

# Thermochemistry of $(\text{H}_2\text{SO}_4)_m (\text{H}_2\text{O})_n (\text{NH}_3)_k$ : A DFT Study

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**Abstract**  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$  nucleation rates in earth's atmosphere are very sensitive to thermodynamics of initial growth steps. However, reliable data on thermochemistry of small  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$  clusters are lacking. This theoretical study is dedicated to the quantum modeling of  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$  clusters using Density Functional Theory (DFT) at PW91PW91 level with the largest Pople 6-311 + + G(3df,3pd) basis set. We have obtained equilibrium geometries, and computed enthalpies, entropies, and Gibbs free energies of  $(\text{H}_2\text{SO}_4)_m (\text{H}_2\text{O})_n (\text{NH}_3)_k$  ( $n = 1, 2$ ;  $m = 1-5$ ;  $k = 0, 1$ ) formation. The obtained results have been compared with earlier theoretical studies. It has been pointed out that the application of PW91PW91 coupled with large 6-311 + + G(3df,3pd) basis set allows to improve the quality of the model predictions, and helps to avoid serious problems with  $\text{H}_2\text{SO}_4$  thermochemistry found in earlier studies.

**Keywords** Binary clusters, ternary clusters, Density Functional Theory, atmospheric nucleation

## Introduction

Quantum methods have been used to study  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$  clusters in the past. However, the quality of quantum predictions was not always satisfactory. The pioneering studies of Ianni and Bandy (1998), (1999) [1,2], in which  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$  structures were identified for the first time, were unable to predict the stability of gas-phase hydrates of sulfuric acid and ammonia bisulfate complex in agreement with experiments. More recent studies of Al Natsheh et al. (2004) [3], Kurten et al. (2006) [4], Nadykto and Yu (2007) [5] showed that insufficient accuracy of water and ammonia affinities to the sulfuric

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acid is caused by deficiencies of the B3LYP in describing intermolecular interactions in hydrogen-bonded complexes. According to Tsuzuki and Luthi (2001) [6], Natsheh et al. (2004, 2006), Kurten et al. (2006), Nadykto et al. (2006) [7], Nadykto and Yu (2007) [5], Nadykto et al. (2007) [8], PW91PW91 functional is a better choice. A comprehensive structural analysis of  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  clusters has been carried out in Ding et al. (2003) [9] using PW91PW91 method with the DNP basis set. The same combination was used in a recent study by Kurten et al. (2007), where a limited number of  $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$  structures were identified. The DNP is similar to 6-31G\*\* basis in Gaussian, but the basis functions are numerical atomic orbitals augmented by polarization functions. This basis does not include diffuse functions. While PW91PW91/DNP adequately describes first two hydration steps, the PW91PW91/DNP dimerization free energy for the sulfuric acid deviates from PW91PW91/6-311 ++ G(3df,3pd) results by  $> 2.5 \text{ kcal mol}^{-1}$  [5]. Such a big deviation, which is probably caused by the basis set quality, may lead to erroneous conclusions about the thermochemistry of the sulfuric acid, which is a key substance controlling the atmospheric nucleation. Thus, the application of a more appropriate, presumably larger, basis set is necessary.

In this paper, the structure, thermochemical properties, and dipole moments of  $(\text{H}_2\text{SO}_4)_m (\text{H}_2\text{O})_n (\text{NH}_3)_k$  ( $n = 1, 2$ ;  $m = 1-5$ ;  $k = 0, 1$ ) clusters have been studied using DFT at PW91PW91 level with large 6-311 ++ G(3df,3pd) basis set. The hydration of  $\text{H}_2\text{SO}_4$  monomer and dimer has been investigated so as the effect of ammonia on stability of  $(\text{H}_2\text{SO}_4)_m (\text{H}_2\text{O})_n$  clusters.

