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

Supporting Information :

Third Dissociation Constant of Phosphoric Acid in H_2O and D_2O from 75 to 300 °C at p = 20.4 MPa using Raman Spectroscopy and a Titanium-Sapphire Flow Cell

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Table S1. The $pQ_{3b,OH,m}$ for the reaction $PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$ in light water at 20.4 MPa.

t (°C)	Solution #	PO_4^{3-} (mol·kg^{-1})	HPO_4^{2-} (mol·kg^{-1})	*I* (mol·kg^{-1})	$pQ_{3b,OH,m}$
75	1a	0.4309 ± 0.0074	0.0708 ± 0.0021	2.9469 ± 0.0416	1.979 ± 0.053
	2a	0.2345 ± 0.0022	0.0582 ± 0.0006	1.7381 ± 0.0122	1.780 ± 0.015
100	1a	0.4602 ± 0.0067	0.1095 ± 0.0021	3.1415 ± 0.0380	2.084 ± 0.085
	1a	0.4196 ± 0.0038	0.0916 ± 0.0009	2.9435 ± 0.0211	1.784 ± 0.023
	2a	0.2252 ± 0.0027	0.0858 ± 0.0012	1.7564 ± 0.0158	1.538 ± 0.017
	2a	0.2260 ± 0.0027	0.0797 ± 0.0011	1.7473 ± 0.0159	1.576 ± 0.018
	3a	0.1019 ± 0.0042	0.0683 ± 0.0026	0.8937 ± 0.0263	1.410 ± 0.040
125	1a	0.4259 ± 0.0059	0.1493 ± 0.0025	3.0841 ± 0.0349	1.617 ± 0.039
	1a	0.3904 ± 0.0036	0.1313 ± 0.0012	2.9063 ± 0.0208	1.455 ± 0.016
	2a	0.2041 ± 0.0029	0.1088 ± 0.0016	1.7178 ± 0.0177	1.286 ± 0.016
	2a	0.2003 ± 0.0025	0.1113 ± 0.0013	1.7077 ± 0.0150	1.251 ± 0.013
	3a	0.0923 ± 0.0044	0.0993 ± 0.0035	0.9174 ± 0.0291	1.410 ± 0.040
150	1a	0.3404 ± 0.0053	0.1751 ± 0.0027	2.7937 ± 0.0323	1.100 ± 0.010
	2a	0.1637 ± 0.0024	0.1376 ± 0.0018	1.6136 ± 0.0157	0.979 ± 0.008
	3a	0.0668 ± 0.0037	0.1058 ± 0.0039	0.8284 ± 0.0267	0.821 ± 0.009
	3a	0.0600 ± 0.0010	0.1019 ± 0.0014	0.7934 ± 0.0795	0.783 ± 0.007
175	1a	0.3067 ± 0.0092	0.2304 ± 0.0052	2.7778 ± 0.0549	0.813 ± 0.020
	2a	0.1358 ± 0.0028	0.1625 ± 0.0023	1.5387 ± 0.0184	0.780 ± 0.013
	2a	0.1409 ± 0.0022	0.1665 ± 0.0018	1.5718 ± 0.0149	0.773 ± 0.010
	3a	0.0581 ± 0.0042	0.1273 ± 0.0061	0.8452 ± 0.0342	0.584 ± 0.044
	3a	0.0457 ± 0.0013	0.1108 ± 0.0020	0.7481 ± 0.0110	0.605 ± 0.017
200	1a	0.2719 ± 0.0049	0.2419 ± 0.0042	2.6498 ± 0.0329	0.716 ± 0.014
	2a	0.1224 ± 0.0020	0.1802 ± 0.0022	1.5227 ± 0.0148	0.637 ± 0.011
	2a	0.1232 ± 0.0025	0.1799 ± 0.0021	1.5256 ± 0.0167	0.642 ± 0.012
	3a	0.0429 ± 0.0029	0.1330 ± 0.0069	0.7908 ± 0.0306	0.413 ± 0.044
225	1a	0.2610 ± 0.0045	0.2862 ± 0.0047	2.7114 ± 0.0324	0.544 ± 0.013
	2a	0.1101 ± 0.0024	0.1980 ± 0.0023	1.5119 ± 0.0169	0.504 ± 0.012
	3a	0.0335 ± 0.0029	0.1502 ± 0.0056	0.7919 ± 0.0273	0.197 ± 0.045
	4a	0.0126 ± 0.0015	0.0868 ± 0.0021	0.4390 ± 0.0121	0.261 ± 0.055
250	1a	0.2509 ± 0.0046	0.2951 ± 0.0053	2.6885 ± 0.0345	0.500 ± 0.014
	2a	0.0976 ± 0.0025	0.1997 ± 0.0024	1.4601 ± 0.0173	0.444 ± 0.014
	3a	0.0312 ± 0.0035	0.1433 ± 0.0056	0.7642 ± 0.0299	0.208 ± 0.055
	4a	0.0077 ± 0.0016	0.0857 ± 0.0020	0.4143 ± 0.0122	0.061 ± 0.090
275	3a	0.0309 ± 0.0040	0.1506 ± 0.0051	0.7812 ± 0.0307	0.159 ± 0.060
	4a	0.0077 ± 0.0014	0.0856 ± 0.0019	0.4140 ± 0.0111	0.061 ± 0.082
	4a	0.0098 ± 0.0011	0.0865 ± 0.0027	0.4256 ± 0.0118	0.154 ± 0.054
300	3a	0.0379 ± 0.0055	0.1253 ± 0.0051	0.7492 ± 0.0376	0.412 ± 0.068
	4a	0.0077 ± 0.0010	0.0847 ± 0.0019	0.4117 ± 0.0093	0.071 ± 0.058
	4a	0.0124 ± 0.0048	0.0902 ± 0.0030	0.4467 ± 0.0291	0.222 ± 0.168

