**Ab Initio Study of Different Acid Molecules Interacting with H$_2$O**

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**Abstract**

Using the Gaussian-03 for *ab initio* calculations, we have studied interaction of different acid molecules with a single water molecule. The molecular and supermolecular optimized structures were found with the Becke-3-Lee-Yang-Parr (B3LYP-hybrid potential) calculations of density-functional theory (DFT) methods as well as the Møller-Plesset second-order perturbation theory, using the basis set of Aug-cc-pVDZ quality and the CRENBL ECP effective core potential for molecules containing heavy iodine atom. Possible isomers of studied acids and supermolecules, consisting of acid molecules coupled with a single water molecule, are shown. Energies, zero-point energies (ZPEs), thermal enthalpies and free energies, as well as the corresponding binding energies for the theoretical methods were calculated. It was found that optimized structures of supermolecular isomers with lowest energies corresponding to the global minimum on the potential energy surfaces can be different for both theories. The simplest structure acids H$_2$S and H$_2$Se, forming acid-water supermolecules, can give clear evidence of disagreement of the two theoretical methods concerning optimization of lowest energy structures, because the B3LYP-DFT method gives the lowest-energy structure for the first supermolecular isomer, but the MP2 method for the second possible isomer. A dramatic difference between potential energy surfaces for both theories applying to the optimized structure finding of the H$_2$SO$_3$-H$_2$O supermolecular isomers was found, because MP2 supermolecular geometries cannot exist for the corresponding B3LYP-DFT ones, for which the frequency characteristics of the supermolecular isomers were also calculated. In general, the binding energies and ZPE ones for the MP2 method are 10-15\% larger than those for the B3LYP-DFT method. However, the thermal free energies for the MP2 method can be significantly smaller than those for the B3LYP-DFT method.

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1. Introduction

One of today recurrent topics of physical chemistry and chemical physics is the theoretical investigation of gas-phase clusters [1-4], including hydrogen-bonded complexes. The interaction of an acid molecule with water can lead to many different structures that could depend on chosen level of theory. It is well-known that the hydration process has important implications in the context of atmospheric chemistry and aerosol, because there occur reaction mechanisms of introduction of substantial amount of gas phase chlorine and bromine compounds into the marine troposphere [5-6]. The development of supersonic jet nozzles allowed extensive studying of different molecular clusters in complicated experiments, for instance, see in Refs. [7-11]. On the other hand, ab initio theoretical studies are widely used in addition to experimental investigations. Thus, a large set of the structural and thermochemical data were obtained in this theoretical study with quantum-mechanical methods.

In Ref. [12] was mentioned that the available structural, spectroscopic, and thermochemical data are still limited for the majority of hydrated halides. That is also true for chlorine-, bromine-, and iodine-containing acids, the recent theoretical and experimental investigations of which can be found in refs. [13-29]. Hypochlorous (HClO), hypobromous (HBrO), and hypo-iodous (HIO) acids are, probably, the simple examples and represent weak acids. Chlorous (HClO₂), bromous (HBrO₂), and iodous (HIO₂) acids of relatively weak-acid family are also well-known. Chloric acid with the chemical formula HClO₃ is known as a strong acid with pKₐ ~ - 1 and oxidizing agent. Bromic acid with the chemical formula HBrO₃ is a key reagent in the well-known Belousov-Zhabotinsky oscillating reaction and has about 62% bromine, 1% hydrogen, and 37% oxygen. Iodic acid with the chemical formula HIO₃ can be obtained as a white solid and is an insoluble compound, unlike chloric acid or bromic acid. Perchloric acid (HClO₄) is an oxoacid of chlorine and is a colorless liquid soluble in water. Perchloric acid is a strong super-acid completely dissociating in an aqueous solution comparable in strength to sulfuric acid (H₂SO₄) or nitric acid (). Perbromic acid (HBrO₄) is a strong acid and
strongly oxidizing, and is the least stable of the halogen (VII) acids. Per-iodic acid (HIO₄) has heavy iodine atom and is widely used in organic chemistry for structural analysis.

On the other hand, there is much work on experimental and theoretical investigations of strong nitric super-acid (HNO₃) that is a highly corrosive and toxic acid that can cause severe burns. Example interesting theoretical and experimental studies of nitric acid can be found in Refs. [30-36] and [37-42], respectively. Also, there exist much theoretical (in general, density-functional theory or DFT) and experimental work on studying the strong sulfur-containing super-acid, H₂SO₄, see Refs. [43-46] as well as Refs. [47-50] of DFT-study. It is thought that due to experimental difficulties in investigations of the Sulfurous acid H₂SO₃, less attention is paid to the acid study [51-52], and it is little known about the so-called Sulfonic acid, which has the same chemical formula H₂SO₃. The sulfur-containing acid with the simplest chemical formula H₂S (Sulfane or Hydrogen sulfide) is a covalent hydride structurally related to water (H₂O) since oxygen and sulfur occur in the same periodic table group. Hydrogen sulfide is weakly acidic, and references on the acid studies can be found in [53-56]. Hydrogen selenide (H₂Se) is the simplest hydride of selenium studied in Ref. [57], a colorless, flammable gas under standard conditions, and soluble in water. The properties of H₂S and H₂Se are similar. The well-known phosphorous-containing acids, phosphoric acid (H₃PO₄) and phosphorous acid (H₃PO₃), were studied in Refs. [58-62]. Phosphoric acid (H₃PO₄) also known as orthophosphoric acid or phosphoric (V) acid, is an inorganic acid and very commonly used as an aqueous solution. Phosphoric acid is also used as the electrolyte in phosphoric-acid fuel cells. Phosphorous acid [63-64], also called phosphonic acid, is one of the well-known and commonly used oxoacids of phosphorus. The other well-known acids are boric acid (H₃BO₃ or B(OH)₃) also called boracic acid or orthoboric acid, and boron oxide hydroxide (metaboric acid) with the chemical formula HBO₂. There is much work on the H₃BO₃ and HBO₂ acids used in medicine, for instance, see Refs. [65-70]. A highly valuable precursor to many chemical compounds ranging from polymers to pharmaceuticals, hydrogen cyanide is a chemical compound with the following chemical formula HCN. A solution of hydrogen cyanide in water is called hydrocyanic acid. Hydrogen cyanide is a colorless, very poisonous, and highly volatile liquid that boils slightly above room temperature at 26 °C (78.8 °F). Recent studies on the weakly acidic hydrogen cyanide can be found in Refs. [71-73]. It is noted that HCN as a simplest nitrile system can act
as both proton donor and proton acceptor systems in cluster formation that can be the case for water and alcohol molecules. The interaction of HCN with water can lead to two different structural motifs.

