Supplementary Material to

An ab Initio, Infrared, and Raman

Investigation of Phosphate Ion Hydration.

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Table S1: Total Energies (au)

	HF/STO-3G	HF/3-21G	HF/A
PO_4^{3-}	-630.8352772	-636.1837371	-639.7078111
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})$ (C_{2v})	-705.9561660	-711.8911464	-715.8090689
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_2$ (D_{2d})	-781.0560376	-787.5819836	-791.9006538
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_2$ (C_s)	-781.0922427	-787.5814101	-791.8994339
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_3$ (C_2)		-863.2593450	-867.9822680
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_3$ (C_{3v} # 1)	-856.1639475	-863.2585094	-867.9809902
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_3$ (C_{3v} # 2)	-856.1201447	-863.2593743	-867.9814993
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_4$ (C_s)		-938.9268442	-944.0569639
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_4$ (D_{2d})	-931.1860657	-938.9267718	-944.0575980
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_5$ (C_{2v})	-1006.2388413	-1014.5862774	-1020.1264494
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_6$ (T_d)	-1081.2670672	-1090.2388652	-1096.1907780
	HF/B	MP2/A	MP2/B
PO_4^{3-}	-639.8131042	-640.5465769	-640.7215422
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})$ (C_{2v})	-715.9035697	-716.8488893	-717.0103785
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_2$ (D_{2d})	-791.9895282	-793.1379650	-793.2941229
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_2$ (C_s)	-791.9881694	-793.1368986	-793.2930774
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_3$ (C_2)	-868.0687041	-869.4150013	-869.5711728
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_3$ (C_{3v} # 1)	-868.0672628	-869.4136519	-869.5697475
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_3$ (C_{3v} # 2)	-868.0677075	-869.4145200	-869.5704734
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_4$ (C_s)	-944.1431154	-945.6835186	-945.8430293
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_4$ (D_{2d})	-944.1441100	-945.6839991	-945.8440132
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_5$ (C_{2v})	-1020.2141068	-1021.9455827	-1022.1111586
$\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_6$ (T_d)	-1096.2809652	-1098.2017125	-1098.3749120

Table S2: PO_4^{3-} - Geometry and Frequencies

Level	Geometry	Frequencies (cm^{-1})			
	PO ($\text{\AA}$)	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(T_2)$	$\nu_4(T_2)$
HF/STO-3G	1.7128	622.2	320.2	879.9	426.6
HF/3-21G	1.6077	889.3	416.2	1132.7	590.1
HF/A	1.5673	922.9	423.1	1062.4	609.6
HF/B	1.5718	901.8	404.2	986.1	577.9
MP2/A	1.5989	837.5	383.9	986.2	550.8
MP2/B	1.6119	792.4	349.1	853.9	493.7

Table S3: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})$ (C_{2v}) Geometry				
	HF		MP2	
	A	B	A	B
P-O (free)	1.5510	1.5577	1.5797	1.5943
P-O (bound)	1.5782	1.5790	1.6130	1.6210
O...H	1.7617	1.8218	1.6973	1.7585
O-H	0.9868	0.9811	1.0243	1.0199
O(PO_4^{3-})...O(H_2O)	2.6881	2.7283	2.6731	2.7139
P...O(H_2O)	3.3086	3.3615	3.2979	3.3599

Table S4: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})$ (C_{2v}) Frequencies

sym	HF		MP2		Mode
	A	B	A	B	
B_1	54.2	59.0	50.5	53.3	HOH trans
B_2	174.8	150.4	178.5	151.3	H...O str.
A_1	291.6	267.4	297.9	269.1	H...O str.
A_2	408.8	396.2	366.5	342.8	PO_4 def.
A_1	459.2	437.5	434.0	394.5	PO_4 def.
B_1	599.0	575.8	538.6	495.4	PO_4 def.
B_2	613.2	587.4	554.3	508.8	PO_4 def.
A_1	618.8	594.5	560.8	513.7	PO_4 def.
A_2	689.3	676.6	689.2	683.7	HOH twist
B_2	747.9	665.9	793.3	695.0	HOH rock
A_1	925.8	909.3	838.8	800.3	PO_4 str.
B_2	999.8	959.3	914.7	834.1	PO_4 str.
A_1	1073.5	1012.4	998.2	892.9	PO_4 str.
B_1	1110.1	1033.0	1041.8	915.7	PO_4 str.
B_1	1203.8	1160.7	1148.6	1102.4	HOH wag
A_1	1962.8	1914.3	1872.7	1781.2	HOH def
B_2	3330.6	3478.9	2792.3	2938.5	OH str.
A_1	3522.3	3583.3	3077.5	3078.3	OH str.

