http://dx.doi.org/10.5012/bkcs.2012.33.6.1998

Monohydrated Sulfuric and Phosphoric Acids with Different Hydrogen Atom Orientations: DFT and *Ab initio* Study

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Received September 16, 2011, Accepted March 22, 2012

We carried out DFT calculations for monohydrated sulfuric and phosphoric acids. We are interested in clusters which differ in orientation of hydrogen atoms only. Such molecular complexes are close in energy, since they lie in the vicinity of the global minimum energy structure on the flat potential energy surface. For monohydrated sulfuric acid we identified four different isomers. The monohydrated phosphoric acid forms five different conformers. These systems are difficult to study from the theoretical point of view, since binding energy differences in several cases are very small. For each structure, we calculated harmonic vibrational frequencies to be sure that if the optimized structures are at the local or global minima on the potential energy surface. The analysis of calculated –OH vibrational frequencies is useful in interpretation of infrared photodissociation spectroscopy experiments. We employed four different DFT functionals in our calculations. For each structure, we calculated binding energies, thermodynamic properties, and harmonic vibrational frequencies. Our analysis clearly shows that DFT approach is suitable for studying monohydrated inorganic acids with different hydrogen atom orientations. We carried out MP2 calculations with aug-cc-pVDZ basis set for both monohydrated acids. MP2 results serve as a benchmark for DFT calculations.

Key Words : Monohydrated sulfuric and phosphoric acids, Density functional theory, Harmonic vibrational frequencies

Introduction

It is hard to imagine a world without solutions, and thus a microscopic representation of hydrated acids underlies our understanding of a broad spectrum of issues, ranging from proton transfer to acid rains (it is strongly related to atmospheric chemistry). Moreover, for many inorganic acids, the path from small hydrated complexes to aqueous solution is associated with very complex solvation process. Small hydrated acid clusters mimic simplified forms of aqueous solution whose evolution shows the transition from microscopic to macroscopic world. The monohydrates of numerous inorganic acids have been investigated, both experimentally and theoretically. The $H_2SO_4\cdots H_2O$ system has been observed by rotational spectroscopy measurements in a supersonic jet.[1] The vibrationally averaged structure of monohydrated of the system has been determined. However, computational chemistry provides detailed information about other possible conformers formed by $H_2SO_4\cdots H_2O$ complex. The $H_3PO_4\cdots H_2O$ clusters have not been studied experimentally.[1] Study of solvation and dissociation phenomena is a really hard issue in contemporary computational chemistry. In majority of cases the number of water molecules which are necessary to dissociate inorganic acid and to stabilize the hydronium cation is large. Such complexes have very complicated geometrical structure and they are really difficult to construct. To simplify this procedure, we usually start from the simplest molecular (monohydrated) complexes and then gradually increase the number of water molecules. In that sense, this paper provides all initial conformations for both inorganic acids. It significantly facilities creation of molecular complexes having larger number of water molecules. Due to high complexity of the hydration/dehydration which requires extensive theoretical studies, the present aim is not to study such phenomena, but we have tried to investigate the monohydrated inorganic acids as the first step towards understanding the hydration phenomenon. This mono-hydration study is vital to preparing the fully anhydrated inorganic acids by de-hydrating the last water molecule.

The hydration/dehydration phenomena of molecular systems including diverse hydrated cations,[2] anions,[3] simple inorganic acids,[4] bases,[5] and salts[6] have already been reported. However, geometrical parameters, infrared (IR) frequencies and thermodynamic properties for hydration of a large family of inorganic acids are still scarce.[7] The monohydrated inorganic acids are very interesting molecular systems to study, both from the experimental and theoretical point of view. We carried out extensive Density Functional Theory (DFT) calculations for monohydrated sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4).[7-16] The main purpose of this research was to identify and characterize the most stable conformers. We investigated isomers which show the difference only in hydrogen atom orientations (H-orientations).

Different H-orientations occur due to specific alignment of water molecule with respect to the inorganic acid, and different orientations of the –OH groups within the inorganic acid. The energy differences and energy barriers between the structures are small, since potential energy surfaces (PES) for both monohydrated acids are very shallow in the vicinity of the global minimum energy structure. Therefore different isomers easily convert to other structures with small energy barriers. The analyses of calculated harmonic vibrational frequencies are important in structure identification during Infrared Photodissociation Spectroscopy (IRPD) experiments.

We carried out MP2 calculations with aug-cc-pVDZ basis set for both monohydrated acids. This allows direct comparison of DFT results with more accurate MP2 approach.