The ± uncertainties shown are propagated experimental standard errors.

Table S2. The $pQ_{3b,OD,m}$ for the reaction $PO_4^{3-} + D_2O \rightleftharpoons DPO_4^{2-} + OD^-$ in heavy water at 20.4 MPa.

t (°C)	Solution #	PO_4^{3-} (mol·kg^{-1})	DPO_4^{2-} (mol·kg^{-1})	I (mol·kg^{-1})	$pQ_{3b,OD,m}$
75	1b	0.2794 ± 0.0039	0.0471 ± 0.0009	1.9701 ± 0.0196	1.507 ± 0.014
	1b	0.4087 ± 0.0030	0.0661 ± 0.0006	2.4697 ± 0.0149	2.047 ± 0.024
	2b	0.1990 ± 0.0017	0.0560 ± 0.0007	1.3565 ± 0.0089	1.698 ± 0.012
	3b	0.0989 ± 0.0033	0.0507 ± 0.0017	0.7421 ± 0.0178	1.536 ± 0.032
100	1b	0.4132 ± 0.0052	0.1066 ± 0.0015	2.5586 ± 0.0261	1.881 ± 0.045
	2b	0.2020 ± 0.0018	0.0832 ± 0.0008	1.4164 ± 0.0095	1.552 ± 0.013
	2b	0.1996 ± 0.0017	0.0815 ± 0.0007	1.4047 ± 0.0090	1.541 ± 0.012
	3b	0.1077 ± 0.0041	0.0800 ± 0.0030	0.8266 ± 0.0240	1.449 ± 0.044
	3b	0.0954 ± 0.0016	0.0693 ± 0.0011	0.7631 ± 0.0091	1.359 ± 0.015
125	1b	0.3847 ± 0.0050	0.1412 ± 0.0020	2.5183 ± 0.0263	1.535 ± 0.029
	2b	0.1726 ± 0.0018	0.1118 ± 0.0011	1.3620 ± 0.0103	1.199 ± 0.010
	2b	0.1781 ± 0.0016	0.1070 ± 0.0009	1.3732 ± 0.0090	1.257 ± 0.009
	3b	0.0776 ± 0.0014	0.0906 ± 0.0014	0.7372 ± 0.0089	1.041 ± 0.013
150	1b	0.3316 ± 0.0045	0.1773 ± 0.0024	2.3923 ± 0.0247	1.046 ± 0.009
	2b	0.1469 ± 0.0022	0.1367 ± 0.0019	1.3144 ± 0.0135	0.918 ± 0.008
	3b	0.0618 ± 0.0019	0.1029 ± 0.0027	0.7026 ± 0.0134	0.784 ± 0.014
175	1b	0.2649 ± 0.0052	0.2137 ± 0.0042	2.2269 ± 0.0307	0.751 ± 0.015
	2b	0.1197 ± 0.0019	0.1640 ± 0.0022	1.2711 ± 0.0125	0.651 ± 0.011