Table S5: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_2$ Geometry

	HF		MP2	
	A	B	A	B
C_s				
P-O (free)	1.5388	1.5460	1.5659	1.5798
P-O (bound to 2)	1.5852	1.5851	1.6228	1.6300
P-O (bound to 1)	1.5631	1.5656	1.5948	1.6033
O...H 2	1.8386	1.8817	1.7713	1.8034
O...H 1	1.7752	1.8264	1.7194	1.7773
O-H 2	0.9761	0.9741	1.0089	1.0110
O-H 1	0.9828	0.9789	1.0162	1.0139
O(PO_4^{3-})...O(H_2O) 2	2.7379	2.7687	2.7172	2.7418
O(PO_4^{3-})...O(H_2O) 1	2.6987	2.7332	2.6860	2.7256
P...O(H_2O)	3.3291	3.3727	3.3149	3.3665
D_{2d}				
P-O (bound)	1.5619	1.5650	1.5935	1.6031
O...H	1.8016	1.8455	1.7424	1.7832
O-H	0.9805	0.9775	1.0140	1.0141
O(PO_4^{3-})...O(H_2O)	2.7147	2.7439	2.7005	2.7285
P...O(H_2O)	3.3163	3.3617	3.3015	3.3538

Table S6: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_2$ (D_{2d}) Frequencies					
sym	HF		MP2		Mode
	A	B	A	B	
E	42.8	47.6	39.6	44.2	HOH trans.
E	173.4	154.4	182.1	158.8	O...H str.
A_1	251.1	234.8	256.1	236.4	O...H str.
B_2	313.1	289.4	331.1	301.7	O...H str.
B_1	396.7	388.4	352.1	336.9	PO_4 def.
A_1	479.3	463.5	453.1	424.4	PO_4 def.
E	604.1	584.5	544.8	509.0	PO_4 def.
B_2	626.7	606.6	569.8	526.8	PO_4 def.
A_2	653.0	655.1	654.4	661.7	HOH twist
B_1	653.5	655.3	652.4	662.4	HOH twist
E	708.1	637.1	759.7	667.6	HOH rock
A_1	935.1	921.4	848.9	816.7	PO_4 str.
E	1048.4	1003.9	968.5	888.9	PO_4 str.
B_2	1077.1	1030.2	1000.5	916.9	PO_4 str.
E	1158.4	1133.1	1104.5	1079.0	HOH wag
B_2	1955.9	1910.1	1872.6	1782.3	HOH def.
A_1	1976.5	1922.7	1897.7	1797.9	HOH def.
E	3469.6	3556.4	2993.1	3048.0	OH str.
B_2	3609.9	3636.7	3196.3	3153.0	OH str.
A_1	3621.3	3645.7	3212.1	3167.1	OH str.

Table S7: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_2$ (C_s) Frequencies