Computational Details

We performed geometry optimization, harmonic frequency analysis, and computed binding energies for the most stable conformers of monohydrated H_2SO_4 and H_3PO_4. Geometry optimization and harmonic frequency calculations were done at the DFT level of theory employing M06-2X,[17] ωB97X-D,[18] B97-D,[19] and B3LYP[20] functionals. Calculations were done by using the Gaussian 09 suite of programs.[21] All the atoms were treated with the correlation consistent aug-cc-pVDZ basis set (which we have denoted as aVDZ).[22] All the reported structures are at the local or global minima without imaginary frequencies. All the conformers were drawn with the Posmol package.[23]

To distinguish different conformers, we use the following notation: A/D_X denotes the role of proton acceptor (A:O)/donor(D:H) by the water molecule, while the subscript "X" denotes the atom/group of each acid interacting with the hydrogen atom of water molecule. The $D_{O(H)}$ structure where a hydrogen atom in water molecule interacts with the -O(H) group in the acid is denoted as D_{OH}, in contrast to the D_O structure where a hydrogen atom in water molecule interacts with a double-bond oxygen (O=) in the acid. The bond distance between two oxygen atoms (one in water molecule and the other in the inorganic acid) is denoted as r_{OO}. The hydrogen bond (H-bond) distance between an oxygen atom in water molecule and a hydrogen atom in the acid is described as r_{OH}. Similarly, r_{XO} determines the distance between central atom X in the acid and an oxygen atom in water molecule.

In all the cases, the central atom X (X = S, P) interacts with the oxygen (O) atom of a water molecule (W_{XO}). To distinguish different conformers exhibiting the same structural motif, we employed Arabic numerals. For all possible conformers, we calculated binding energies ($-\Delta E_e$), BSSE-corrected binding energies ($-\Delta_e$(BSSE)), zero-point-energy (ZPE) corrected binding energies ($-\Delta E_0$), and binding enthalpies ($-\Delta H_r$) and free binding energies ($-\Delta G_r$) at standard conditions (298.16 K and 1 bar). For energy comparison between different isomers to find the most stable structures, our discussion will be based on the DFT/aVDZ ΔE_0 values.

It is necessary to compare DFT results with more accurate quantum chemical approach. Thus, we carried out extensive MP2/aVDZ calculations for both monohydrated acids. We optimized geometries of all conformers at the MP2/aVDZ level of theory. We also performed harmonic vibrational frequency analysis to assure that all optimized conformers are global/local minimum energy structures (without imaginary frequencies). We computed thermodynamical properties at standard conditions. The MP2/aVDZ results serve as a benchmark which allows us to justify the reliability of different DFT functionals.

The BSSE errors at the MP2/aVDZ level of theory are significantly larger in comparison with DFT BSSE values. The double-zeta quality basis set is far too small for correlated calculations which converge very slowly with the basis set size. Since, we carried out MP2 calculations with aug-cc-pVTZ (aVTZ) basis set. The BSSE errors are significantly smaller at this level of theory. We employed Kim *et al.*[24] extrapolation procedure to compute MP2/CBS (Complete Basis Set) binding energies for both monohydrated acids.

Discussion of Results

Table 1 contains information about binding energies, BSSE-corrected binding energies, ZPE-corrected binding energies, and binding enthalpies and Gibbs free binding energies at standard conditions (289.16 K and 1 bar). All the reported structures differ in H-orientations only, since they are close in energy and possess similar, however, not identical geometrical parameters. Despite the slight differences in geometry, in some cases the relative energy differences between conformers are not negligible.

In the case of monohydrated sulfuric acid, the most stable AD_OW_{SO}(I) and AD_OW_{SO}(II) structures are almost isoenergetic (the energy difference does not exceed ~0.4 kJ/mol). Both conformers vary in slightly different orientation of the water molecule with respect to the position of sulfuric acid. Although these structures have almost the same binding energy, their geometrical parameters slightly differ. In the case of AD_OW_{SO}(I) conformer, r_{OH} and r_{OO} distances are slightly longer while compared to AD_OW_{SO}(II) structure. Simultaneously the r_{XO} distance is slightly shorter. It clearly shows that PES in this particular region is almost flat. The third conformer AD_OW_{SO}(III) is slightly less stable. In this case, the binding energy difference is about 4 kJ/mol lower in comparison with AD_OW_{SO}(I-II) structures.

The $AD_{OH}{}^2W_{SO}$ structure is relatively less stable when

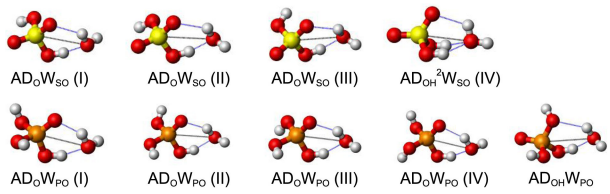

Figure 1. DFT/aVDZ optimized structures of monohydrated inorganic acids. The lowest energy structure for each chemical species is denoted in bold. Dashed blue lines represent hydrogen bonds.

