

Supporting Information

Microhydrated Dihydrogen Phosphate Clusters Probed by Gas Phase Vibrational Spectroscopy and First Principles Calculations

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Table S1. Assignment of the low frequency spectra for $n=2, 3, 4, 5, 6, 8, 10$, and 12 .

Label	Exp.	n	Harmonic	140K	180K	Assignment
G	1666	2		1700-1800	1600-1700	1600-1700 Water scissoring
	1673	3	
	1664	4				
	1670	5				
	1661	6				
	1649	8				
	1652	10				
H	1663	12				
	1284	2	1305(2-4)	1200-1300	1241	Antisymmetric P=O
	1268	3	-			stretching
	1249	4	1235(4-3)	1167	1161	
	1216	5	-			
	1207	6	1210(6-2) 1182(6-4) 1156(6-5)	1197	1141	
	1216	8	-			
	1231	10	-			
	1234	12	-			
	1138	6	1121(6-1) 1119(6-3)	1064	1084	Antisymmetric P=O stretching mode
H'	1132	8	-			of (m,m) type
	1132	10	-			isomers
	1123	12	-			
I	1089	2	1065(2-1) 1059(2-2) 1058(2-3) 1081(2-4)	1024	1047	Symmetric P=O stretching
	1084	3	-			
	1086	4	1049(4-1) 1071(4-2) 1058(4-3) 1065(4-4)	1041	1021	
	1084	5	-			
	1077	6	1054(6-1) 1063(6-2) 1060(6-3) 1060(6-4) 1057(6-5)	1004	1017	
	1071	8	-			
	1074	10	-			

	1073	12	-			
K	837	2	800(2-1) 839(2-2) 836(2-3) 833(2-4)	774	754	Antisymmetric P-OH stretching
	853	3	-			
	885	4	844(4-1) 850(4-2) 865(4-3) 857(4-4)	821	817	
	912	5	-			
	924	6	937(6-1) 901(6-2) 950(6-3) 856(6-4) 930(6-5)	887	851	
	962	8	-			
	968	10	-			
	979	12	-			
L	812	2	781(2-1) 793(2-2) 780(2-3) 788(2-4)	730	727	Symmetric P-OH stretching
	816	3	-			
	827	4	801(4-1) 777(4-2) 813(4-3) 782(4-4)	760	747	
	835	5	-			
	842	6	840(6-1) 824(6-2) 842(6-3) 799(6-4) 839(6-5)	807	777	
	-	8	-			
	-	10	-			
	-	12	-			
M	550- 1000	6-12	550-1000			Water wagging and rocking

Table S2. Populations of each isomers in $\text{H}_2\text{PO}_4^-(\text{H}_2\text{O})$ at 140 and 180K with different hydrogen bond distance threshold. The identification of a configuration as with a certain isomer depends on the threshold value. But it does not change the overall trend.

Cutoff(Å)	2.4		2.5		2.6	
T(K)	140	180	140	180	140	180
1-1:	6	1	7	1	8	2
1-2:	66	45	72	51	76	55
1-3:	28	50	20	44	15	38
1-4/5:	1	3	1	4	1	5