sym	HF		MP2		Mode
	A	B	A	B	
A'	49.7	51.1	48.3	52.2	HOH trans.
A''	55.3	61.1	51.0	55.2	HOH trans.
A'	142.8	124.8	151.3	131.6	O...H asym. str.
A''	197.4	169.5	214.4	181.0	O...H asym. str.
A''	271.6	254.4	277.2	257.2	O...H sym. str.
A'	281.9	261.3	288.6	265.9	O...H sym. str.
A'	421.4	408.0	388.6	363.0	PO_4 def.
A''	460.8	443.8	435.8	404.2	PO_4 def.
A'	596.7	578.3	535.9	500.6	PO_4 def.
A''	615.6	596.2	558.9	520.3	PO_4 def.
A'	620.5	600.2	561.9	523.2	PO_4 def.
A''	635.9	626.1	639.2	644.4	HOH twist
A'	650.6	632.7	650.5	658.2	HOH twist
A''	688.4	635.9	736.1	660.0	HOH rock
A'	699.4	651.7	748.3	675.8	HOH rock
A'	926.9	914.1	837.5	802.9	PO_4 str.
A'	996.4	965.6	908.2	847.4	PO_4 str.
A''	1057.4	1014.4	977.9	901.1	PO_4 str.
A'	1121.3	1058.6	1057.1	953.2	PO_4 str.
A''	1138.5	1109.8	1088.5	1059.1	HOH wag
A'	1171.4	1132.4	1115.8	1080.9	HOH wag
A''	1944.8	1904.1	1860.9	1779.0	HOH def.
A'	1983.3	1932.1	1904.3	1810.5	HOH def.
A''	3456.9	3547.6	2988.8	3059.2	OH str. (1)
A'	3478.1	3563.7	3022.8	3087.2	OH str. (1)
A''	3644.5	3668.6	3226.3	3175.9	OH str. (2)
A'	3667.6	3689.2	3254.3	3202.2	OH str. (2)

Table S8: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_3$ Geometry

	HF		MP2	
	A	B	A	B
C_2				
P-O 2	1.5706	1.5717	1.6050	1.6122
P-O 1	1.5503	1.5539	1.5799	1.5887
O (C_2) ... H	1.8432	1.8825	1.7838	1.8183
O...H 2	1.8726	1.9081	1.8067	1.8257
O...H 1	1.8103	1.8454	1.7624	1.8000
O-H (C_2)	0.9739	0.9726	1.0043	1.0067
O-H 2	0.9721	0.9712	1.0030	1.0066
O-H 1	0.9778	0.9760	1.0083	1.0095
O(PO_4^{3-})...O(H_2O) (C_2)	2.7434	2.7713	2.7257	2.7517
O(PO_4^{3-})...O(H_2O) 2	2.7628	2.7866	2.7410	2.7554
O(PO_4^{3-})...O(H_2O) 1	2.7226	2.7460	2.7138	2.7398
P...O(H_2O) (C_2)	3.3537	3.3879	3.3409	3.3782
P...O(H_2O)	3.3371	3.3751	3.3193	3.3626
C_{3v} # 1				
P-O (bound to 3)	1.5904	1.5895	1.6316	1.6374
P-O (bound to 1)	1.5510	1.5544	1.5803	1.5892
O...H 3	1.9118	1.9474	1.8352	1.8572
O...H 1	1.7859	1.8277	1.7421	1.7874
O-H 3	0.9689	0.9684	0.9993	1.0033
O-H 1	0.9794	0.9773	1.0092	1.0100
O(PO_4^{3-})...O(H_2O) 3	2.7889	2.8154	2.7596	2.7778
O(PO_4^{3-})...O(H_2O) 1	2.7070	2.7357	2.7002	2.7328
P...O(H_2O)	3.3571	3.3912	3.3438	3.3803
C_{3v} # 2				
P-O (unb.)	1.5291	1.5359	1.5554	1.5674
P-O (bound)	1.5716	1.5724	1.6061	1.6126
O...H	1.8438	1.8825	1.7833	1.8177
O-H	0.9741	0.9728	1.0046	1.0069
O(PO_4^{3-})...O(H_2O)	2.7438	2.7712	2.7251	2.7512
P...O(H_2O)	3.3454	3.3800	3.3287	3.3706