Table 1. DFT/aVDZ and MP2/aVDZ binding energies ($-\Delta E_e$), BSSE-corrected binding energies ($-\Delta E_e$(BSSE)), ZPE-corrected binding energies ($-\Delta E_0$), binding enthalpies ($-\Delta H_r$) and free binding energies ($-\Delta G_r$) [in kJ/mol] at room temperature (298.16 K) and 1 bar for various conformers of monohydrated H_2SO_4 and H_3PO_4

Method	acid⋯water	Conformer	$-\Delta E_e$($-\Delta E_e$(BSSE))	$-\Delta E_o$	$-\Delta H_r$	$-\Delta G_r$
M06-2X	$H_2SO_4 \cdots H_2O$	**AD_OW_{SO}**(I)	61.09(58.51)	51.90	54.91	15.96
		AD_OW_{SO}(II)	61.19(58.72)	51.48	54.59	14.93
		AD_OW_{SO}(III)	56.47(54.01)	47.19	50.15	11.99
		$AD_{OH}{}^2W_{SO}$	58.33(54.75)	47.03	50.59	8.94
	$H_3PO_4 \cdots H_2O$	**AD_OW_{PO}**(I)	61.59(58.86)	51.50	54.62	15.46
		AD_OW_{PO}(II)	60.68(57.78)	50.56	53.77	13.85
		AD_OW_{PO}(III)	58.65(55.81)	48.95	51.98	12.68
		AD_OW_{PO}(IV)	57.94(55.40)	48.46	51.62	12.39
		$AD_{OH}W_{PO}$	45.42(42.79)	35.65	38.16	-0.19
ωB97X-D	$H_2SO_4 \cdots H_2O$	**AD_OW_{SO}**(I)	57.27(54.83)	46.40	50.15	7.84
		AD_OW_{SO}(II)	57.29(54.94)	46.69	50.34	8.21
		AD_OW_{SO}(III)	52.55(50.17)	42.31	45.80	5.18
		$AD_{OH}{}^2W_{SO}$	50.48(46.91)	38.74	42.72	-1.15
	$H_3PO_4 \cdots H_2O$	**AD_OW_{PO}**(I)	57.90(55.17)	46.90	50.49	10.89
		AD_OW_{PO}(II)	56.81(53.88)	46.26	49.39	10.73
		AD_OW_{PO}(III)	54.98(52.08)	44.57	47.81	8.50
		AD_OW_{PO}(IV)	54.13(51.60)	43.72	47.15	8.01
		$AD_{OH}W_{PO}$	42.26(39.85)	32.51	35.03	-2.56
B97-D	$H_2SO_4 \cdots H_2O$	**AD_OW_{SO}**(I)	51.64(49.29)	41.21	44.55	4.25
		AD_OW_{SO}(II)	51.41(49.19)	41.11	44.44	4.05
		AD_OW_{SO}(III)	46.52(44.31)	36.73	39.73	1.04
		$AD_{OH}{}^2W_{SO}$	46.52(44.32)	36.71	39.72	1.00
	$H_3PO_4 \cdots H_2O$	**AD_OW_{PO}**(I)	52.49(49.90)	41.70	45.11	6.04
		AD_OW_{PO}(II)	51.39(48.58)	40.75	43.92	4.86
		AD_OW_{PO}(III)	49.90(47.12)	39.44	42.73	3.13
		AD_OW_{PO}(IV)	49.29(46.82)	39.13	42.41	3.55
		$AD_{OH}W_{PO}$	40.12(37.67)	30.01	32.60	-4.57
B3LYP	$H_2SO_4 \cdots H_2O$	**AD_OW_{SO}**(I)	51.14(48.78)	40.80	44.28	3.28
		AD_OW_{SO}(II)	51.29(48.99)	40.96	44.47	3.33
		AD_OW_{SO}(III)	46.73(44.42)	36.62	39.99	0.04
		$AD_{OH}{}^2W_{SO}$	41.79(38.43)	30.60	34.11	-5.79
	$H_3PO_4 \cdots H_2O$	**AD_OW_{PO}**(I)	51.99(49.26)	41.07	44.62	4.87
		AD_OW_{PO}(II)	50.89(47.97)	40.42	43.54	4.70
		AD_OW_{PO}(III)	49.15(46.23)	38.62	42.02	1.95
		AD_OW_{PO}(IV)	48.27(45.69)	38.09	41.48	2.13
		$AD_{OH}W_{PO}$	36.04(33.71)	26.54	28.94	-8.10
MP2	$H_2SO_4 \cdots H_2O$	**AD_OW_{SO}**(I)	53.08(44.32)	43.52	46.23	7.96
		AD_OW_{SO}(II)	53.27(44.39)	43.48	46.27	7.85
		AD_OW_{SO}(III)	48.32(39.68)	39.06	41.53	4.82
		$AD_{OH}{}^2W_{SO}$	47.63(38.19)	37.10	40.08	0.39
	$H_3PO_4 \cdots H_2O$	**AD_OW_{PO}**(I)	54.85(45.62)	43.97	47.49	8.13
		AD_OW_{PO}(II)	54.02(44.52)	43.27	46.60	6.72
		AD_OW_{PO}(III)	51.72(42.36)	41.13	44.52	4.27
		AD_OW_{PO}(IV)	50.53(41.57)	40.39	43.76	4.58
		$AD_{OH}W_{PO}$	40.01(31.84)	30.31	32.88	-5.20