2. Ab initio calculations

All the calculations were performed using the GAUSSIAN-03 program [74], see also the famous books [75-77]. The minimum-energy molecular structures of all supermolecular isomers were completely optimized by using density-functional theory (DFT [78]) calculations employing Becke’s three-parameter exchange potential [79-80] and the Lee-Yang-Parr correlation functional [81] (B3LYP) as well as the Møller-Plesset [82] second-order perturbation theory (MP2) calculations employing Dunning’s augmented basis set [83-84] of the Aug-cc-pVDZ quality. In a supermolecule consisting of two molecules (for instance, in the water dimer) basis functions from one molecule can help compensate for the basis set incompleteness on the other molecule, and vice versa. This effect is known as basis set superposition error (BSSE) which will be zero in the case of a complete basis set. An approximate way of assessing the BSSE is the counterpoise (CP) correction method [85-86], in which the BSSE can be estimated as the difference between monomer energies with the regular basis and the energies calculated with the full set of basis functions for the whole supermolecules studied in this paper. In addition to the binding energies ($\Delta E$), zero-point energies ($\Delta ZPE$), the enthalpies ($\Delta H$), and the Gibbs free energies ($\Delta G$) at 298K and 1 atm are also reported for both the B3LYP and MP2 theoretical methods.

Average relativistic effective potential (AREP) and spin-orbit (SO) operators for the chemical elements of the second transition row have been published in Ref. [87], in which particular attention was focused on the portioning of the core and valence space, as well as Gaussian basis sets with contraction coefficients for the lowest energy state of each atom were introduced. Discussion of the details and complete review were given in Ref. [88]. More general reviews on the subject of effective core potentials can be also found in the literature [89-90]. The effective core potential of Ref. [87] called CRENBL ECP was used in this report to calculate structural and energetic properties of (super)-molecules containing the heavy iodine atom possessing the atomic number 53 in the periodic table of chemical elements of Mendeleev.
3. Results and discussion

It was found with the B3LYP-DFT methods using the basis set of Aug-CC-pVDZ quality that three possible isomers for the chemical formula H$_2$SO$_3$ can exist. The most stable of them, the so-called Sulfurous acid (H$_2$SO$_3$) possesses the lowest energy on the potential energy surface, and its molecular structure is shown in Figure 1a with both hydrogen atoms rotated towards the third molecular oxygen, which is not coupled with a hydrogen atom. The second, less stable H$_2$SO$_3$ isomer has its ground state energy by about 1 kcal/mol smaller and opposite-directed hydrogen atoms (see the Table and Figure 1). The so-called Sulfonic acid being the third possible H$_2$SO$_3$ isomer is the most “unstable” with its local minimum energy value of by about Hartrees that is ~ 1 kcal/mol smaller. However, a Sulfonic acid single molecule can have the strongest coupling with a single water molecule (H$_2$O) with a 10% larger binding energy $E_B$ compared with the other two isomers. Indeed, it is possible to suggest a 10% difference in energy can be treated as non-significant, and hence, one deals here with an isoenergetic case like studied in Refs. [Kim, others?]. Using the Moeller-Plesset second-order perturbation theory (MP2) [], obtained binding energies are always larger than corresponding those calculated at the hybrid B3LYP-DFT level of theory. Moreover, some optimized structures shown in Figure 1 cannot be found with the MP2-method, for instance, the structure shown in Table 1 with the largest binding energy Eb for the most stable H$_2$SO$_3$ isomer. That can be explained by the way that the potential energy surfaces (PESs) for both commonly-used methods can give even qualitatively different results concerning structure optimization. Also, for Sulfonic acid it was found that the water oxygen can interact with the H$_2$SO$_3$ molecular hydrogen coupled with sulfur atom. That is natural because an H$_2$O-molecule can readily interact with an H$_2$S-molecule [], if a sulfur atom is placed instead of an oxygen atom in a water dimer. However, in the case of O=HS-interaction for the H$_2$SO$_3$-H$_2$O complex system the twice binding energy can be obtained compared with the relatively more simple system of O-HS-interaction: an H$_2$S-H$_2$O-system.

Calculations were done with the B3LYP-DFT method, using the basis set of Aug-CC-pVDZ quality. Energy of water monomer is $E_w$(B3LYP-DFT/Aug-CC-pVDZ) = − 76.4446427 atomic units (Hartrees). It is
noted that the energy difference between the parallel-like and anti-parallel-like hydrogen orientations for H$_3$PO$_4$ is as high as the following value: $\Delta E_M(H_3PO_4, \text{B3LYP-DFT/Aug-CC-pVDZ}) = E_M(\text{anti-parallel}) - E_M(\text{parallel}) \sim 0.90$ kcal/mol. The same value for Phosphonic acid H$_3$PO$_3$ is as follows: $\Delta E_M(H_3PO_3, \text{B3LYP-DFT/Aug-CC-pVDZ}) = E_M(\text{anti-parallel}) - E_M(\text{parallel}) = \sim 1.79$ kcal/mol. This difference between the parallel-like and anti-parallel-like hydrogen orientations for Sulfuric acid H$_2$SO$_4$ two possible hydrogen orientations is as high as the following value: $\Delta E_M(H_2SO_4, \text{B3LYP-DFT/Aug-CC-pVDZ}) = E_M(\text{anti-parallel}) - E_M(\text{parallel}) \sim -1.13$ kcal/mol. The same value for Sulfurous acid H$_2$SO$_3$ is as follows: $\Delta E_M(H_2SO_3, \text{B3LYP-DFT/Aug-CC-pVDZ}) = E_M(\text{anti-parallel}) - E_M(\text{parallel}) \sim 0.93$ kcal/mol. Using the MP2 calculations, these values for H$_3$PO$_4$ are as follows: $\Delta E_M(H_3PO_4, \text{MP2/Aug-CC-pVDZ}) \sim 0.98$ kcal/mol; the value for Phosphonic acid H$_3$PO$_3$ is as follows: $\Delta E_M(H_3PO_3, \text{MP2/Aug-CC-pVDZ}) \sim 1.88$ kcal/mol; for Sulfuric acid H$_2$SO$_4$ one can calculate $\Delta E_M(H_2SO_4, \text{MP2/Aug-CC-pVDZ}) \sim -1.17$ kcal/mol; for Sulfurous acid H$_2$SO$_3$ is as follows: $\Delta E_M(H_2SO_3, \text{MP2/Aug-CC-pVDZ}) \sim 0.81$ kcal/mol.