Table S9: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_3$ (C_2) Frequencies

sym	HF		MP2		Mode
	A	B	A	B	
<i>B</i>	42.2	45.8	39.4	44.2	HOH trans.
<i>A</i>	47.0	50.6	45.4	50.4	HOH trans.
<i>B</i>	50.4	54.1	47.7	55.3	HOH trans.
<i>B</i>	129.0	114.7	138.5	123.0	O...H asym str.
<i>A</i>	165.9	148.1	178.9	159.3	O...H asym str.
<i>B</i>	201.2	177.2	221.5	194.2	O...H asym str.
<i>A</i>	239.1	226.7	243.9	229.4	O...H sym str.
<i>A</i>	264.2	248.8	269.9	254.8	O...H sym str.
<i>B</i>	295.1	277.1	311.3	290.7	O...H sym str.
<i>A</i>	413.7	403.3	380.3	360.9	PO_4 def.
<i>A</i>	473.1	461.1	447.3	425.0	PO_4 def.
<i>B</i>	597.0	581.8	537.3	507.8	PO_4 def.
<i>A</i>	597.3	601.5	600.9	617.5	HOH twist
<i>B</i>	612.2	595.4	617.6	626.7	HOH twist
<i>A</i>	612.7	595.8	554.6	523.8	PO_4 def.
<i>A</i>	621.5	605.6	622.0	633.6	HOH twist
<i>B</i>	625.5	608.7	568.2	532.5	PO_4 def.
<i>B</i>	641.4	604.8	686.6	630.5	HOH rock
<i>A</i>	660.0	629.9	709.1	646.1	HOH rock
<i>B</i>	663.1	623.2	712.1	653.1	HOH rock
<i>A</i>	935.5	925.4	846.7	820.1	PO_4 str.
<i>B</i>	1015.3	987.7	927.0	870.5	PO_4 str.
<i>A</i>	1055.8	1021.6	977.0	913.6	PO_4 str.
<i>B</i>	1081.9	1071.0	1039.7	1025.3	HOH wag
<i>B</i>	1095.0	1048.5	1020.7	949.3	PO_4 str.
<i>A</i>	1115.1	1095.4	1063.2	1047.6	HOH wag
<i>B</i>	1136.0	1107.0	1080.1	1059.6	HOH wag

Table S9: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_3$ (C_2) Frequencies (cont.)

sym	HF		MP2		Mode
	A	B	A	B	
<i>A</i>	1942.2	1902.6	1863.1	1782.7	HOH def.
<i>B</i>	1955.6	1912.6	1876.9	1791.7	HOH def.
<i>A</i>	1992.9	1940.7	1918.6	1825.2	HOH def.
<i>B</i>	3565.6	3612.9	3141.6	3150.8	HOH str. asym.
<i>A</i>	3571.2	3617.4	3151.2	3159.3	HOH str. asym.
<i>B</i>	3616.3	3663.0	3193.9	3196.6	HOH str. asym.
<i>A</i>	3707.9	3714.2	3317.1	3248.0	HOH str. sym.
<i>B</i>	3719.7	3728.3	3321.0	3251.0	HOH str. sym.
<i>A</i>	3733.1	3738.1	3346.0	3278.1	HOH str. sym.

Table S10: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_3$ (C_{3v} # 1) Frequencies					
sym	HF		MP2		Mode
	A	B	A	B	
E	47.3	49.1	46.0	47.7	HOH trans.
A_2	53.6	66.0	43.2	57.2	HOH trans.
A_1	113.6	98.3	124.9	108.8	O...H asym. str.
E	184.4	158.7	206.8	176.5	O...H asym. str.
E	256.6	243.6	259.8	246.0	O...H sym. str.
A_1	281.4	260.9	294.7	271.4	O...H sym. str.
E	445.1	432.4	417.8	393.7	PO_4 def.
A_2	577.0	583.9	581.5	593.6	HOH twist
E	600.6	587.7	544.0	513.6	PO_4 def.
E	612.2	594.0	610.4	620.2	HOH twist
A_1	626.3	609.2	567.1	534.0	PO_4 def.
E	637.9	616.2	681.6	632.5	HOH rock
A_1	651.0	602.8	695.0	637.1	HOH rock
A_1	924.2	915.1	828.0	797.7	PO_4 str.
A_1	996.4	973.5	908.2	862.1	PO_4 str.
A_2	1073.6	1060.8	1021.7	1008.2	HOH wag
E	1083.9	1045.3	1016.0	944.9	PO_4 str.
E	1128.6	1100.0	1070.3	1044.8	HOH wag
E	1944.9	1906.5	1865.4	1786.2	HOH def.
A_1	1994.2	1943.2	1919.4	1829.1	HOH def.
E	3538.7	3587.8	3138.1	3150.0	HOH str. 1
A_1	3562.8	3607.6	3173.2	3179.8	HOH str. 1
E	3763.3	3770.6	3360.3	3288.6	HOH str. 3
A_1	3790.1	3796.5	3394.5	3326.0	HOH str. 3