compared to AD_OW_{SO} isomers. Its structure is characterized by three H-bonds, two of them are formed by –O(H) groups which belong to the sulfuric acid and the oxygen atom of water molecule. The calculated r_{XO} distances for $AD_{OH}{}^2W_{SO}$ conformer are significantly shorter in comparison with AD_OW_{SO} motifs. It seems that B97-D functional cannot properly describe $AD_{OH}{}^2W_{SO}$ structure. In this case, the water molecule has completely different orientation, thus the

Table 2. MP2/aVDZ binding energies ($-\Delta E_e$), BSSE-corrected binding energies ($-\Delta E_e$(BSSE)), MP2/aVTZ binding energies ($-\Delta E_e$), BSSE-corrected binding energies ($-\Delta E_e$(BSSE)) and MP2/CBS binding energies for various conformers of monohydrated H_2SO_4 and H_3PO_4

MP2		aVDZ	aVTZ	CBS
$H_2SO_4\cdots H_2O$	**AD_OW_{SO}(I)**	53.08(44.32)	54.43(49.91)	52.26
	AD_OW_{SO}(II)	53.27(44.39)	54.22(49.68)	51.90
	AD_OW_{SO}(III)	48.32(39.68)	49.48(44.99)	47.22
	$AD_{OH}{}^2W_{SO}$	47.63(38.19)	47.24(42.68)	44.57
$H_3PO_4\cdots H_2O$	**AD_OW_{PO}(I)**	54.85(45.62)	55.96(51.24)	53.60
	AD_OW_{PO}(II)	54.02(44.52)	54.52(49.83)	52.06
	AD_OW_{PO}(III)	51.72(42.36)	52.32(47.63)	49.85
	AD_OW_{PO}(IV)	50.53(41.57)	52.04(47.32)	49.73
	$AD_{OH}W_{PO}$	40.01(31.84)	38.37(34.13)	35.09

corresponding binding energies and geometrical parameters are very close to the AD_OW_{SO}(III) conformer. It is important to note that the order in terms of binding energies for AD_OW_{SO}(I) and AD_OW_{SO}(II) isomers is not always preserved at different DFT levels. We suppose that additional stabilization of these complexes is caused by dispersion interactions. However, the r_{XO} distances are similar for DFT functionals with and without empirical dispersion. We found one additional structure, which is characterized by D_O motif. This structure is ~30 kJ/mol less stable than AD_OW_{SO} conformers, thus this complex is not discussed.

In the case of monohydrated phosphoric acid, we could identify five conformers which differ in H-orientations only. Contrary to the sulfuric acid, the two most stable conformers are slightly different in binding energy (the difference is about ~1 kJ/mol), however, their structures are very similar to AD_OW_{SO}(I) and AD_OW_{SO}(II) conformers. The order of conformers in terms of binding energies is conserved at different DFT levels. The AD_OW_{SO}(I) conformer has slightly longer r_{OH} and r_{OO} distances. Two other conformers which are characterized by AD_OW_{PO} motif are slightly less stable. The $AD_{OH}W_{PO}$ conformer is significantly less stable while compared to AD_OW_{PO} motifs. The geometry of $AD_{OH}W_{PO}$ structure is substantially different. The r_{XO} distances as well as r_{OH} distances are significantly longer in comparison with AD_OW_{PO} structures. Similarly to the monohydrated sulfuric acid, PES in the vicinity of the global minimum for monohydrated phosphoric acid is very flat, however, the relative binding energy differences are slightly larger. It is important to note that absolute values of binding energies are different for various DFT functionals. It is well known that B3LYP approach usually underestimates binding energy values. B97-D binding energies are similar to B3LYP values. M06-2X as well as ωB97X-D binding energies are significantly larger in comparison with B3LYP and M06-2X functionals.

We calculated harmonic vibrational frequencies for both monohydrated acids. We are interested in stretching frequencies of –OH vibrations.