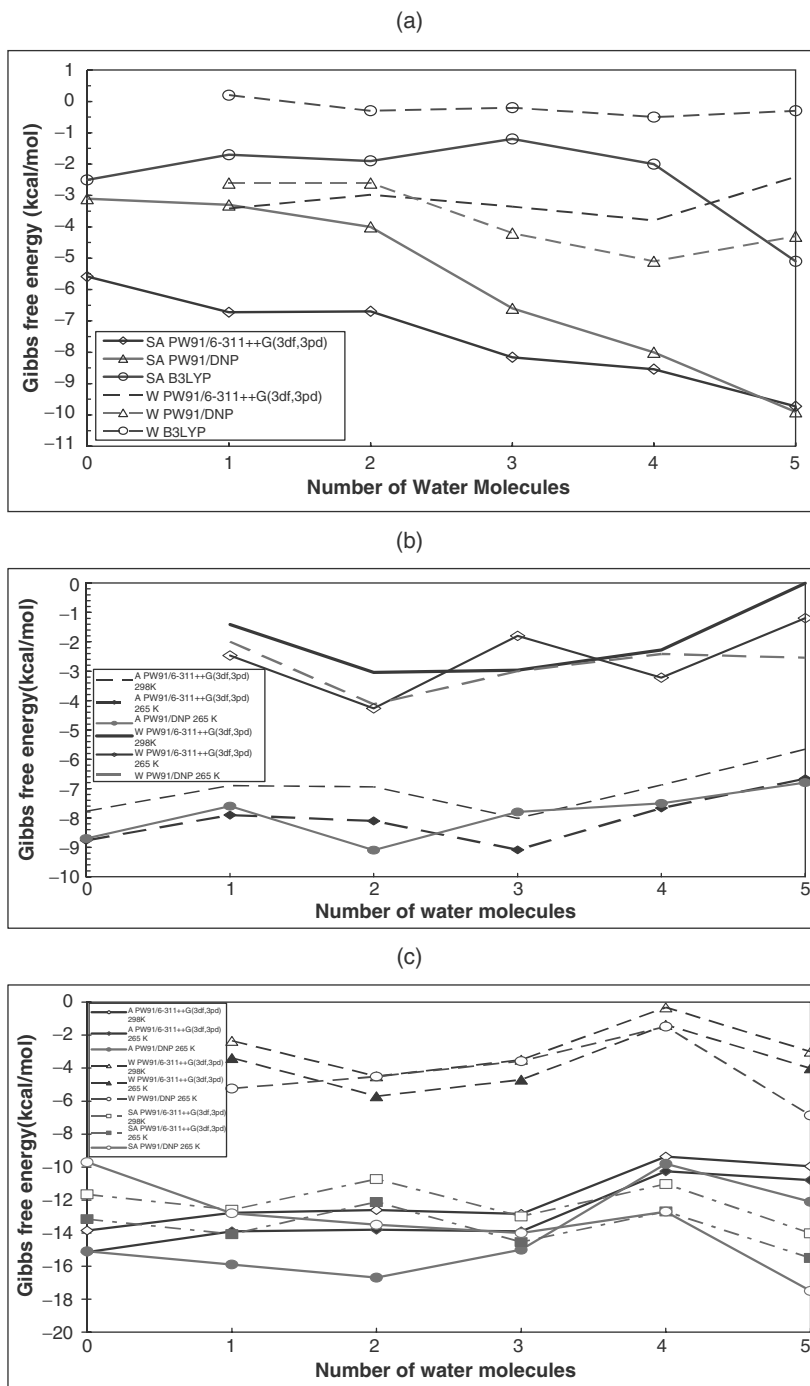
## Results and Discussion

At present time, the experimental data are available for  $(\text{H}_2\text{SO}_4) (\text{H}_2\text{O})$  only. Table 1 presents a comparison of optimized  $(\text{H}_2\text{SO}_4) (\text{H}_2\text{O})$  geometries at different levels of theory with experimental data. As seen from Table 1, PW91PW91/6-311

**Table 1** Comparison of  $(\text{H}_2\text{SO}_4) (\text{H}_2\text{O})$  geometry obtained using ab initio and DFT methods with experiments