Table S11: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_3$ (C_{3v} # 2) Frequencies

sym	HF		MP2		Mode
	A	B	A	B	
A_1	47.9	47.7	46.4	50.8	HOH trans.
E	50.9	53.6	48.5	52.3	HOH trans.
E	137.4	122.9	146.6	132.9	O...H asym. str.
A_2	216.3	185.3	243.1	205.9	O...H asym. str.
E	260.3	246.9	265.5	250.8	O...H sym. str.
A_1	270.7	252.1	283.9	265.3	O...H sym. str.
E	444.3	431.1	417.9	393.2	PO_4 def.
A_1	597.0	582.4	535.6	505.2	PO_4 def.
A_2	595.8	590.8	603.8	615.0	HOH twist
E	613.7	600.9	615.5	630.7	HOH twist
E	619.2	603.4	562.9	529.6	PO_4 def.
A_2	639.2	604.9	681.4	628.1	HOH rock
E	658.6	625.3	705.4	654.8	HOH rock
A_1	931.3	921.8	841.2	816.0	PO_4 str.
E	1013.0	987.3	924.5	870.5	PO_4 str.
E	1092.6	1070.8	1046.9	1029.6	HOH wag
A_1	1113.2	1116.6	1060.5	1062.0	HOH wag
A_1	1169.6	1074.1	1104.3	989.2	PO_4 str.
E	1945.9	1907.3	1866.6	1788.1	HOH def.
A_1	1997.5	1946.4	1923.4	1831.3	HOH def.
A_2	3587.9	3640.3	3151.2	3160.5	HOH str. asym.
E	3621.1	3668.8	3197.4	3200.4	HOH str. asym.
E	3704.9	3711.6	3318.5	3254.1	HOH str. sym.
A_1	3725.8	3729.9	3345.4	3280.9	HOH str. sym.

Table S12: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_4$ Geometry

	HF		MP2	
	A	B	A	B
C_s				
P-O 3	1.5770	1.5769	1.6147	1.6198
P-O 1	1.5406	1.5443	1.5686	1.5767
P-O 2	1.5596	1.5611	1.5916	1.5981
O2...H6	1.9118	1.9437	1.8439	1.8682
O2...H12	1.9471	1.9786	1.8700	1.8827
O3...H14	1.8147	1.8415	1.7765	1.8058
O4...H8	1.8475	1.8801	1.7967	1.8257
O4...H16	1.8753	1.9041	1.8178	1.8389
O2...O7	2.7917	2.8150	2.7668	2.7856
O2...O13	2.8147	2.8368	2.7845	2.7940
O3...O13	2.7273	2.7455	2.7230	2.7446
O4...O7	2.7482	2.7715	2.7345	2.7574
O4...O15	2.7663	2.7862	2.7489	2.7645
P...O7	3.3750	3.4008	3.3613	3.3872
P...O13	3.3680	3.3965	3.3518	3.3796
P...O15	3.3525	3.3839	3.3316	3.3690
D_{2d}				
P-O	1.5589	1.5606	1.5910	1.5976
O...H	1.8759	1.9039	1.8192	1.8396
O(PO_4^{3-})...O(H_2O)	2.7670	2.7861	2.7501	2.7652
P...O(H_2O)	3.3663	3.3935	3.3505	3.3782