The IR spectrum is characterized by one very intense peak which originates from the –OH vibration of the inorganic acid. The other peaks are coupled vibrations of acidic –OH groups and –OH stretching modes of water molecule. It is important to note that AD_OW_{XO} (X = S, P) –OH stretching vibrational frequencies are similar, since structure identification of these isomers during IRPD experiments appears to be very difficult. It should be feasible to distinguish AD_OW_{XO} (X = S, P) forms from significantly less stable $AD_{OH}{}^2W_{SO}$ and $AD_{OH}W_{PO}$ structures. We intentionally left harmonic vibrational frequencies unscaled. It enables the direct comparison of harmonic vibrational frequencies calculated at different DFT levels of theory. Table 4 clearly shows that B97-D frequencies are significantly smaller than those given by the other DFT functionals.

Potential energy surfaces for monohydrated H_2SO_4, and H_3PO_4 are relatively broad and flat. It is a well known fact that the harmonic approximation usually fails while PES is relatively broad and flat. Thus, we carried out computations of anharmonic frequencies at the B3LYP/aVDZ level of theory (Table 5). The largest deviations between anharmonic and harmonic frequencies are observed for very intense vibrations which originate from the –OH stretching mode of the inorganic acid. However, several harmonic –OH vibrational frequencies exhibit large deviations from their anharmonic equivalents.

The comparison of DFT approach with MP2 exhibits that DFT binding energies and geometrical parameters are close to MP2 results. The analysis of ZPE-corrected binding energies ($-\Delta E_0$) shows that B97D/aVDZ results are very close to MP2/aVDZ values (the largest difference does not exceed ~3 kJ/mol). In the case of ωB97X-D functional, binding energy differences are insignificantly larger as compared with B97D (by ~1 kJ/mol). The B3LYP functional slightly underestimates binding energies. The binding energies at the M06-2X/aVDZ level of theory are slightly overestimated. It seems that in terms of binding energies the performance of DFT functionals with empirical dispersion (B97D and ωB97X-D) is slightly better than that of M06-2X and B3LYP. We checked out calculated geometrical parameters of monohydrated acids. When we compare MP2 and DFT computed bond lengths (r_{XO}, r_{OO}, and r_{OH}), the best agreement can be observed for the ωB97X-D functional (the largest deviation never exceeds 0.07 Å). Although B97D functional gives accurate values of binding energies, it tends to overestimate the hydrogen bond lengths (the largest deviation is 0.17 Å). The distances given by M06-2X functional are close to MP2 results (the largest bond length

Table 3. Selected interatomic distances [Å] for monohydrated H_2SO_4 and H_3PO_4. r_{XO} denotes the X(acid)···OH_2 distance; r_{OH} denotes either H(acid)···OH_2 or O(acid)···HOH distance; r_{OO} denotes the =O(acid)···OH_2 distance

Method	acid···water	Conformer	r_{XO}	r_{OO}	r_{OH}
M06-2X	H_2SO_4···H_2O	**AD_OW_{SO}(I)**	3.25	2.83	2.12
		AD_OW_{SO}(II)	3.27	2.81	2.10
		AD_OW_{SO}(III)	3.30	2.78	2.08
		$AD_{OH}{}^2W_{SO}$	3.00	2.73	2.12
	H_3PO_4···H_2O	**AD_OW_{PO}(I)**	3.21	2.77	1.92
		AD_OW_{PO}(II)	3.20	2.76	1.92
		AD_OW_{PO}(III)	3.20	2.78	1.93
		AD_OW_{PO}(IV)	3.19	2.78	1.95
		$AD_{OH}W_{PO}$	3.26	4.72	2.23
ωB97X-D	H_2SO_4···H_2O	**AD_OW_{SO}(I)**	3.30	2.88	2.18
		AD_OW_{SO}(II)	3.30	2.87	2.16
		AD_OW_{SO}(III)	3.33	2.81	2.11
		$AD_{OH}{}^2W_{SO}$	3.03	2.76	2.15
	H_3PO_4···H_2O	**AD_OW_{PO}(I)**	3.23	2.78	1.93
		AD_OW_{PO}(II)	3.23	2.78	1.91
		AD_OW_{PO}(III)	3.22	2.78	1.93
		AD_OW_{PO}(IV)	3.21	2.80	1.95
		$AD_{OH}W_{PO}$	3.37	4.80	2.28
B97-D	H_2SO_4···H_2O	**AD_OW_{SO}(I)**	3.37	3.01	2.33
		AD_OW_{SO}(II)	3.38	3.00	2.32
		AD_OW_{SO}(III)	3.41	2.94	2.27
		$AD_{OH}{}^2W_{SO}$	3.41	2.94	2.28
	H_3PO_4···H_2O	**AD_OW_{PO}(I)**	2.28	2.85	2.00
		AD_OW_{PO}(II)	3.28	2.84	1.98
		AD_OW_{PO}(III)	3.28	2.86	2.02
		AD_OW_{PO}(IV)	3.27	2.88	2.04
		$AD_{OH}W_{PO}$	3.40	4.87	2.40
B3LYP	H_2SO_4···H_2O	**AD_OW_{SO}(I)**	3.33	2.88	2.17
		AD_OW_{SO}(II)	3.33	2.87	2.16
		AD_OW_{SO}(III)	3.35	2.83	2.13
		$AD_{OH}{}^2W_{SO}$	3.07	2.79	2.20
	H_3PO_4···H_2O	**AD_OW_{PO}(I)**	3.24	2.79	1.93
		AD_OW_{PO}(II)	3.24	2.77	1.92
		AD_OW_{PO}(III)	3.23	2.79	1.94
		AD_OW_{PO}(IV)	3.21	2.80	1.95
		$AD_{OH}W_{PO}$	3.44	4.85	2.80
MP2	H_2SO_4···H_2O	**AD_OW_{SO}(I)**	3.30	2.87	2.16
		AD_OW_{SO}(II)	3.30	2.88	2.17
		AD_OW_{SO}(III)	3.26	2.82	2.13
		$AD_{OH}{}^2W_{SO}$	3.04	2.77	2.18
	H_3PO_4···H_2O	**AD_OW_{PO}(I)**	3.23	2.79	1.94
		AD_OW_{PO}(II)	3.23	2.78	1.93
		AD_OW_{PO}(III)	3.22	2.80	1.95
		AD_OW_{PO}(IV)	3.21	2.81	1.97
		$AD_{OH}W_{PO}$	3.36	4.82	2.25