The interaction energies $E_B$ of different molecules with a single water molecular, where $E_T$ represents the total energy of a sample molecule plus a single water molecule, $E_C$ is the corrected energy with the basis set superposition error (BSSE) correction, $E_{BSSE}$. Using the values of $E_{BSSE}$ and $E_{BC}$, the binding energy is:

$$E_{BC} = E_C - E_M - E_w,$$

and the binding energy is:

$$E_{BA} = (E_B + E_{BC} \pm E_{BSSE})/2$$

BSSE from the book

4. Conclusions
In this report, we have investigated the structural and energetic characteristics of the interaction of single acid molecules with a single water molecule. Both commonly-used theoretical methods, the Becke’s three-parameter exchange potential with the Lee-Yang-Parr correlation functional and the second-order Møller-Plesset perturbation theory, have shown good agreement for optimized structures’ finding and binding energies’ calculations, using the same Dunning’s basis set of Aug-cc-pVDZ quality and the CRENBL ECP effective core potential for molecules containing heavy iodine atom. However, some MP2 optimized structures of the acid-water supermolecules cannot be found for the corresponding B3LYP-DFT calculations that can be explained by the fact of uniqueness of each potential energy surface for the theoretical methods. That is even dramatic for the Sulfurous acid-water (H$_2$SO$_3$-H$_2$O) supermolecular isomers, because the corresponding MP2 optimized structures cannot be found for the B3LYP-DFT ones with the smallest and highest (most stable structure) binding energies.

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References

[1] Bernstein, E. R., Ed. Atomic and Molecular Clusters; Elsevier: Amsterdam, 1990.
[2] Scheiner, S. Hydrogen bonding: A theoretical perspective; Oxford University Press: Oxford, 1997.
[3] Wilson, K. R.; Cavalleri, M.; Rude, B. S.; Schaller, R. D.; Catalon, T.; Nilsson, A.; Saykally, R. J.; Pettersson, L. G. M. J. Phys. Chem. B 2005, 109, 10194.
[4] Zwier, T. S. Annu. Rev. Phys. Chem. 1996, 47, 205.
[5] E. M. Knipping, M. J. Lakin, K. L. Foster, P. Jungwirth, D. J. Tobias, R. B. Gerber, D. Dabdub, B. J. Finlayson-Pitts, Science 288, 301 (2000).
[6] S. W. Hunt, M. Roeselová, W. Wang, L. M. Wingen, E. M. Knipping, D. J. Tobias, D. B. Finlayson-Pitts, J. Phys. Chem. A 108, 11559 (2004).
[7] J. R. R. Verlet, A. E. Bragg, A. Kammrath, O. Cheshnovsky, D. M. Neumark, Science 307, 93 (2005).
[8] N. I. Hammer, J.-W. Shin, J. M. Headrick, E. G. Diken, J. R. Roscioli, G. H. Weddle, M. A. Johnson, Science 306, 675 (2004);
[9] J. M. Lisy, Int. Rev. Phys. Chem. 16, 267 (1997);
[10] G. N. Patwari, J. M. Lisy, J. Chem. Phys. 118, 8555 (2003);
[11] B. Brutschy, Chem. Rev. Washington, D.C. 100, 3891 (2000);
[12] A. C. Olleta, H. M. Lee, K. S. Kim, “Ab initio study of hydrated sodium halides NaX(H2O)1–6 (X=F, Cl, Br, and I)” JOURNAL OF CHEMICAL PHYSICS 124, 024321 (2006).
[13] B.F. Minaev, H. Agren, “Ab initio study of the singlet–triplet transitions in hypobromous acid” Journal of Molecular Structure (Theochem) 492 (1999) 53 – 66.
[14] J. Orphal, Q. Kou, F. K. Tchana, O. Pirali, J.-M. Flaud, “The ν3 bands of HOBr around 16 μm measured by high-resolution Fourier-transform spectroscopy” Journal of Molecular Spectroscopy 221 (2003) 239–243.
[15] J. Orphal, J.-M. Flaud, Q. Kou, F. K. Tchana, O. Pirali, “The far infrared rotational spectrum of HOBr: line positions and intensities” Journal of Molecular Structure 742 (2005) 153–159.
[16] T. J. Lee, J. S. Francisco, “The proton affinity of HOBr” Chemical Physics Letters 251 (1996) 400–404.
[17] L. Wang, J.-Y. Liu, Z.-S. Li, C.-C. Sun, “Ab initio and DFT theoretical studies and rate constants calculation on the reactions O (3P) atoms with HOX (X = Cl, Br)” Chemical Physics Letters 411 (2005) 225–232.
[18] J. Urban, “Optimal sub-millimeter bands for passive limb observations of stratospheric HBr, BrO, HOCI, and HO2 from space” Journal of Quantitative Spectroscopy & Radiative Transfer 76 (2003) 145–178.
[19] A. F. Jalbout, M. Solimannejad, “Reliability of gaussian based ab initio methods in the calculations of HClO and HOCl decomposition channels” Journal of Molecular Structure (Theochem) 626 (2003) 87–90.
[20] J. Hauschildt, J. Weiß, C. Beck, S.Yu. Grebenshchikov, R. Dueren, R. Schinke, J. Koput, “Unimolecular dissociation of HOCI: unexpectedly broad distribution of rate constants” Chemical Physics Letters 300 (1999) 569–576.
[21] A.F. Jalbout, X.H. Li, M. Solimannejad, “Thermochemical stability of the HO2–HOCI complex” Chemical Physics Letters 420 (2006) 204–208.
[22] M. Solimannejad, I. Alkorta, J. Elguero, “Stabilities and properties of O3–HOCI complexes: A computational study” Chemical Physics Letters 449 (2007) 23–27.
[23] G. Rothenberg, R. M. H. Beadnall, J. E. McGrady, J. H. Clark, “Competing bromination and oxidation pathways in acid bromate solutions: an experimental and theoretical study” J. Chem. Soc., Perkin Trans. 2, 2002, 630–635.
[24] K. Gupta, D.R. Roy, V. Subramanian, P.K. Chattaraj, “Are strong Brønsted acids necessarily strong Lewis acids?” Journal of Molecular Structure: THEOCHEM 812 (2007) 13–24.
[25] A. F. Jalbout, M. Solimannejad, J.K. Labanowski, “Thermochemical stability of the HO2–HClO4 complex” Chemical Physics Letters 379 (2003) 503–506.
[26] A. H. Otto, S. Schrader, T. Steiger, M. Schneider, “Gas-phase deprotonation energies of sulfuric acid, perchloric acid, chlorosulfuric acid and fluorosulfuric acid” J. Chem. Soc., Faraday Trans., 1997, 93(22), 3927 – 3930.
[27] A. D. Boesea, J.M.L. Martin, “Anharmonic force fields of perchloric acid, HClO4, and perchloric anhydride, Cl2O7. An extreme case of inner polarization” Journal of Molecular Structure 780–781 (2006) 310–316.
[28] Greenwood, N. N.; Earnshaw, A. (1997). *Chemistry of the Elements*, 2nd Edition, Oxford:Butterworth-Heinemann. ISBN 0-7506-3365-4.