	3b	0.0385 ± 0.0016	0.1055 ± 0.0048	0.6189 ± 0.0175	0.531 ± 0.033
200	1b	0.2402 ± 0.0042	0.2540 ± 0.0040	2.2178 ± 0.0261	0.561 ± 0.012
	1b	0.2304 ± 0.0025	0.2235 ± 0.0023	2.1095 ± 0.0154	0.652 ± 0.008
	2b	0.1035 ± 0.0015	0.1744 ± 0.0017	1.2292 ± 0.0100	0.535 ± 0.009
	2b	0.1002 ± 0.0012	0.1706 ± 0.0014	1.2073 ± 0.0079	0.540 ± 0.007
	3b	0.0359 ± 0.0039	0.1502 ± 0.0095	0.7089 ± 0.0370	0.196 ± 0.061
	3b	0.0333 ± 0.0011	0.1313 ± 0.0028	0.6559 ± 0.0106	0.279 ± 0.019
225	1b	0.2385 ± 0.0047	0.2806 ± 0.0050	2.2706 ± 0.0304	0.472 ± 0.014
	2b	0.0877 ± 0.0010	0.1941 ± 0.0018	1.2095 ± 0.0080	0.370 ± 0.007
	3b	0.0315 ± 0.0017	0.1386 ± 0.0049	0.6653 ± 0.0180	0.208 ± 0.032
250	1b	0.2259 ± 0.0055	0.3030 ± 0.0063	2.2699 ± 0.0365	0.382 ± 0.016
	2b	0.0765 ± 0.0019	0.1992 ± 0.0026	1.1755 ± 0.0133	0.287 ± 0.013
	2b	0.0781 ± 0.0012	0.1966 ± 0.0024	1.1760 ± 0.0104	0.308 ± 0.010
	3b	0.0289 ± 0.0029	0.1513 ± 0.0069	0.6832 ± 0.0274	0.095 ± 0.052
	3b	0.0249 ± 0.0010	0.1372 ± 0.0031	0.6355 ± 0.0109	0.115 ± 0.022
	4b	0.0040 ± 0.0010	0.0800 ± 0.0019	0.3225 ± 0.0082	-0.199 ± 0.109
275	3b	0.0218 ± 0.0017	0.1454 ± 0.0047	0.6410 ± 0.0174	0.007 ± 0.039
	4b	0.0058 ± 0.0008	0.0703 ± 0.0013	0.3077 ± 0.0063	0.071 ± 0.064
	4b	0.0053 ± 0.0010	0.0732 ± 0.0016	0.3120 ± 0.0078	-0.006 ± 0.087
300	3b	0.0144 ± 0.0022	0.0664 ± 0.0033	0.4337 ± 0.0162	0.501 ± 0.072
	4b	0.0048 ± 0.0010	0.0818 ± 0.0020	0.3295 ± 0.0084	-0.146 ± 0.090
	4b	0.0030 ± 0.0010	0.0809 ± 0.0020	0.3201 ± 0.0085	-0.343 ± 0.144

The ± uncertainties shown are propagated experimental standard errors.