Table S13: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_4$ (C_s) Frequencies

sym	HF		MP2	Mode
	A	B	A	
A'	42.6	45.5	41.0	HOH trans.
A''	44.5	49.4	38.6	HOH trans.
A'	48.8	49.3	47.4	HOH trans.
A''	49.3	54.6	46.9	HOH trans.
A'	110.4	96.6	122.0	O...H str. asym.
A''	132.6	120.8	142.7	O...H str. asym.
A'	176.4	156.6	197.3	O...H str. asym.
A''	203.3	177.5	230.7	O...H str. asym.
A'	229.8	220.1	233.7	O...H str. sym.
A''	245.1	235.3	249.1	O...H str. sym.
A'	259.3	244.3	272.1	O...H str. sym.
A'	280.9	266.5	295.9	O...H str. sym.
A''	429.7	419.8	402.0	PO_4 def.
A'	460.7	451.4	434.9	PO_4 def.
A''	547.8	557.5	554.2	HOH twist
A''	576.3	564.7	583.2	HOH twist
A'	580.3	565.7	580.4	HOH twist
A''	589.6	573.8	591.1	HOH twist
A''	594.7	587.9	636.2	HOH rock
A'	598.8	575.4	645.6	HOH rock
A'	605.0	587.8	541.9	PO_4 def.
A''	607.4	598.1	547.9	PO_4 def.
A'	615.9	593.7	660.7	HOH rock
A''	626.9	603.9	671.1	HOH rock
A'	627.9	612.4	568.9	PO_4 def.

Table S13: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_4$ (C_s) Frequencies (cont.)

sym	HF		MP2	Mode
	A	B	A	
A''	935.5	928.5	843.3	PO_4 str.
A'	1011.0	992.1	921.0	PO_4 str.
A''	1030.9	1024.1	982.9	HOH wag
A''	1041.8	1016.9	963.4	PO_4 str.
A'	1053.0	1038.2	1006.2	HOH wag
A'	1074.9	1051.6	1020.8	HOH wag
A''	1089.2	1072.1	1033.0	HOH wag
A'	1129.5	1092.4	1061.8	PO_4 str.
A'	1939.5	1902.3	1862.1	HOH def.
A''	1943.9	1907.8	1866.5	HOH def.
A'	1953.2	1913.2	1876.2	HOH def.
A'	2001.8	1951.8	1929.0	HOH def.
A'	3622.8	3640.4	3251.7	HOH str. asym.
A''	3666.6	3691.6	3267.4	HOH str. asym.
A'	3690.0	3709.7	3307.9	HOH str. asym.
A''	3696.7	3721.4	3302.9	HOH str. asym.
A'	3763.8	3758.6	3393.0	HOH str. sym.
A''	3787.5	3785.6	3412.7	HOH str. sym.
A'	3798.5	3797.2	3420.2	HOH str. sym.
A'	3828.2	3829.5	3448.2	HOH str. sym.

Table S14: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_4$ (D_{2d}) Frequencies

sym	HF		MP2	Mode
	A	B	A	
A_2	30.0	36.3	24.9	HOH trans.
B_2	50.0	51.3	48.7	HOH trans.
E	50.6	54.7	47.6	HOH trans.
B_2	113.9	100.8	124.9	O...H str. asym.
E	161.1	143.9	176.5	O...H str. asym.
A_2	203.4	185.6	225.9	O...H str. asym.
B_1	218.7	212.0	223.1	O...H str. sym.
A_1	236.8	224.9	242.0	O...H str. sym.
E	278.9	265.0	295.0	O...H str. sym.
A_1	413.3	405.6	378.7	PO_4 def.
B_1	474.0	466.2	450.8	PO_4 def.
B_1	562.4	573.8	561.8	HOH twist
E	576.4	569.6	579.5	HOH twist
B_2	595.8	588.2	536.6	PO_4 def.
A_1	598.4	609.7	595.3	HOH twist
A_2	600.8	561.6	644.9	HOH rock
E	610.3	587.4	656.8	HOH rock
E	621.0	608.2	561.7	PO_4 def.
B_2	623.4	575.4	667.0	HOH rock
A_1	941.8	933.8	853.0	PO_4 str.
A_2	1030.9	1025.4	983.7	HOH wag
B_2	1037.3	1008.8	956.5	PO_4 str.
E	1045.9	1027.4	973.6	PO_4 str.
E	1083.8	1062.2	1024.3	HOH wag
B_2	1102.3	1082.5	1047.8	HOH wag
B_1	1934.2	1897.0	1857.2	HOH def.
E	1952.6	1913.2	1875.8	HOH def.
A_1	2000.0	1949.4	1027.5	HOH def.
A_2	3672.3	3699.2	3269.4	HOH str. asym.
E	3691.3	3716.4	3293.4	HOH str. asym.
B_2	3709.5	3734.2	3314.7	HOH str. asym.
B_1	3758.5	3752.3	3390.2	HOH str. sym.
E	3765.6	3759.4	3398.0	HOH str. sym.
A_1	3784.7	3776.8	3423.0	HOH str. sym.