difference never exceeds 0.1 Å). Our analysis clearly shows that the ωB97X-D functional gives the best results (very close to MP2 values) among analyzed various DFT functionals. However, it is noteworthy that other DFT functionals give results which are close to MP2 values.

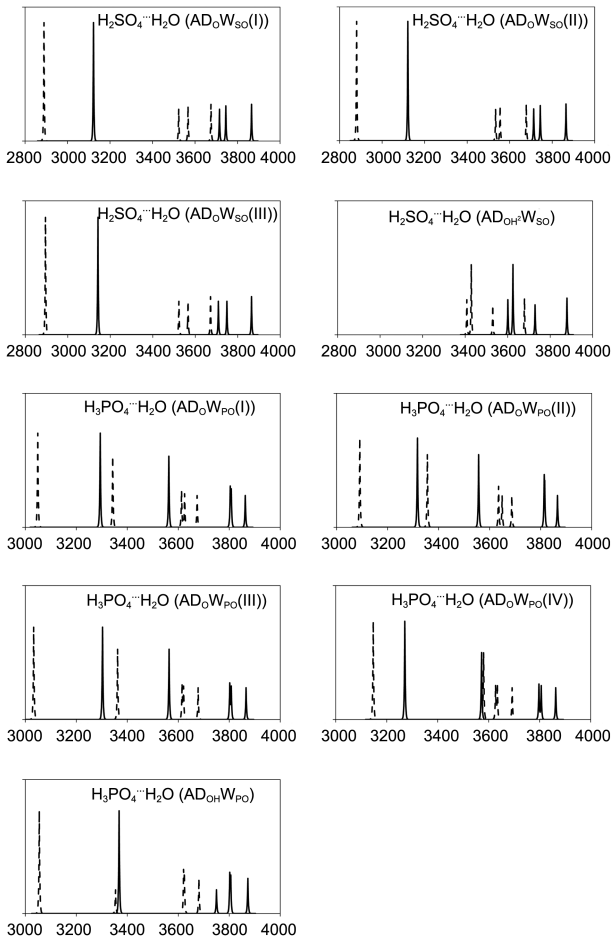

Figure 2. B3LYP/aVDZ harmonic (solid line) and anharmonic vibrational frequencies (dashed line) of monohydrated inorganic acids.

The BSSE errors given by MP2/aVDZ calculations are significantly larger when compared with DFT BSSE values. It is due to the basis set incompleteness for correlated calculations. Thus, we carried out MP2 computations with aVTZ basis set. The substantial improvement of the basis set significantly reduces the BSSE errors (by ~50%). By using Kim's extrapolate scheme, we computed MP2/CBS binding energies for both monohydrated acids. It is important to note that the energetic order of conformers is conserved at the MP2/CBS level of theory. Moreover, MP2/CBS values are very close to the BSSE-corrected MP2/aVDZ binding energies. The largest deviation between BSSE-corrected MP2/aVDZ binding energies and MP2/CBS values does not exceed ~5 kJ/mol ($AD_{OH}W_{PO}$ structure). However, for many other conformers the differences are significantly smaller.