[29] King, R. B. (Ed.) (1994) Encyclopedia of Inorganic Chemistry, Vol. 2, p. 658. Chichester: Wiley.

[30] Y. D. Liu, R. Zhong, “Theoretical studies on HOONO, HONOO, and HNO₃ isomers and their isomerization reactions” *Journal of Molecular Structure: THEOCHEM* 765 (2006) 143–149.

[31] M. Walker, C. A. Morrison, D. R. Allan, “Nitrilic acid monohydrates at high pressure: An experimental and computational study” *Physical Review B* 72, 224106 (2005).

[32] R. D’Auria, R. P. Turco, K. N. Houk, “Effects of Hydration on the Properties of Protonated-Water-Nitric Acid Clusters” J. Phys. Chem. A 2004, 108, 3756-3765.

[33] F.-M. Tao, “Gas phase proton transfer reaction of nitric acid-ammonia and the role of water” J. Chem. Phys. 108 (1), 193 – 202 (1998).

[34] M.-T. Nguyen, A. J. Jamka, R. A. Cazar, F.-M. Tao, “Structure and stability of the nitric acid–ammonia complex in the gas phase and in water” J. Chem. Phys. 106 (21), 8710 – 8717 (1997).

[35] Y. Miller, G.M. Chaban, R.B. Gerber, “Theoretical study of anharmonic vibrational spectra of HNO₃, HNO₃-H₂O, HNO₄: Fundamental, overtone and combination excitations” *Chemical Physics* 313 (2005) 213–224.

[36] D. J. Donaldson, J. J. Orlando, S. Amann, G. S. Tyndall, R. J. Proos, B. R. Henry, V. Vaida, “Absolute Intensities of Nitric Acid Overtones” J. Phys. Chem. A 1998, 102, 5171-5174.

[37] K. J. Feierabenda, D. K. Havey, M. E. Varner, J. F. Stanton, V. Vaida, “A comparison of experimental and calculated spectra of HNO3 in the near-infrared using Fourier transform infrared spectroscopy and vibrational perturbation theory” J. Chem. Phys. 124, 124323 (2006).

[38] S. Imai, M. Takahashi, K. Matsuba, Asuha, Y. Ishikawa, H. Kobayashi, “FORMATION AND ELECTRICAL CHARACTERISTICS OF SILICON DIOXIDE LAYERS BY USE OF NITRIC ACID OXIDATION METHOD” Acta Physica Slovaca 55(3) 305 - 313 (2005).

[39] X. Zhang, E. L. Mereand, A. W. Castleman, Jr., “Reactions of Water Cluster Ions with Nitric Acid” J. Phys. Chem. 1994, 98, 3554-3557.

[40] P. R. Fleming, M.-G. Li, T. R. Rizzo, “Infrared spectroscopy of vibrationally excited HONO₂: Shedding light on the dark states of intramolecular vibrational energy redistribution” J. Chem. Phys. 94(4) 2425 – 2437 (1991).

[41] A. Sinha, R.L.V. Wal, F.F. Crim, “The vibrationally mediated photodissociation dynamics of Nitric Acid” J. Chem. Phys. 91(5) 2929 – 2938 (1989).

[42] A. Sinha, R.L.V. Wal, F.F. Crim, “State-resolved unimolecular reactions: The vibrational overtone initiated decomposition of Nitric Acid” J. Chem. Phys. 92(1) 401 – 410 (1990).

[43] T. Loerting, K. R. Liedl, “Toward elimination of discrepancies between theory and experiment: The rate constant of the atmospheric conversion of SO₃ to H₂SO₄” PNAS (2000) 97(16) 8874 – 8878.

[44] Laura J. Larson, Mayuso Kuno, and Fu-Ming Tao, “Hydrolysis of sulfur trioxide to form sulfuric acid in small water clusters” JOURNAL OF CHEMICAL PHYSICS 112, 20 8830 – 8838 (2000)

[45] D. L. Fiacco, S. W. Hunt, K. R. Leopold, “Microwave Investigation of Sulfuric Acid Monohydrate” J. Am. Chem. Soc. 2002, 124, 4504-4511

[46] A. Aguzzi, M. J. Rossi, “The kinetics of the uptake of HNO₃ on ice, solid H₂SO₄-H₂O and solid ternary solutions of H₂SO₄-HNO₃-H₂O in the temperature range 180-211 K” Phys. Chem. Chem. Phys., 2001, 3, 3707 – 3716.

[47] H. Arstila, K. Laasonen, A. Laaksonen, “Ab initio study of gas-phase sulphuric acid hydrates containing 1 to 3 water molecules” J. Chem. Phys. 108 (3), 1031 - 1039 (1998).

[48] A. R. Bandy, J. C. Ianni, “Study of the Hydrates of H₂SO₄ Using Density Functional Theory” J. Phys. Chem. A 1998, 102, 6533-6539.

[49] P. Beichert, O. Schrems, “Complexes of Sulfuric Acid with Hydrogen Chloride, Water, Nitric Acid, Chlorine Nitrate, and Hydrogen Peroxide: An ab Initio Investigation” J. Phys. Chem. A 1998, 102, 10540-10544.