	MP2*	Re	Ianni		Natsheh	Nadykto Yu	exp.**
			Bandy	Ding			
R(H1-O2)	0.967	0.975		0.978	0.98	0.976	0.95
R(O2-S)	1.579	1.636	1.611	1.634	1.63	1.614	1.578
R(O3-S)	1.557	1.603		1.604	1.59	1.576	1.567
R(O4-S)	1.43	1.466	1.439	1.463	1.46	1.446	1.464
R(O5-S)	1.42	1.458	1.43	1.453	1.44	1.435	1.41
R(H6-O3)	0.997	1.009	0.999	1.023	1.03	1.022	1.04
R(H6-O8)	1.654	1.651	1.682	1.621	1.61	1.61	1.645
R(H9-O8)	0.976					0.98	0.98
R(H10-O8)	0.96					0.97	0.98
R(H9-O4)	2.15	2.23	2.207	2.141		2.05	2.04

\* MP2(full)/6-311 ++ G(3df,3pd), present study; \*\* Fiacco et al. (2003) [10].



**Figure 1** Changes of Gibbs free energies associated with the formation of (a)  $(\text{H}_2\text{SO}_4)_2 (\text{H}_2\text{O})_n$ ; (b)  $(\text{H}_2\text{SO}_4) (\text{NH}_3) (\text{H}_2\text{O})_n$ ; (c)  $(\text{H}_2\text{SO}_4)_2 (\text{NH}_3) (\text{H}_2\text{O})$ . Abbreviations B3LYP, PW91/DNP, and PW91/6-311 + + G(3df,3pd) refers to studies Ianni and Bandy(2000), Ding et al.(2003) (a) and Kurten et al. (2007)(b,c), and the present study, respectively. Gibbs free energy changes were calculated at  $P = 101.3 \text{ kPa}$ .  $T = 298.15 \text{ K}$  unless specified

+ + G(3df,3pd) predictions are in best overall agreement with experiments. Another important detail is that PW91PW91/6-311 + + G(3df,3pd) is the only method that predicts longest R(H9-O4) bond length controlling the  $(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n$  stability in agreement with experiment data. The difference in the (H9-O4) bond length between PW91PW91/6-311 + + G(3df,3pd) and PW91PW91/DNP is considerable, and may be attributed to the difference in the basis set quality.

Another important detail is that a vast majority of clusters studied here is highly polar. Due to high polarity, they may be involved in the dipole-charge interaction with airborne ions enhancing the ion-mediated nucleation rates.

Figure1 presents the comparison of Gibbs free energy changes associated with the formation of  $(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n(\text{NH}_3)_k$  complexes by addition of water (W), sulfuric acid (S), and ammonia (A). As seen from Figure1(a), both Ianni and Bandy (2000) [11], and Ding et al. (2003) underestimate the affinity of sulfuric acid to  $(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n$  complexes by 1–5 kcal mol<sup>-1</sup> per step.

While B3LYP/6-311 + + G(2d,2p) predictions of Ianni and Bandy (2000) [11] consistently deviate from our results, the PW91/DNP energies at  $n = 4,5$  are quite close to ours. This suggests that PW91/DNP results could probably be used to approximate the thermochemistry of larger  $(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n$  complexes, for which a more rigorous treatment would be prohibitively expensive.

The comparison of theoretical affinities with average experimental value of -8.9 kcal mol<sup>-1</sup> for  $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_n$  ( $n = 1-10$ ;  $T = 242\text{K}$ ) leads us to conclude that the present results are in better agreement with experiments than the previous studies. The difference between hydration free energies obtained using B3LYP/6-311 + + G(2d,2p) and those obtained using PW91 with DNP and 6-311 + + G(3df,3pd) basis sets is very large. The difference between PW91/DNP and PW91/6-311 + + G(3df,3pd) is a lot smaller, yet it exceeds ~ 1 kcal mol<sup>-1</sup> per step on average. As seen from Figure 1(b), affinities of ammonia to hydrated sulfuric acid and H<sub>2</sub>O affinities to  $(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n(\text{NH}_3)_k$  predicted by two PW91 studies are quite close. However, thermochemical properties of  $(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_n(\text{NH}_3)_k$  (Figure1(c)), especially NH<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> affinities, are predicted by PW91/DNP with much less success. The performance of DNP basis set is quite different from that of 6-311 + + G(3df,3pd), and it is clear that the application of more accurate 6-311 + + G(3df,3pd) basis set leads to a significant improvement in the quality of the model predictions.

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