1384982332
H,0,0.9067665007,0.9820622777,0.2054087118
H,0,-3.1929109484,-0.2559897434,-0.2164795691
O,0,-0.0591619556,-3.473266934,0.0161013905
H,0,0.9151759412,-3.5292731784,0.1428347807
Cl,0,-1.7004104495,2.2002591136,-0.025383987
N,0,-2.784714537,-2.8291298733,-0.330809787
O,0,-2.543769446,-3.7663748572,-1.070236255
O,0,-3.8393111088,-2.6338383157,0.2597929657
N,0,1.9696894131,-1.401318063,0.2787248133
O,0,2.3264045123,-2.5925814279,0.3224015881
O,0,2.7444460537,-0.4684274368,0.3649194574

Conjugate base

C,0,-1.7618141166,-1.8414832064,-0.1538405784
C,0,-0.3537520174,-2.3022871226,-0.0427239555
C,0,0.5739352621,-1.1524564708,0.1141320001
C,0,0.1581266345,0.1707104474,0.1494030714
C,0,-1.1858829228,0.4879051988,0.0361179478
C,0,-2.1386527456,-0.5068235066,-0.1140745299
H,0,0.9062814616,0.9417676083,0.2668773372
H,0,-3.1885335598,-0.2661681549,-0.2029553206
O,0,-0.0035636471,-3.4765534384,-0.0757561684
Cl,0,-1.6926073718,2.1870041558,0.0840685909
N,0,-2.8520428638,-2.7917658038,-0.3148836376
O,0,-2.6110647885,-3.9929729496,-0.3595227845
O,0,-4.0109974964,-2.3397638341,-0.4030415454
N,0,2.0087946186,-1.3578579891,0.2427838896
O,0,2.4652044613,-2.4955050788,0.2224776736
O,0,2.7326035817,-0.3504764651,0.3713879896

β-naphthol



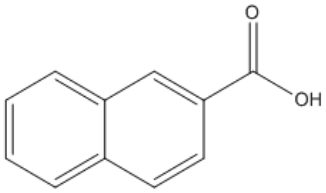
Acid

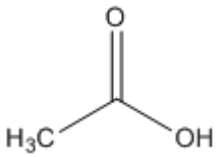
C,0,2.9275809635,0.3773547551,-0.0000149562
C,0,1.8708021406,1.2593710531,-0.0000840843
C,0,0.5313473156,0.7898489142,-0.0000629808
C,0,0.285121529,-0.6207405817,-0.0000721434
C,0,1.3982787756,-1.50493634,0.0000139017
C,0,2.6856667319,-1.0176951926,0.000053542
H,0,-0.4056123814,2.7435248,0.0000632873
H,0,3.9480650939,0.7468935687,0.0000206675
H,0,2.0482068956,2.3313896826,-0.0001006232

Conjugate base

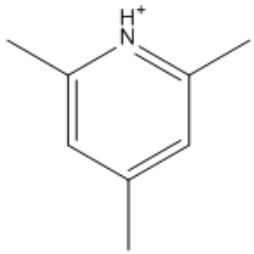
C,0,2.8847082151,0.4146639911,0.0005865472
C,0,1.806645998,1.2747644869,0.0000346844
C,0,0.4770985979,0.7846222156,-0.0007360298
C,0,0.2430379188,-0.632563344,-0.001020895
C,0,1.3817466752,-1.4923332204,-0.0006555356
C,0,2.6617601873,-0.9843057497,0.0001699665
H,0,-0.4980615927,2.7192663282,-0.0008127931
H,0,3.8983343133,0.8024808761,0.0013789708
H,0,1.9642130093,2.3506451519,0.0003680073

	C,0,-0.5838293315,1.6718960915,0.0000181189	C,0,-0.6583330845,1.6433638189,-0.0007619766
	C,0,-1.0539113281,-1.094184095,-0.0001034259	C,0,-1.0824552687,-1.127013467,-0.0008212868
	H,0,1.2169005759,-2.5760325956,0.0000881099	H,0,1.2225870509,-2.5674945878,-0.0008145711
	H,0,3.5249197759,-1.7065310891,0.0001101267	H,0,3.511094394,-1.6615347501,0.0006190526
	C,0,-2.1065236738,-0.2057901702,-0.0000306419	C,0,-2.205244899,-0.2801947547,0.000252322
	C,0,-1.8695632182,1.1931596971,0.0000686695	C,0,-1.9334557964,1.141011242,-0.000320768
	H,0,-1.2430431938,-2.1660196314,-0.0001201641	H,0,-1.2429804215,-2.2034231343,-0.0004449601
	H,0,-2.7215663951,1.8670232928,0.0001439848	H,0,-2.7882490636,1.8140612449,0.000026576
	O,0,-3.4176626999,-0.592081489,-0.0000501408	O,0,-3.4361562334,-0.7160243477,0.0029605824
	H,0,-3.4889085757,-1.5684456704,0.0001515549	