[50] S. Re, Y. Osamura, K. Morokuma, “Coexistence of Neutral and Ion-Pair Clusters of Hydrated Sulfuric Acid H₂SO₄(H₂O)ₙ (n = 1-5) - A Molecular Orbital Study” J. Phys. Chem. A 1999, 103, 3535-3547.

[51] A. F. Voegele, C. S. Tautermann, T. Loerting, A. Hallbrucker, E. Mayer, K. R. Liedl, “About the Stability of Sulfurous Acid (H₂SO₃) and Its Dimer” Chem. Eur. J. 2002, 8, No. 24 , 5644 – 5651.
[52] E. Bishenden, D. J. Donaldson, “Ab Initio Study of SO₂ + H₂O” J. Phys. Chem. A 1998, 102, 4638–4642.
[53] G. Tarczay, A. G. Csaszar, “Ab initio rovibrational spectroscopy of hydrogen sulfide” JOURNAL OF CHEMICAL PHYSICS 115, 3 1229 – 1242 (2001).
[54] M. RAIONDI, G. F. TANTARDINI, M. SIMONETTA, “Ab initio valence bond calculations. IV. H₂S, SH and related ions” MOLECULAR PHYSICS, 1975, 30, 3, 703-712.
[55] M. W. Wong, “Vibrational frequency prediction using density functional theory” Chemical Physics Letters 256 (1996) 391-399.
[56] Pak, C.-H.; Lee, H. M.; Kim, J. C.; Kim, D.-W.; Kim, K. S. “A. M. W. Wong, “Vibrational frequency prediction using density functional theory” Letters Gaussian03 (RevisionA.1), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Skoroz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 2003.
Aleksey A. Zakharenko, S. Karthikyan, K.S. Kim, “Ab Initio Study of Different Acid Molecules Interacting with H$_2$O” E-mail: kim@postech.ac.kr

[75] D.C. Young, *Computational chemistry*, Wiley, 398 pages (2001).

[76] Hehre, W. G.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley-Interscience Publication, John Wiley & Sons: New York-Chichester-Brisbane-Toronto-Singapore, 1986.

[77] J. B. Foresman, A. Frisch, “Exploring chemistry with electronic structure methods: a guide to using Gaussian” Gaussian, Inc., Pittsburgh, PA, USA (2000) 302 pages.

[78] R.G. Parr, W. Yang, “density-functional theory of atoms and molecules” Oxford university Press, New York, Clarendon Press, Oxford (1989) 333 pages.

[79] Becke, A. D.; *J. Chem. Phys.* 1993, 98, 1372.

[80] Becke, A. D.; *J. Chem. Phys.* 1993, 98, 5648.

[81] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* 1988, 37, 785.

[82] C. Møller, M.S. Plesset, Note on an Approximation Treatment for Many-Electron Systems, *Physical Review* 46(7) 618 – 622 (1934).

[83] Dunning (Jr.), T. H. *J. Chem. Phys.* 1989, 90, 1007–1023.

[84] Woon, D. E., Dunning (Jr.), T. H., *J. Chem. Phys.* 1993, 98, 1358–1371.

[85] F. Jensen, Introduction to computational chemistry, John Wiley & Sons, Chichester-New York-Weinheim-Brisbane-Singapore-Toronto (1999) 429 pages.

[86] F.B. van Duijneveldt, J.G.C.M. van Duijneveldt-van de Rijdt, J.H. van Lenthe, *Chem. Rev.* 94, 1873 (1994).

[87] L.A. LaJohn, P.A. Christiansen, R.B. Ross, T. Atashroo, W.C. Ermler, “Ab initio relativistic effective potentials with spin-orbit operators. III. Rb through Xe” *J. Chem. Phys.*, 87, 2812 – 2824 (1987).

[88] L.F. Pacios, P.A. Christiansen, *J. Chem. Phys.*, 82, 2664 (1985).

[89] M. Krauss, W.J. Stevens, *Annu. Rev. Phys. Chem.* 35, 357 (1984).

[90] P.A. Christiansen, W.C. Ermler, K.S. Pitzer, *Annu. Rev. Phys. Chem.* 36, 407 (1985).
Table 1. The energies of molecules and supermolecules as well as binding energies. The lowest energies and lowest binding energies are shown bold, and the MP2 calculations are shown italic compared with the B3LYP-DFT calculations. The MP2 calculations are given above the corresponding B3LYP-DFT energies. Note that some MP2 structures for the B3LYP ones were not found, and hence, their energies were not introduced in the Table. Here the energies (E), zero point energies (ZPE), thermal enthalpies (H), and thermal free energies (G) are given in the Hartree energy units, and the corresponding binding energies $\Delta E$, $\Delta ZPE$, $\Delta H$, and $\Delta G$ are given in kcal/mol. The CRENBL ECP effective core potential was used to calculate energies of supermolecules containing the heavy iodine atom. In the first column of the table, the labels in the parentheses for the (super)-molecular isomers corresponds to those for the (super)-molecular structures shown in Figures 1 and 2.