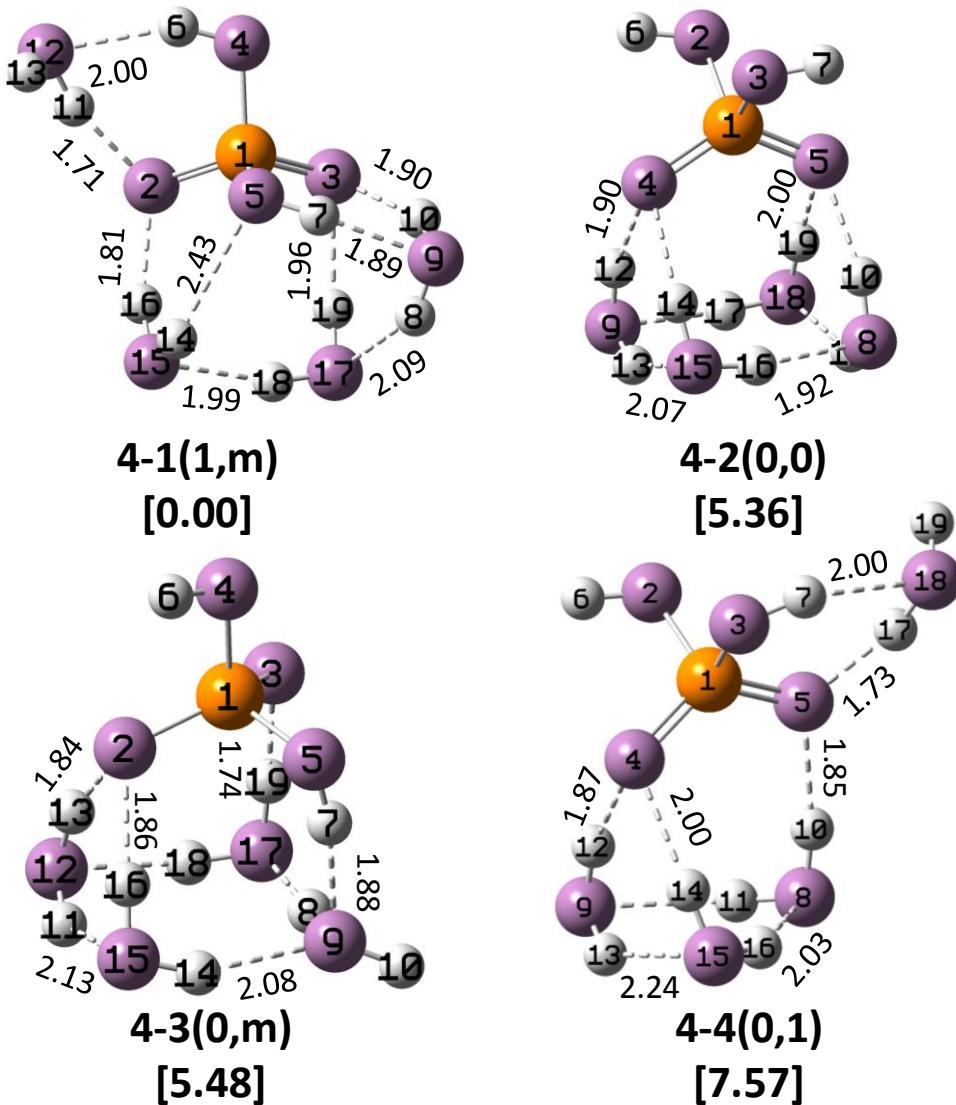


Figure S1. Four 0 K structures at $n = 4$, optimized at the MP2/aug-cc-pVDZ level. The relative energies listed in the square brackets are in kJ/mol and the hydrogen bond distances are in angstrom.