Concluding Remarks

We carried out DFT calculations for monohydrated sulfuric and phosphoric acids. These systems are difficult to study because PES in the vicinity of the global minimum energy structure is relatively flat. In the case of monohydrated

Table 4. DFT/aVDZ and MP2/aVDZ harmonic vibrational frequencies ν of -OH stretching modes [cm^{-1}]. The subscripts denote IR intensities [10 kJ/mol]

Method	acid⋯water	Conformer	
M06-2X	$H_2SO_4 \cdots H_2O$	**AD_OW_{SO}**(I)	3108_{135} 3771_{11} 3800_{14} 3931_{14}
		AD_OW_{SO}(II)	3118_{143} 3771_{11} 3827_{14} 3934_{14}
		AD_OW_{SO}(III)	3120_{141} 3766_{11} 3819_{13} 3934_{15}
		$AD_{OH}{}^2W_{SO}$	3666_{1} 3690_{50} 3793_{9} 3945_{14}
	$H_3PO_4 \cdots H_2O$	**AD_OW_{PO}**(I)	3359_{84} 3644_{42} 3869_{16} 3872_{11} 3936_{11}
		AD_OW_{PO}(II)	3388_{76} 3644_{41} 3873_{24} 3875_{4} 3941_{12}
		AD_OW_{PO}(III)	3369_{81} 3648_{40} 3860_{14} 3872_{12} 3951_{11}
		AD_OW_{PO}(IV)	3321_{94} 3655_{37} 3863_{17} 3867_{9} 3937_{11}
		$AD_{OH}W_{PO}$	3487_{75} 3818_{5} 3858_{15} 3864_{13} 3935_{12}
ωB97X-D	$H_2SO_4 \cdots H_2O$	**AD_OW_{SO}**(I)	3241_{120} 3799_{9} 3834_{12} 3949_{12}
		AD_OW_{SO}(II)	3241_{122} 3791_{9} 3832_{13} 3946_{13}
		AD_OW_{SO}(III)	3255_{118} 3789_{10} 3837_{12} 3948_{13}
		$AD_{OH}{}^2W_{SO}$	3680_{1} 3703_{46} 3798_{10} 3962_{13}
	$H_3PO_4 \cdots H_2O$	**AD_OW_{PO}**(I)	3415_{80} 3660_{43} 3891_{15} 3893_{9} 3948_{10}
		AD_OW_{PO}(II)	3429_{69} 3652_{46} 3897_{24} 3898_{1} 3951_{10}
		AD_OW_{PO}(III)	3413_{73} 3651_{43} 3887_{12} 3894_{10} 3951_{10}
		AD_OW_{PO}(IV)	3388_{83} 3663_{39} 3886_{14} 3890_{9} 3948_{10}
		$AD_{OH}W_{PO}$	3477_{83} 3830_{5} 3888_{15} 3891_{10} 3951_{11}
B97-D	$H_2SO_4 \cdots H_2O$	**AD_OW_{SO}**(I)	3023_{122} 3659_{8} 3661_{4} 3792_{9}
		AD_OW_{SO}(II)	3023_{125} 3657_{5} 3660_{8} 3791_{10}
		AD_OW_{SO}(III)	3054_{122} 3655_{5} 3667_{8} 3794_{11}
		$AD_{OH}{}^2W_{SO}$	3056_{122} 3656_{5} 3667_{8} 3794_{11}
	$H_3PO_4 \cdots H_2O$	**AD_OW_{PO}**(I)	3157_{88} 3502_{36} 3721_{9} 3726_{8} 3782_{8}
		AD_OW_{PO}(II)	3179_{78} 3492_{38} 3733_{7} 3734_{12} 3784_{8}
		AD_OW_{PO}(III)	3167_{83} 3507_{34} 3717_{7} 3725_{7} 3784_{8}
		AD_OW_{PO}(IV)	3139_{95} 3519_{31} 3712_{7} 3724_{8} 3728_{8}
		$AD_{OH}W_{PO}$	3224_{92} 3678_{3} 3721_{9} 3723_{7} 3794_{9}
B3LYP	$H_2SO_4 \cdots H_2O$	**AD_OW_{SO}**(I)	3122_{125} 3715_{9} 3745_{11} 3866_{12}
		AD_OW_{SO}(II)	3121_{127} 3713_{9} 3744_{11} 3865_{12}
		AD_OW_{SO}(III)	3142_{123} 3709_{10} 3749_{10} 3865_{13}
		$AD_{OH}{}^2W_{SO}$	3601_{11} 3625_{44} 3729_{8} 3879_{12}
	$H_3PO_4 \cdots H_2O$	**AD_OW_{PO}**(I)	3294_{79} 3563_{45} 3804_{12} 3808_{10} 3863_{9}
		AD_OW_{PO}(II)	3317_{71} 3557_{47} 3814_{15} 3816_{9} 3866_{9}
		AD_OW_{PO}(III)	3303_{76} 3564_{44} 3802_{11} 3808_{9} 3866_{9}
		AD_OW_{PO}(IV)	3271_{86} 3572_{40} 3797_{11} 3806_{10} 3863_{9}
		$AD_{OH}W_{PO}$	3368_{94} 3750_{5} 3802_{12} 3806_{10} 3873_{11}
MP2	$H_2SO_4 \cdots H_2O$	**AD_OW_{SO}**(I)	3174_{117} 3723_{6} 3732_{12} 3887_{14}
		AD_OW_{SO}(II)	3174_{114} 3724_{8} 3731_{11} 3886_{13}
		AD_OW_{SO}(III)	3208_{111} 3726_{7} 3741_{11} 3890_{14}
		$AD_{OH}{}^2W_{SO}$	3602_{1} 3625_{45} 3734_{6} 3899_{13}
	$H_3PO_4 \cdots H_2O$	**AD_OW_{PO}**(I)	3331_{76} 3601_{37} 3802_{12} 3806_{11} 3882_{11}
		AD_OW_{PO}(II)	3358_{67} 3595_{39} 3809_{11} 3812_{14} 3885_{11}
		AD_OW_{PO}(III)	3339_{73} 3600_{36} 3805_{11} 3809_{11} 3885_{11}
		AD_OW_{PO}(IV)	3312_{83} 3611_{33} 3797_{13} 3801_{10} 3882_{11}
		$AD_{OH}W_{PO}$	3403_{83} 3752_{5} 3794_{12} 3803_{11} 3894_{12}