β-naphthoic acid	**Acid**	**Conjugate base**
	C,0,3.6298429184,0.1870490086,-0.00017754	C,0,-3.5877448109,0.169669424,-0.0014142923
	C,0,2.6618562603,1.1649707852,0.0000108836	C,0,-2.6264474536,1.1544076177,-0.0000043032
	C,0,1.2852189986,0.8192775518,0.0001395374	C,0,-1.2457418671,0.8209832272,0.0014576431
	C,0,0.9204916041,-0.5656334867,0.0001813348	C,0,-0.8663396045,-0.5593481469,0.0018368502
	C,0,1.9450969698,-1.5513634044,-0.0000165979	C,0,-1.8846170754,-1.5517456103,0.000661334
	C,0,3.269547093,-1.1830913671,-0.0002347571	C,0,-3.213654845,-1.1967475357,-0.0010954601
	H,0,0.5317910265,2.8493150194,0.0002005939	H,0,-0.5041347329,2.855252188,0.0017115218
	H,0,4.6797341153,0.4632133763,-0.0002665788	H,0,-4.6399853832,0.4368837016,-0.0029510271
	H,0,2.9397835635,2.2150244172,0.0000944631	H,0,-2.9129382885,2.2024615124,-0.0004579763
	C,0,0.2553197903,1.7989542145,0.00018818	C,0,-0.2212775813,1.8060825353,0.0017994976
	C,0,-0.4516734777,-0.9124049383,0.0003362179	C,0,0.5129135902,-0.8935860059,0.0024835475
	H,0,1.6631681571,-2.6003610983,0.000022336	H,0,-1.5946027995,-2.5987783591,0.0006652311
	H,0,4.046245774,-1.9411941148,-0.0004577746	H,0,-3.9825065531,-1.9630663757,-0.0023470332
	C,0,-1.4322838248,0.0602768962,0.0002671697	C,0,1.4924647766,0.0776985452,0.0014164793
	C,0,-1.0678303423,1.4354053272,0.000183739	C,0,1.1042060345,1.4451055627,0.0013871573
	H,0,-0.7368787234,-1.9593778896,0.0003828954	H,0,0.8043607837,-1.938563779,0.0023792431
	H,0,-1.8418379425,2.1926817463,0.0001326624	H,0,1.8807355743,2.200778686,0.000821004
	C,0,-2.855940248,-0.3701029864,0.0001514399	C,0,2.9707264673,-0.3029343702,-0.0015802002
	O,0,-3.2276027194,-1.5288296715,0.0006270057	O,0,3.2570767446,-1.5323711309,0.0033377978
	O,0,-3.7184448426,0.6624679589,-0.0007029014	O,0,3.8088970234,0.6414063137,-0.0100420146
	H,0,-4.6366121504,0.3031296554,-0.0010610313	

acetic acid	**Acid**	**Conjugate base**
	C,0,-1.394472763,-0.1225919158,-0.0001026627	C,0,-1.3520713803,-0.0380037111,0.0056661301
	H,0,-1.9282062766,0.8261342004,-0.002636762	H,0,-1.7269733566,-1.0258935029,0.2775611411
	H,0,-1.672011046,-0.70926521,-0.8804213824	H,0,-1.7603307994,0.7158537519,0.682434445
	H,0,-1.6725700962,-0.7043779018,0.8833621598	H,0,-1.7074915955,0.1985763701,-1.0033587445
	C,0,0.088146893,0.1218665737,0.0002201341	C,0,0.1800326303,0.0027659919,0.0068471823
	O,0,0.6213318017,1.2120002323,0.0023123356	O,0,0.8004065465,-1.09450128,-0.0885750731
	O,0,0.7887494295,-1.0273198035,-0.0018170697	O,0,0.729182955,1.13985538,0.0779239191
	H,0,1.7519270576,-0.8139581752,-0.0004997528	

s-collidine



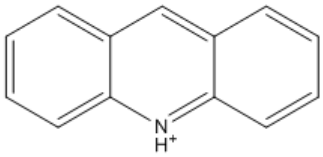
Acid (protonated)

C,0,0.7266552768,-1.2021632975,-0.0083239166
C,0,0.72675968,1.2027849294,-0.0111453402
N,0,-1.2895172464,0.0003834779,0.0044816359
H,0,1.2464693151,-2.1539498478,-0.015368766
H,0,1.2465432474,2.1545418672,-0.0202258736
C,0,-1.5014684957,-2.4333254085,0.0038501476
H,0,-0.8725601759,-3.3233187525,0.0032928279
H,0,-2.1441953464,-2.4557462658,0.8903005041
H,0,-2.148179208,-2.4575272496,-0.8796892118
C,0,-0.6563177671,-1.1998439235,0.0007016536
C,0,2.9443513468,-0.0003801362,0.0094055134
H,0,3.3474698859,-0.8807040051,-0.4956974905
H,0,3.3488836483,0.9015582232,-0.4542360467
H,0,3.2937313522,-0.0258374445,1.0489486924
C,0,-1.5014700997,2.4339924395,-0.001840162
H,0,-2.1494766213,2.4551109395,0.8807598629
H,0,-0.8725285968,3.3239459827,0.0025284688
H,0,-2.1429074977,2.4595334939,-0.8892110791
C,0,1.4446258429,0.0004035467,-0.0114041445
C,0,-0.6564371642,1.200438673,-0.0019797005
H,0,-2.3191893762,0.0003527583,0.009117425