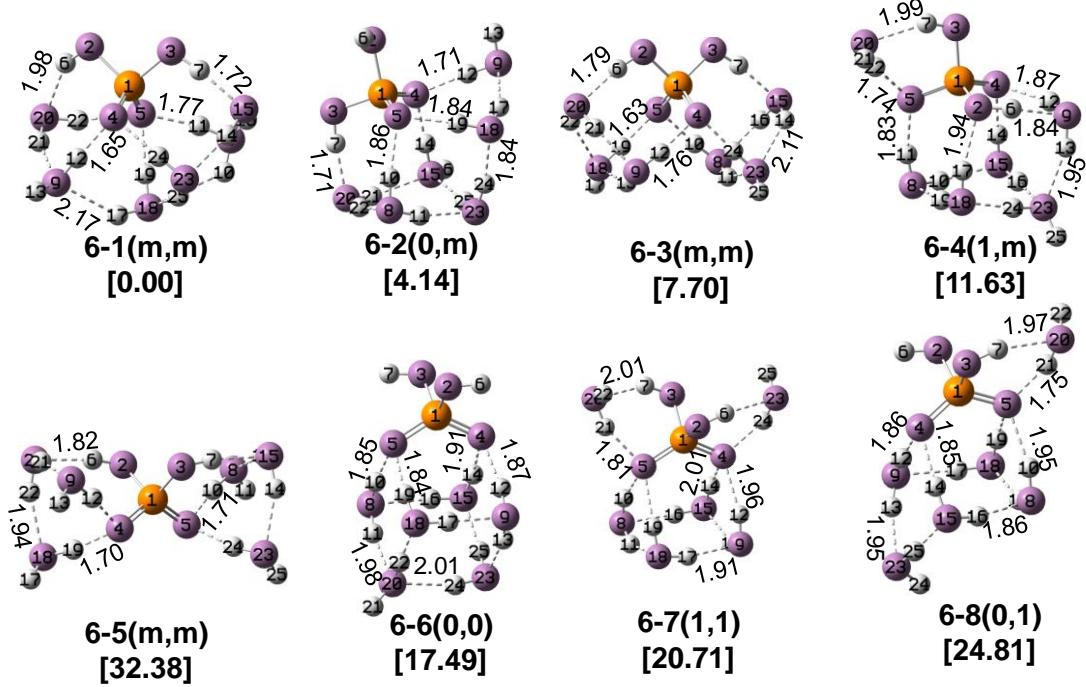


Figure S2. Eight 0 K structures at $n = 6$, optimized at the MP2/aug-cc-pVDZ level. The relative energies listed in the square brackets are in kJ/mol and the hydrogen bond distances are in angstrom.