| Name                   | E, Hartrees | ZPE     | H       | G       | $\Delta E$, kcal/mol | $\Delta ZPE$ | $\Delta H$ | $\Delta G$ |
|------------------------|-------------|---------|---------|---------|-----------------------|--------------|------------|------------|
| $H_2O(MP2)$            | -76.26091   | -76.23958 | -76.23580 | -76.25723 | -                     | -            | -          | -          |
| $H_2O$                 | -76.4446    | -76.42341 | -76.41963 | -76.44106 | -                     | -            | -          | -          |
| $H_2SO_4d(MP2)$        | -699.06475  | -699.02675 | -699.02045 | -699.05525 | -                     | -            | -          | -          |
| $H_2SO_4(\text{trans})$| -700.28055  | -700.24300 | -700.23659 | -700.27159 | -                     | -            | -          | -          |
| $H_2SO_4-H_2O(MP2)$    | -775.34588  | -775.28290 | -775.27385 | -775.31551 | -12.69                | -10.40       | -11.05     | -1.903     |
| $H_2SO_4-H_2O(1U11t)$  | -776.74293  | -776.68058 | -776.67145 | -776.71327 | -11.13                | -8.89        | -9.56      | -0.385     |
| $H_2SO_4-H_2O(p)$      | -775.35959  | -775.28288 | -775.27387 | -775.31548 | -12.73                | -10.39       | -11.06     | -1.879     |
| $H_2SO_4-H_2O(1U111t)$ | -776.74287  | -776.68052 | -776.67139 | -776.71327 | -11.09                | -8.85        | -9.51      | -0.384     |
| $H_2SO_4(MP2)$         | -699.06289  | -699.02522 | -699.01867 | -699.05429 | -                     | -            | -          | -          |
| $H_2SO_4(cis)$         | -700.27875  | -700.24148 | -700.23486 | -700.27064 | -                     | -            | -          | -          |
| $H_2SO_4-H_2O(MP2)$    | -775.34407  | -775.28120 | -775.27206 | -775.31432 | -11.55                | -9.34        | -9.92      | -1.15      |
| $H_2SO_4-H_2O(1U11c)$  | -776.74119  | -776.67894 | -776.66975 | -776.71206 | -10.04                | -7.86        | -8.49      | 0.37       |
| $H_2SO_4-H_2O(1U12c)$  | -775.34380  | -775.28045 | -775.27151 | -775.31263 | -11.38                | -8.87        | -9.58      | -0.09      |
| $H_2SO_4-H_2O(1U12t)$  | -776.73931  | -776.67662 | -776.66750 | -776.70970 | -8.86                 | -6.40        | -7.08      | 1.85       |
| $H_2SO_4-H_2O(1U11c)$  | -775.33002  | -775.26908 | -775.25847 | -775.30624 | -2.74                 | -1.73        | -1.40      | 3.92       |
| $H_2SO_4-H_2O(1U10c)$  | -776.72768  | -776.66750 | -776.65661 | -776.70670 | -1.56                 | -0.09        | -0.24      | 3.74       |
| $H_2SO_4(MP2)$         | -624.01878  | -623.98708 | -623.98107 | -624.01499 | -                     | -            | -          | -          |
| $H_2SO_4(p)$           | -625.07765  | -625.04605 | -625.00460 | -625.07395 | -                     | -            | -          | -          |
| $H_2SO_4-H_2O(MP2)$    | -700.29837  | -700.24089 | -700.23255 | -700.27197 | -11.72                | -8.93        | -9.84      | 0.16       |
| $H_2SO_4-H_2O(1U12sp)$ | -701.53721  | -701.48106 | -701.47170 | -701.51191 | -9.36                 | -6.71        | -7.55      | 1.95       |
| $H_2SO_4-H_2O(1U12c)$  | -700.29665  | -700.23982 | -700.23114 | -700.27185 | -10.64                | -8.26        | -8.95      | 0.23       |
| $H_2SO_4-H_2O(1U11sp)$ | -701.53700  | -701.48042 | -701.47177 | -701.51228 | -9.23                 | -6.87        | -7.60      | 1.71       |
| $H_2SO_4-H_2O(1U12sp)$ | -701.52625  | -701.47145 | -701.46138 | -701.50787 | -2.48                 | -1.24        | -1.08      | 4.49       |
| $H_2SO_4-H_2O(1U10sp)$ | -701.52244  | -701.46871 | -701.45785 | -701.50718 | -0.09                 | 0.48         | 1.14       | 4.92       |
| $H_2SO_4-H_2O(1U00sp)$ | -701.53796  | -701.48116 | -701.47264 | -701.51291 | -9.83                 | -7.34        | -8.15      | 1.32       |
| $H_2SO_4-H_2O(1U11sp)$ | -700.28656  | -700.23131 | -700.22154 | -700.26485 | -4.31                 | -2.92        | -2.93      | 4.63       |
| $H_2SO_4-H_2O(1U02sp)$ | -701.52574  | -701.47097 | -701.46092 | -701.50615 | -2.16                 | -0.94        | -0.79      | 5.56       |
| $H_2SO_4-H_2O(1U12sp)$ | -700.28563  | -700.23057 | -700.22062 | -700.26629 | -3.73                 | -2.46        | -2.35      | 3.73       |
| $H_2SO_4-H_2O(1U01sp)$ | -701.53700  | -701.48042 | -701.47177 | -701.51228 | -9.23                 | -6.87        | -7.60      | 1.71       |
Aleksey A. Zakharenko, S. Karthikyan, K.S. Kim, “Ab Initio Study of Different Acid Molecules Interacting with H₂O” E-mail: kim@postech.ac.kr

| Acid Molecule | E(dbar) | E(dbar) | E(dbar) | E(dbar) | E(dbar) | E(dbar) |
|---------------|---------|---------|---------|---------|---------|---------|
| HSO₃(1U11pa)  | -567.90391 | -567.86147 | -567.85460 | -567.89029 | -567.89029 | -567.89029 |
| HSO₃(1U11pa)  | -568.94357 | -568.90125 | -568.89438 | -568.90000 | -568.90000 | -568.90000 |
| HSO₃(1U11pa)  | -568.94758 | -568.90518 | -568.89847 | -568.93371 | -568.93371 | -568.93371 |
| HSO₃(1U11pa)  | -644.18446 | -644.11649 | -644.10713 | -644.14904 | -644.14904 | -644.14904 |
| HSO₃(1U11pa)  | -645.40428 | -645.33671 | -645.32729 | -645.36926 | -645.36926 | -645.36926 |
| HSO₃(1U11pa)  | -645.39751 | -645.33138 | -645.32078 | -645.36788 | -645.36788 | -645.36788 |
| HSO₃(1U11pa)  | -645.40214 | -645.33612 | -645.32567 | -645.37153 | -645.37153 | -645.37153 |
| HSO₃(1U11pa)  | -644.18322 | -644.11566 | -644.10618 | -644.14827 | -644.14827 | -644.14827 |
| HSO₃(1U11pa)  | -645.40248 | -645.33611 | -645.32587 | -645.37113 | -645.37113 | -645.37113 |
| HSO₃(1U11pa)  | -645.46926 | -644.11665 | -644.10732 | -644.14901 | -644.14901 | -644.14901 |
| HSO₃(1U11pa)  | -645.40431 | -645.33669 | -645.32733 | -645.36905 | -645.36905 | -645.36905 |