Table S15: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_5$ Geometry				
	HF		MP2	
	A	B	A	B
P-O 3	1.5660	1.5664	1.6008	1.6055
P-O 2	1.5497	1.5516	1.5797	1.5858
O2...H7	1.9097	1.9375	1.8510	1.8726
O2...H9	1.9441	1.9682	1.8763	1.8908
O4...H14	1.8741	1.8971	1.8266	1.8435
O2...O6	2.7923	2.8127	2.7719	2.7896
O2...O10	2.8153	2.8320	2.7896	2.8001
O4...O10	2.7678	2.7838	2.7553	2.7692
P...O6	3.3939	3.4143	3.3793	3.3969
P...O10	3.3872	3.4083	3.3698	3.3893

Table S16: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_5$ (C_{2v}) Frequencies

sym	HF		Mode
	A	B	
A_2	35.1	40.6	HOH trans.
B_1	45.2	49.8	HOH trans.
B_2	46.8	49.8	HOH trans.
B_1	50.0	52.5	HOH trans.
A_1	50.5	51.8	HOH trans.
B_2	107.6	94.7	O...H str. asym.
A_1	108.0	95.9	O...H str. asym.
B_1	150.5	137.3	O...H str. asym.
A_2	186.1	169.7	O...H str. asym.
B_2	194.0	169.4	O...H str. asym.
A_2	215.7	208.7	O...H str. sym.
A_1	221.8	214.1	O...H str. sym.
A_1	245.4	233.2	O...H str. sym.
B_1	259.9	249.5	O...H str. sym.
B_2	270.4	258.8	O...H str. sym.
A_1	429.7	422.5	PO_4 def.
A_2	457.6	451.6	PO_4 def.
A_2	514.1	528.2	HOH twist
B_1	538.8	540.5	HOH twist
B_2	549.5	534.8	HOH twist
A_2	557.6	535.1	HOH twist
B_2	559.5	548.1	HOH rock
A_2	564.8	571.4	HOH rock
A_1	568.3	550.4	HOH twist
B_1	573.5	555.4	HOH rock
B_2	579.7	563.4	HOH rock
A_1	583.9	583.0	HOH rock
A_1	607.1	595.3	PO_4 def.
B_1	608.9	598.4	PO_4 def.
B_2	624.3	612.8	PO_4 def.

Table S16: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_5$ (C_{2v}) Frequencies (cont.)

sym	HF		Mode
	A	B	
A_1	941.7	936.1	PO_4 str.
B_1	991.5	987.9	HOH wag
A_2	991.9	991.0	HOH wag
B_2	1011.1	1031.8	HOH wag
A_1	1034.9	1015.8	PO_4 str.
B_1	1038.0	1022.2	HOH wag
B_2	1045.3	999.7	PO_4 str.
A_1	1075.9	1056.2	HOH wag
B_1	1105.8	1077.7	PO_4 str.
A_2	1932.5	1897.7	HOH def.
A_1	1939.8	1905.6	HOH def.
B_2	1948.8	1911.9	HOH def.
B_1	1949.7	1913.3	HOH def.
A_1	2006.0	1958.1	HOH def.
A_2	3725.2	3732.1	HOH str. asym.
B_2	3731.6	3737.8	HOH str. asym.
B_1	3745.7	3751.9	HOH str. asym.
A_1	3751.5	3763.0	HOH str. asym.
B_2	3775.0	3786.7	HOH str. asym.
A_1	3821.5	3810.2	HOH str. sym.
A_2	3830.3	3823.1	HOH str. sym.
B_1	3832.4	3825.4	HOH str. sym.
B_2	3843.5	3838.9	HOH str. sym.
A_1	3854.9	3847.4	HOH str. sym.