Conjugate base (neutral)

C,0,0.6919916765,-1.1929900684,-0.00940871
C,0,0.6922101573,1.1927930193,-0.0094578626
N,0,-1.38785696,0.0001050509,0.0063722602
H,0,1.2075069567,-2.1497242845,-0.0181997336
H,0,1.2079061143,2.1494328173,-0.0182556695
C,0,-1.5204079207,-2.4241648917,0.0017005086
H,0,-0.8833662564,-3.3106753036,0.0078626897
H,0,-2.1732459306,-2.4569310229,0.8796697708
H,0,-2.1647978264,-2.4640142459,-0.8823775607
C,0,-0.7043360204,-1.1565685857,0.000709018
C,0,2.9254387165,-0.0002363317,0.0079741382
H,0,3.329474698,-0.8896073695,-0.4818561489
H,0,3.3295366347,0.8872212614,-0.4852815801
H,0,3.2925102526,0.0018229433,1.0409413039
C,0,-1.5198824712,2.4244339967,0.001709217
H,0,-2.1736017217,2.4566990911,0.8790331834
H,0,-0.8826464089,3.3107944688,0.0091338892
H,0,-2.1633702175,2.4650813992,-0.8829982302
C,0,1.418794902,-0.0001717136,-0.0117114101
C,0,-0.7040973749,1.1566567693,0.0007019266

acridine



Acid (protonated)

C,0,-7.1325069485,-1.3601094557,-0.0353676643
C,0,-5.7639910371,-1.3961869555,-0.0460022081
C,0,-5.0130648266,-0.1847080168,-0.0301726807
C,0,-5.7211159636,1.0589828792,-0.0030975964
C,0,-7.1321843112,1.0773009216,0.0075332799
C,0,-7.8153871864,-0.1147905908,-0.0084615773
C,0,-3.6153624765,-0.1574164528,-0.0399017082
C,0,-3.6464999809,2.2741177087,0.0031297147
C,0,-2.9079527454,1.0482888516,-0.0238538304
C,0,-1.4839306462,1.1107109459,-0.0331548822
H,0,-0.924712391,0.180435671,-0.0536119635
C,0,-0.846071427,2.3219535473,-0.0164978638
C,0,-1.5983495112,3.5266250149,0.0101999138
C,0,-2.9723374866,3.5137878686,0.0200197644
H,0,-3.0655591146,-1.0959978952,-0.0604307705
H,0,-7.7050790953,-2.2812463162,-0.047397133
H,0,-5.2260377088,-2.3389174286,-0.0665231196
H,0,-7.6555707466,2.0285667689,0.0281011495
H,0,-8.9008404787,-0.1052609343,-0.0003649
H,0,0.2374592621,2.3708218607,-0.0235562595
H,0,-1.0757764954,4.4780006757,0.0231233543
H,0,-3.5461255436,4.4355327027,0.040436345
N,0,-5.0048124018,2.2145439977,0.0120091052
H,0,-5.5254791179,3.1033855684,0.0314621931

Conjugate base (neutral)

C,0,-7.136198796,-1.3515178395,-0.0340380246
C,0,-5.7689738964,-1.3965319822,-0.0531837652
C,0,-5.003087554,-0.1908504649,-0.0318141182
C,0,-5.6883171077,1.0789160243,0.0104188855
C,0,-7.1178162226,1.0796595139,0.0292249442
C,0,-7.8151997176,-0.0981812661,0.0075834136
C,0,-3.6069998393,-0.1772845234,-0.0498500231
C,0,-3.6926076419,2.2521324053,0.0146357851
C,0,-2.9162415065,1.0359423172,-0.0274046486
C,0,-1.4902129175,1.118820356,-0.0441428174
H,0,-0.9154713683,0.1973853684,-0.0757254117
C,0,-0.8646804125,2.3353154535,-0.0207864149
C,0,-1.6297178609,3.5380737918,0.0206532297
C,0,-2.9981058436,3.5015108829,0.0379298209
H,0,-3.055910286,-1.1146059997,-0.081562333
H,0,-7.7139082176,-2.2701667592,-0.0504061291
H,0,-5.2432685789,-2.3467938662,-0.0848699723
H,0,-7.6262806564,2.039179688,0.0609831489
H,0,-8.9007886638,-0.0849466138,0.0221724623
H,0,0.2190159929,2.3933560595,-0.0336439976
H,0,-1.113371566,4.4930370365,0.0386271398
H,0,-3.5893220085,4.4123838525,0.0695131727
N,0,-5.0367857946,2.254567506,0.032847696