sulfuric acid we identified four different conformers, the monohydrated phosphoric acid forms five different molecular complexes. All these structures are compact and close in energy, which means that they are located near the global minimum energy conformer. They differ in H-orientations only. We performed DFT calculations using four different DFT functionals. It seems that DFT approach is an appropriate tool to study such specific molecular systems. At the

Table 5. B3LYP/aVDZ harmonic and anharmonic vibrational frequencies of -OH stretching modes [cm^{-1}]. The subscripts denote IR intensities [10 kJ/mol]

acid⋯water	Conformer	ν_{harm}	ν_{anharm}
$H_2SO_4 \cdots H_2O$	**AD_OW_{SO}(I)**	3122_{125} 3715_9 3745_{11} 3866_{12}	2889_{125} 3523_9 3567_{11} 3675_{12}
	AD_OW_{SO}(II)	3121_{127} 3713_9 3744_{11} 3865_{12}	2880_{127} 3534_9 3555_{11} 3678_{12}
	AD_OW_{SO}(III)	3142_{123} 3709_{10} 3749_{10} 3865_{13}	2895_{123} 3523_{10} 3566_{10} 3672_{13}
	$AD_{OH}{}^2W_{SO}$	3601_{11} 3625_{44} 3729_8 3879_{12}	3408_{11} 3429_{44} 3530_8 3679_{12}
$H_3PO_4 \cdots H_2O$	**AD_OW_{PO}(I)**	3294_{79} 3563_{45} 3804_{12} 3808_{10} 3863_9	3049_{79} 3343_{45} 3613_{12} 3625_{10} 3674_9
	AD_OW_{PO}(II)	3317_{71} 3557_{47} 3814_{15} 3816_9 3866_9	3091_{71} 3356_{47} 3635_{15} 3649_9 3687_9
	AD_OW_{PO}(III)	3303_{76} 3564_{44} 3802_{11} 3808_9 3866_9	3033_{76} 3362_{44} 3615_{11} 3621_9 3678_9
	AD_OW_{PO}(IV)	3271_{86} 3572_{40} 3797_{11} 3806_{10} 3863_9	3147_{86} 3580_5 3634_{11} 3627_{10} 3692_9
	$AD_{OH}W_{PO}$	3368_{94} 3750_5 3802_{12} 3806_{10} 3873_{11}	3055_{94} 3354_5 3621_{12} 3624_{10} 3681_{11}

B97-D level, we were not able to find $AD_{OH}{}^2W_{SO}$ structure. We computed harmonic vibrational frequencies for all possible structures. The analysis of –OH vibrational modes shows that the identification of those clusters during IRPD experiments appear to be very difficult. The comparision of various DFT functionals with MP2 approach clearly shows that the ω97X-D functional gives values (binding energies as well as geometrical parameters) which are very close to MP2 results. However, other DFT functionals give only slightly worse results.

Acknowledgments. This study was supported by research funds from Chosun University 2011.

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