-657.90943 -567.86678 -567.86054 -567.89518 -567.89518 -567.89518

HPO₃(1U11pa) -643.01739 -642.96931 -642.96206 -642.99877 -642.99877 -642.99877

HPO₃(1U11pa) -644.21347 -644.16560 -644.15825 -644.19526 -644.19526 -644.19526

HPO₃(1U11pa) -719.30076 -719.22718 -719.21745 -719.26078 -719.26078 -719.26078

HPO₃(1U11pa) -720.67652 -720.60332 -720.59356 -720.63672 -720.63672 -720.63672

HPO₃(1U11pa) -720.67610 -720.60310 -720.59316 -720.63684 -720.63684 -720.63684

HPO₃(1U11pa) -720.67581 -720.60270 -720.59292 -720.63598 -720.63598 -720.63598

HPO₃(1U11pa) -567.90391 -567.86147 -567.85460 -567.89029 -567.89029 -567.89029

HPO₃(1U11pa) -568.94357 -568.90125 -568.89438 -568.90000 -568.90000 -568.90000

HPO₃(1U11pa) -568.94758 -568.90518 -568.89847 -568.93371 -568.93371 -568.93371

HPO₃(1U11pa) -644.18446 -644.11649 -644.10713 -644.14904 -644.14904 -644.14904

HPO₃(1U11pa) -645.40428 -645.33671 -645.32729 -645.36926 -645.36926 -645.36926

HPO₃(1U11pa) -645.39751 -645.33138 -645.32078 -645.36788 -645.36788 -645.36788

HPO₃(1U11pa) -645.40214 -645.33612 -645.32567 -645.37153 -645.37153 -645.37153

HPO₃(1U11pa) -644.18322 -644.11566 -644.10618 -644.14827 -644.14827 -644.14827

HPO₃(1U11pa) -645.40248 -645.33611 -645.32587 -645.37113 -645.37113 -645.37113

HPO₃(1U11pa) -645.46926 -644.11665 -644.10732 -644.14901 -644.14901 -644.14901

HPO₃(1U11pa) -645.40431 -645.33669 -645.32733 -645.36905 -645.36905 -645.36905

-657.90943 -567.86678 -567.86054 -567.89518 -567.89518 -567.89518

HPO₃(p) -656.94195 -656.89975 -656.89348 -656.92811 -656.92811 -656.92811

HPO₃(p) -644.17778 -644.11144 -644.10152 -644.14318 -644.14318 -644.14318

HPO₃(p) -645.39076 -645.32528 -645.31505 -645.36061 -645.36061 -645.36061

HPO₃(p) -644.17744 -644.11119 -644.10116 -644.14617 -644.14617 -644.14617

HPO₃(p) -645.39128 -645.32568 -645.31552 -645.36118 -645.36118 -645.36118

HPO₃(p) -644.19121 -644.12295 -644.11437 -644.15495 -644.15495 -644.15495

-758.508 -57.39 -5.79 -3.59

-13.10 -10.41 -11.32 -1.59
### Study of Different Acid Molecules Interacting with H\(_2\)O

| Molecule                  | Energy (MP2) (kJ/mol) | Energy (ap) (kJ/mol) | Energy (lower) (kJ/mol) | Difference (kJ/mol) |
|---------------------------|-----------------------|----------------------|-------------------------|---------------------|
| H\(_2\)PO\(_4\)          | -116.5                | -9.85                | -9.89                   | 0.03                |
| H\(_2\)PO\(_4\)         | -8.95                 | 0.03                 |                         |                     |

*Note: The energies are calculated using different methods and may not be directly comparable.*
| Compound | E(Im) (MP2) | E(lower) (MP2) | E(Im) (O2) | E(lower) (O2) |
|----------|-------------|----------------|-------------|--------------|
| HClO | -611.51052 | -611.47432 | -611.46641 | -611.50439 |
| HClO | -612.44142 | -612.40527 | -612.39740 | -612.43541 |
| HClO | -611.51815 | -611.48040 | -611.47330 | -611.51093 |
| HClO | -612.44900 | -612.41150 | -612.40439 | -612.44175 |
| HClO | -612.44866 | -612.41129 | -612.40410 | -612.44155 |
| HClO | -612.44182 | -612.40519 | -612.39757 | -612.43642 |
| HClO | -610.18816 | -610.17178 | -610.16702 | -610.19764 |
| HClO | -611.11090 | -611.09481 | -611.09004 | -611.12068 |
| HClO | -686.46664 | -686.42488 | -686.41756 | -686.45463 |
| HClO | -687.57126 | -687.53009 | -687.52275 | -687.55988 |
| HClO | -686.45729 | -686.41738 | -686.40891 | -686.44910 |
| HClO | -687.56005 | -687.52075 | -687.51203 | -687.55340 |
| HClO | -686.45759 | -686.41714 | -686.40887 | -686.44959 |
| HClO | -687.56239 | -687.52259 | -687.51415 | -687.55583 |
| HClO | -686.45686 | -686.41712 | -686.40847 | -686.44953 |
| HClO | -687.56127 | -687.52192 | -687.51322 | -687.55510 |
| HClO | -686.46643 | -686.42462 | -686.41730 | -686.45435 |
| HClO | -687.57116 | -687.52998 | -687.52262 | -687.55979 |
| HClO | -685.16792 | -685.14761 | -685.14185 | -685.17556 |
| HClO | -686.25447 | -686.23468 | -686.22896 | -686.26246 |
| HClO | -761.43748 | -761.39420 | -761.38432 | -761.42923 |
| HClO | -762.70492 | -762.66217 | -762.65230 | -762.69701 |
| HClO | -761.44438 | -761.39861 | -761.39033 | -761.43047 |
| HClO | -762.71406 | -762.66919 | -762.66992 | -762.70097 |
| HClO | -761.43935 | -761.39526 | -761.38601 | -761.42847 |
| HClO | -762.70444 | -762.66140 | -762.65175 | -762.69539 |
| HClO | -762.70421 | -762.66145 | -762.65159 | -762.69686 |
| HClO | -760.12789 | -760.10182 | -760.09586 | -760.13022 |
| HClO | -761.37488 | -761.35035 | -761.34483 | -761.37832 |
| HClO | -761.37538 | -761.35051 | -761.34434 | -761.37920 |
| HClO | -856.40671 | -856.35574 | -856.34688 | -856.38876 |
| HClO | -837.83628 | -837.78690 | -837.77781 | -837.82028 |
| HClO | -856.40759 | -856.35641 | -856.34763 | -856.38932 |
| HClO | -837.83693 | -837.78749 | -837.77835 | -837.82164 |
| HClO | -837.82204 | -837.77456 | -837.76395 | -837.81232 |
| HBrO | -2648.03692 | -2648.02755 | -2648.02363 | -2648.05194 |
| HBrO | -2648.13700 | -2648.12430 | -2648.12037 | -2648.14850 |
| HBrO | -2649.84942 | -2649.84097 | -2649.83699 | -2649.86543 |
| HBrO | -2649.94485 | -2649.93216 | -2649.92822 | -2649.95636 |
| HBrO | -2724.40604 | -2724.37000 | -2724.36219 | -2724.40063 |
| HBrO | -2726.39582 | -2726.35974 | -2726.35201 | -2726.39024 |
| HBrO | -2724.41033 | -2724.37308 | -2724.36584 | -2724.40560 |
| HBrO | -2726.40017 | -2726.36306 | -2726.35586 | -2726.39456 |
| HBrO | -2724.40994 | -2724.37277 | -2724.36549 | -2724.40447 |
| HBrO | -2726.39995 | -2726.36299 | -2726.35669 | -2726.39461 |
| HBrO | -2724.40489 | -2724.36825 | -2724.36073 | -2724.40061 |
| HBrO | -2726.39441 | -2726.35811 | -2726.35043 | -2726.39120 |