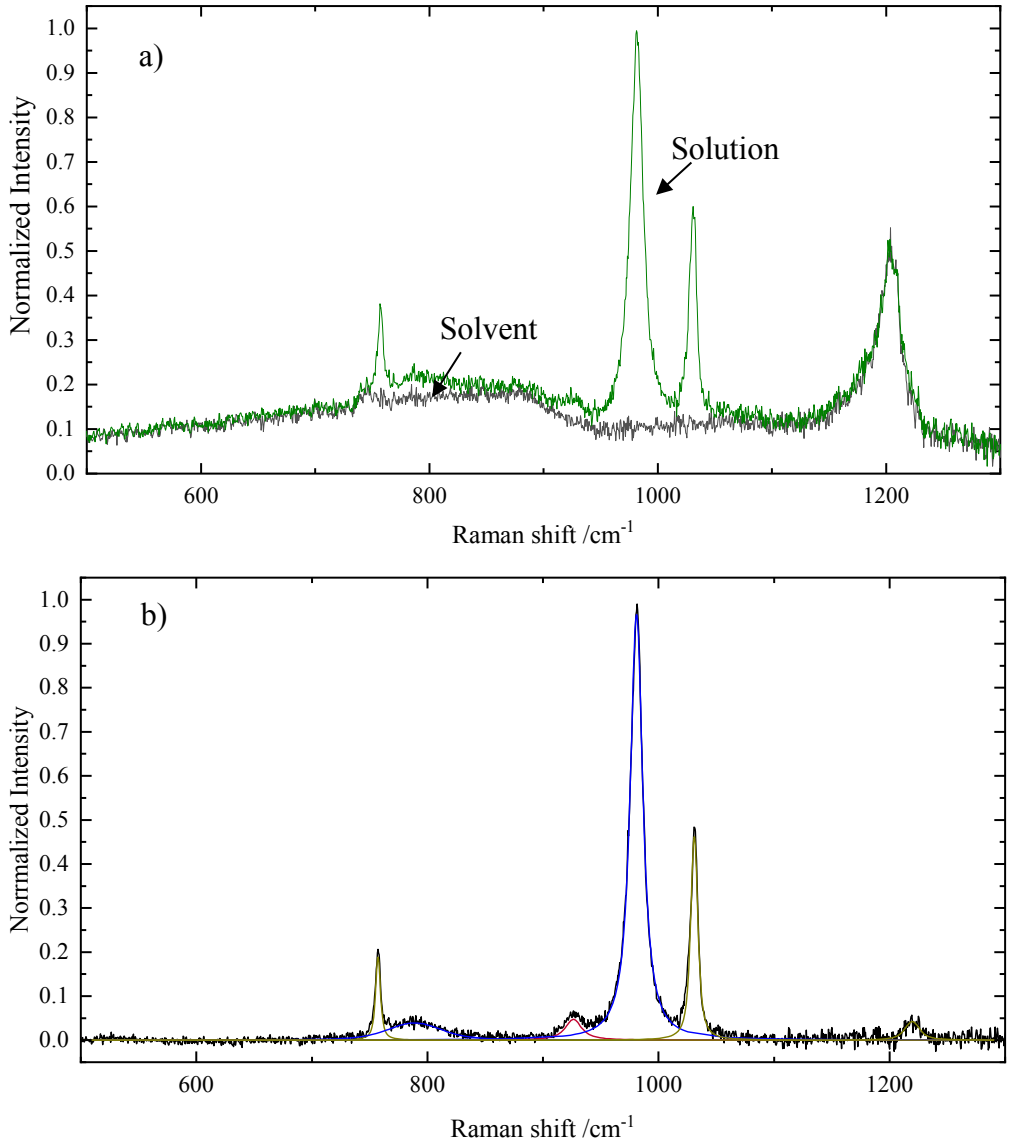

Figure S1. a) The reduced isotropic Raman spectrum of 0.1665 mol·kg^{-1} K_2HPO_4, 0.1527 mol·kg^{-1} KOD, 0.035 mol·kg^{-1} KCF_3SO_3 in D_2O (green) and pure D_2O solvent (black) at 275 °C and 20.4 MPa. b) The resulting solvent-subtracted spectrum (black) with Voigt functions fitted to the peaks of $CF_3SO_3^-$ (yellow), HPO_4^{2-} (blue), and PO_4^{3-} (red). Note that the D_2O solvent peak at 1200 cm^{-1} subtracts cleanly away leaving the $CF_3SO_3^-$ peak visible at 1230 cm^{-1}.