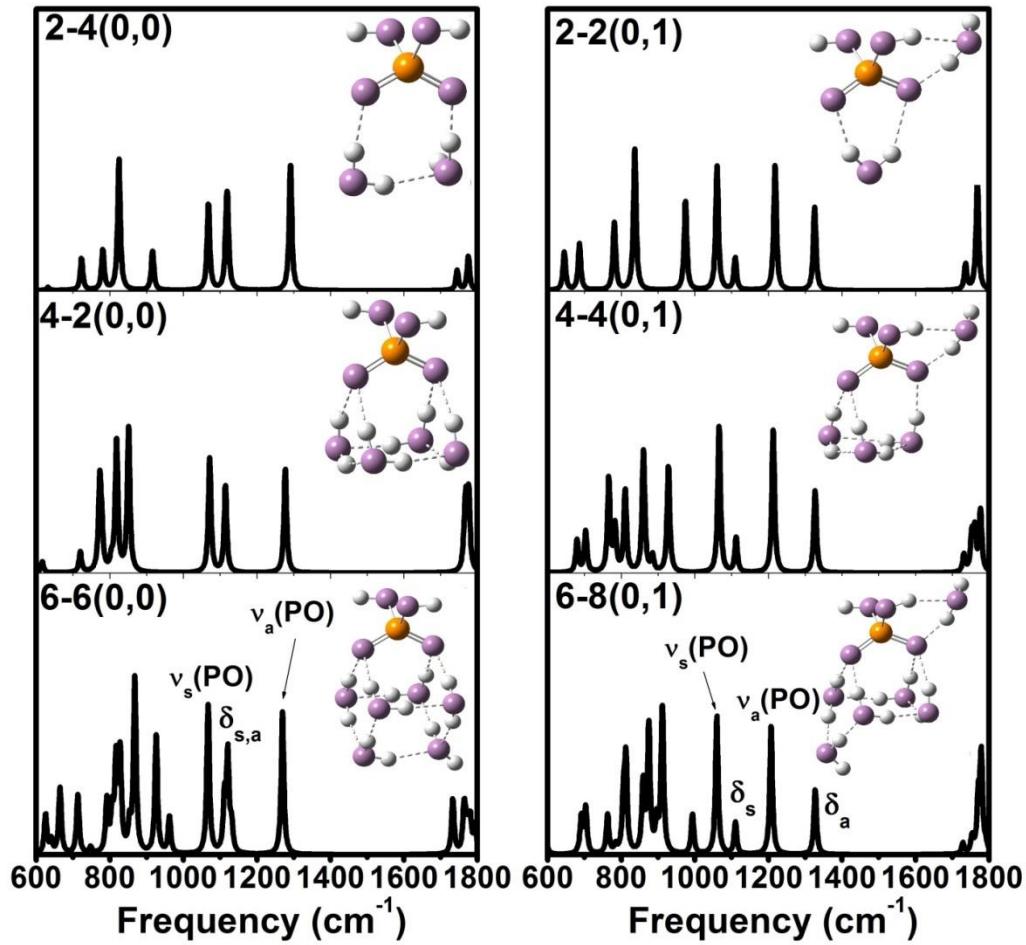


Figure S3. The harmonic peaks for P=O stretching and POH bending, calculated at the MP2/aug-cc-pVDZ level, for **(0,0)** and **(0,1)** structures with $n = 2, 3, 4$ and 6 . The same solvation pattern for the POH groups produces very similar spectra, regardless the value of n .

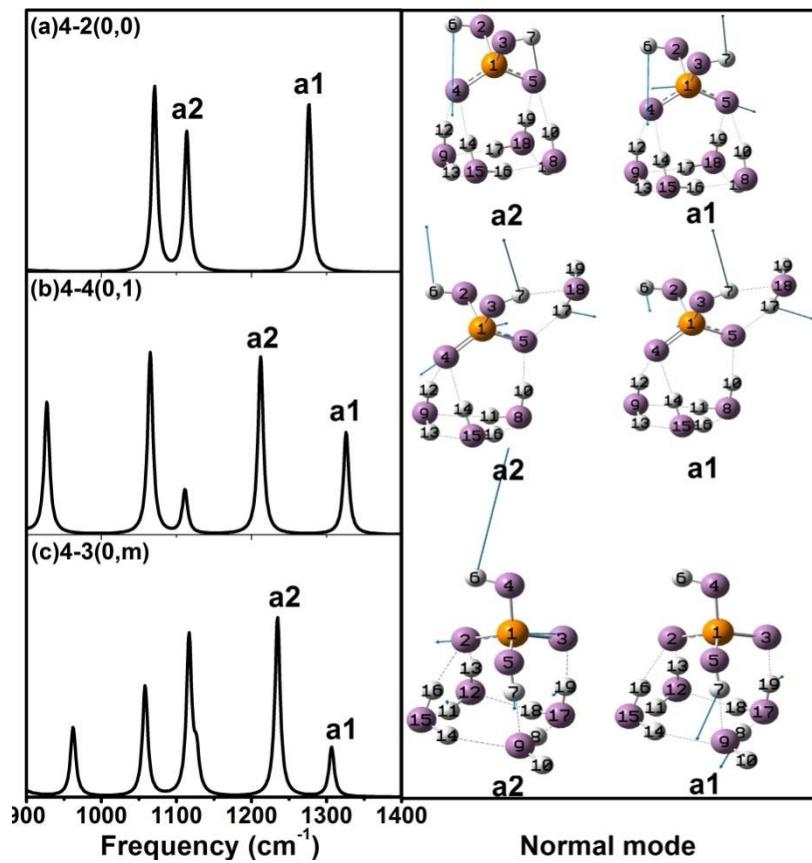


Figure S4. Comparison of the harmonic spectra, calculated at the MP2/aug-cc-pVDZ level, for three isomers at $n = 4$, **4-2 (0,0)**, **4-4 (0,1)**, and **4-3 (0,m)**. The blue arrows in the right show the magnitudes of the displacement vectors for a harmonic mode. Notice for **4-3 (0,m)**, the a1 peak is due to the bending of the solvated POH, decoupled from P=O stretching.