Table S17: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_6$ Geometry				
	HF		MP2	
	A	B	A	B
P-O	1.5568	1.5575	1.5894	1.5937
O ... H	1.9374	1.9571	1.8805	1.8917
O ... O	2.8129	2.8266	2.7934	2.8021
P ... O	3.4082	3.4236	3.3912	3.4019

Table S18: $\text{PO}_4^{3-} \cdot (\text{H}_2\text{O})_6$ (T_d) Frequencies

sym	HF		Mode
	A	B	
T_1	40.2	45.4	HOH trans.
T_2	51.0	52.7	HOH trans.
T_2	104.9	92.9	O...H str. asym.
T_1	183.5	164.5	O...H str. asym.
E	200.3	196.7	O...H str. sym.
A_1	227.0	216.4	O...H str. sym.
T_2	251.7	242.9	O...H str. sym.
E	440.9	436.5	PO_4 def.
A_2	478.6	497.9	HOH twist
T_1	516.9	507.4	HOH twist
E	546.4	561.4	HOH twist
T_1	528.7	532.7	HOH rock
T_2	547.5	523.0	HOH rock
T_2	612.3	603.4	PO_4 def.
A_1	946.3	942.2	PO_4 str.
T_1	953.9	956.1	HOH wag
T_2	1007.8	996.0	HOH wag
T_2	1068.6	1051.1	PO_4 str.
E	1929.9	1897.5	HOH def.
T_2	1945.0	1911.1	HOH def.
A_1	2008.6	1963.3	HOH def.
T_1	3810.8	3814.4	HOH str. asym.
T_2	3834.9	3833.9	HOH str. asym.
E	3853.1	3836.6	HOH str. sym.
T_2	3859.9	3848.6	HOH str. sym.
A_1	3880.0	3864.0	HOH str. sym.

Table S19: Total Energies (au)

	UHF/B	UMP2/B	PMP2/B
PO_4^{2-}	-640.0762847	-640.9746794	-640.9866694
$\text{PO}_4^{2-} \cdot (\text{H}_2\text{O})$ (C_{2v})	-716.1620429	-717.2127117	-717.2238670
$\text{PO}_4^{2-} \cdot (\text{H}_2\text{O})_2$ (D_{2d})	-792.1887226	-793.4842390	-793.4949407
$\text{PO}_4^{2-} \cdot (\text{H}_2\text{O})_3$ (C_2)	-868.2663595	-868.2421070	-868.2561928
$\text{PO}_4^{2-} \cdot (\text{H}_2\text{O})_4$ (D_{2d})	-944.3093074	-945.9541386	-945.9645724
$\text{PO}_4^{2-} \cdot (\text{H}_2\text{O})_5$ (C_{2v})	-1020.3595042	-1022.2005976	-1022.2110186
$\text{PO}_4^{2-} \cdot (\text{H}_2\text{O})_6$ (T_d)	-1096.3721345	-1098.4377307	-1098.4473687
PO_4^-	-640.0645962	-641.0473880	-641.0858586
$\text{PO}_4^- \cdot (\text{H}_2\text{O})$ (C_{2v})	-716.2119344	-717.2113744	-717.3137287
$\text{PO}_4^- \cdot (\text{H}_2\text{O})_2$ (D_{2d})	-792.2125971	-793.4217508	-793.5222923
$\text{PO}_4^- \cdot (\text{H}_2\text{O})_3$ (C_2)	-868.2594669	-869.6534511	-869.7534630
$\text{PO}_4^- \cdot (\text{H}_2\text{O})_4$ (D_{2d})	-944.2823166	-945.8716783	-945.9746952
$\text{PO}_4^- \cdot (\text{H}_2\text{O})_5$ (C_{2v})	-1020.3056380	-1022.0939645	-1022.1932919
$\text{PO}_4^- \cdot (\text{H}_2\text{O})_6$ (T_d)	-1096.2054243	-1098.3150504	-1098.4110762