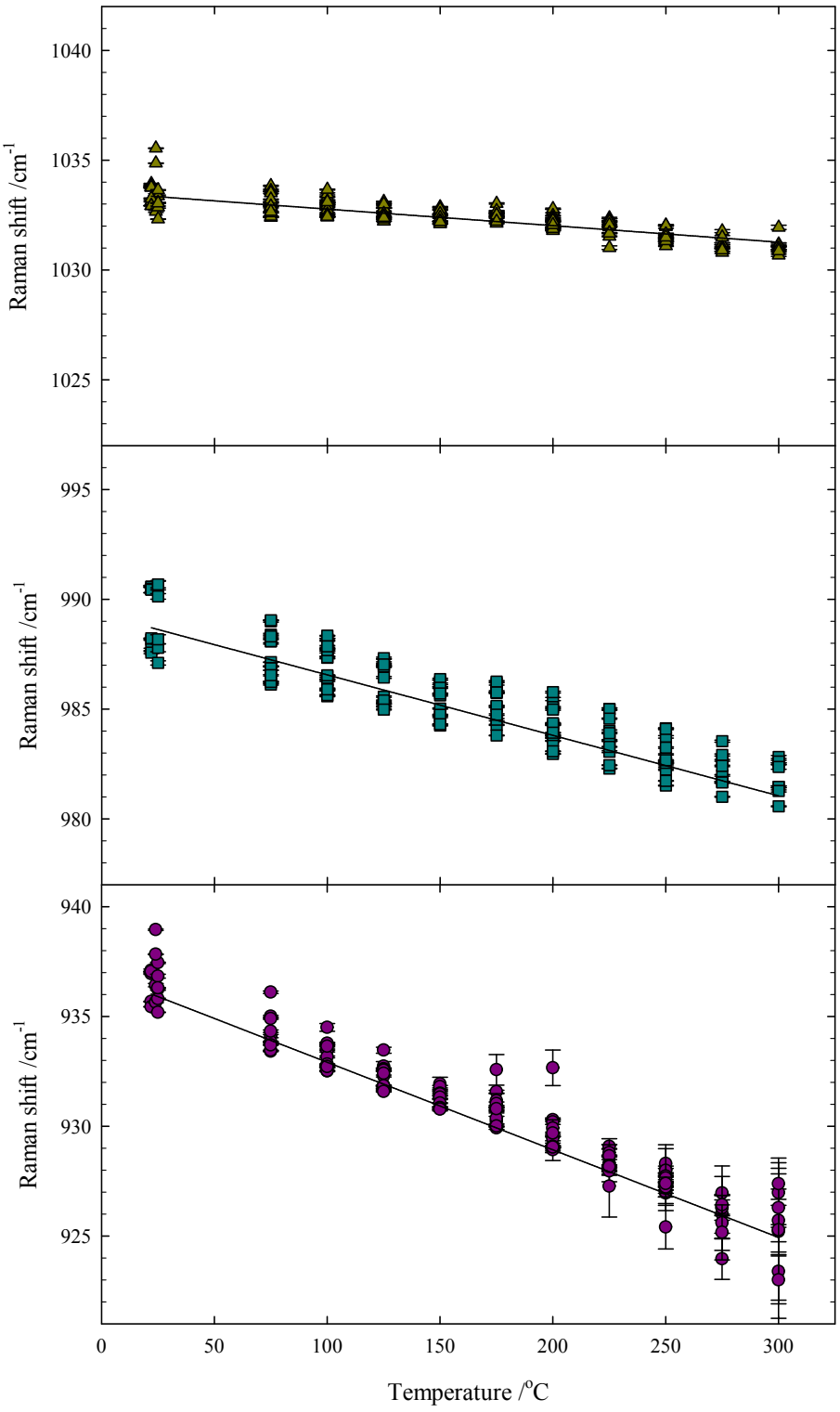

Figure S2. The temperature dependence of the Raman shift for the strongest vibrational modes of ▲ $CF_3SO_3^-$, ■ HPO_4^{2-}, and ● PO_4^{3-} at 20.4 ± 0.4 MPa in D_2O and H_2O.

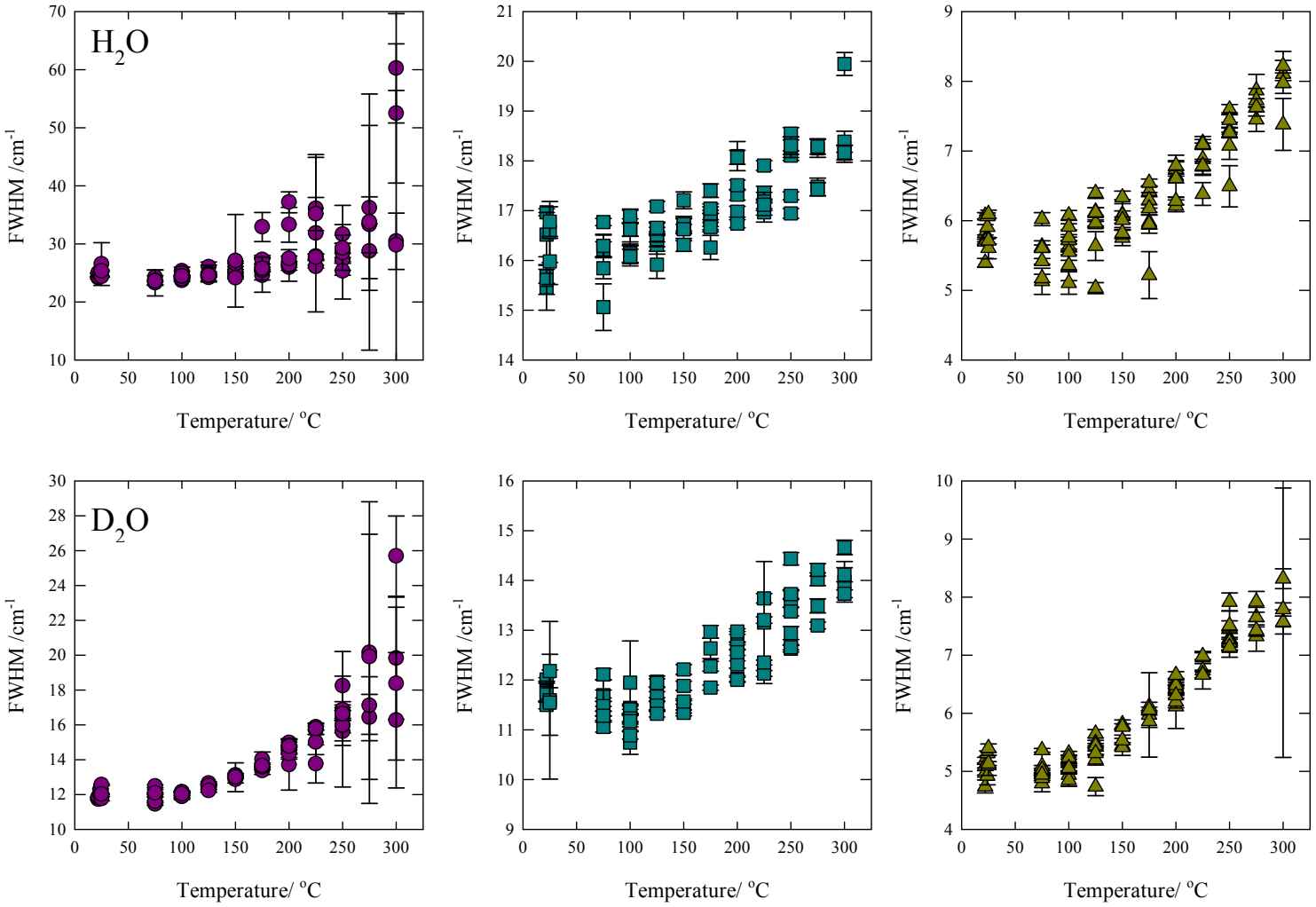

Figure S3. The temperature dependence of the full widths at half maximum (FWHM) for the strongest vibrational modes of PO_4^{3-}, HPO_4^{2-}, and $CF_3SO_3^-$ at 20.4 ± 0.4 MPa in **(top)** H_2O and **(bottom)** D_2O.

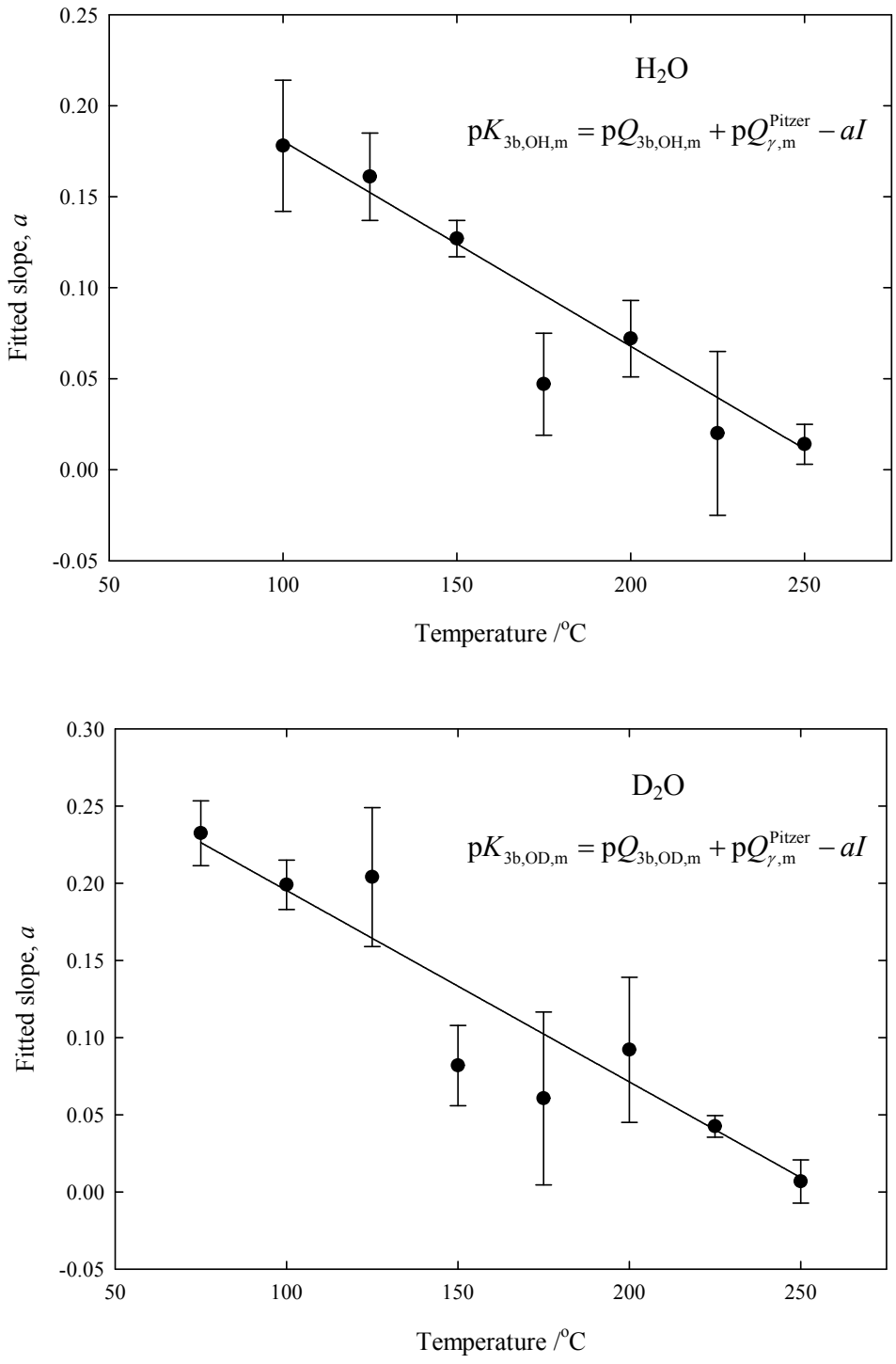

Figure S4. The fitted slope values of the Pitzer model equilibrium constant dependence on ionic strength from Table 3 plotted against temperature in **(top)** H_2O and **(bottom)** D_2O.