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| Compound                      | E(-2021 a.u.)   | E(-2022 a.u.)   | E(-2023 a.u.)   | E(-2024 a.u.)   | Ref.   |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|--------|
| HBrO (MP2)                    | -185.20818      | -185.19959      | -185.1964       | -185.2248       | -      |
| HBrO (MP2) lower              | -185.30649      | -185.29229      | -185.2892       | -185.3180       | -      |
| HIO (lower)                   | -187.17718      | -187.16945      | -187.1654       | -187.1948       | -      |
| HIO (MP2)                     | -263.7721       | -263.54127      | -263.5335       | -263.5722       | -      |
| HIO (1U00)                    | -263.72435      | -263.68827      | -263.6806       | -263.7190       | -      |
| HIO (1U00)                    | -263.57697      | -263.54015      | -263.5327       | -263.5728       | -      |
| HIO (1U00)                    | -263.72299      | -263.68624      | -263.6789       | -263.7185       | -      |
| HIO (1U00)                    | -263.57682      | -263.54014      | -263.5335       | -263.5711       | -      |
| HIO (1U00)                    | -263.72284      | -263.68630      | -263.6788       | -263.7190       | -      |
| HIO (1U00)                    | -263.57525      | -263.53853      | -263.53127      | -263.5706       | -      |
| HIO (1U00)                    | -263.72052      | -263.68408      | -263.67670      | -263.71635      | -      |
| HBrO (MP2)                    | -263.28542      | -263.26985      | -263.26492      | -263.29780      | -      |
| HBrO                          | -263.42021      | -263.40494      | -263.39996      | -263.43293      | -      |
| HBrO (1U11)                   | -336.56710      | -336.52635      | -336.51883      | -336.55797      | -      |
| HBrO (1U11)                   | -338.88078      | -338.84062      | -338.83293      | -338.87253      | -      |
| HBrO (1U01)                   | -336.55992      | -336.52040      | -336.51209      | -336.55298      | -      |
| HBrO (1U01)                   | -338.87410      | -338.83499      | -338.82655      | -338.86794      | -      |
| HBrO (1U02)                   | -336.56063      | -336.52069      | -336.51251      | -336.55431      | -      |
| HBrO (1U10)                   | -338.87577      | -338.83651      | -338.82809      | -338.87080      | -      |
| HBrO (1U10)                   | -336.56240      | -336.52253      | -336.51445      | -336.55480      | -      |
| HBrO (1U10)                   | -338.87822      | -338.83856      | -338.83054      | -338.87070      | -      |

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| Molecule              | Energy (MP2)         | Energy (i''1U11) | Energy (i1U20) | Energy (i1U11) | Energy (MP2) | Energy (i''1U11) | Energy (i1U20) | Energy (i1U11) |
|-----------------------|----------------------|------------------|----------------|----------------|----------------|------------------|----------------|----------------|
| HIO₂·H₂O              | -336.56686           | -336.52608       | -336.51857     | -336.55768     | -12.88         | -10.45           | -11.20         | -1.66          |
| HIO₂·H₂O(i''1U11)     | -338.8068            | -338.84052       | -338.83280     | -338.87246     | -9.93          | -7.64            | -8.29          | 0.96           |
| HIO₃                  | -355.30904           | -335.29070       | -335.28445     | -335.32090     |                |                 |                |                |
| HIO₃(i''1U11)         | -337.61367           | -337.59580       | -337.58945     | -337.62628     |                |                 |                |                |
| HIO₃·H₂O              | -411.58734           | -411.54460       | -411.53516     | -411.57956     | -10.91         | -8.99            | -9.36          | 0.90           |
| HIO₃·H₂O(i''1U11)     | -414.07321           | -414.03101       | -414.02145     | -414.06603     | -9.35          | -7.40            | -7.76          | 0.83           |
| HIO₃·H₂O(MP2)         | -411.59080           | -411.54665       | -411.53827     | -411.57979     | **-13.08**     | **-10.28**       | **-11.31**     | **-1.04**      |
| HIO₃·H₂O(i''1U11)     | -414.07642           | -414.03295       | -414.02450     | -414.06608     | **-11.37**     | **-8.62**        | **-9.67**      | **0.79**       |
| HIO₄·H₂O              | -410.27638           | -410.25449       | -410.24721     | -410.28727     |                |                 |                |                |
| HIO₄·H₂O(MP2)         | -410.27643           | -410.25448       | -410.24729     | -410.28583     | **-0.03**      | -                | -              |                |
| HIO₄                  | -412.75468           | -412.73355       | -412.72706     | -412.76382     |                | -                | -              | -              |
| HIO₄(i''1U11)         | -412.75486           | -412.73359       | -412.72631     | -412.76497     | **-0.11**      | -                | -              |                |
| HIO₄·H₂O(MP2)         | -486.55877           | -486.51160       | -486.50197     | -486.54731     | **-13.449**    | **-11.013**      | **-11.850**    | **-2.663**     |
| HIO₄·H₂O(i''1U11)     | -489.21846           | -489.17216       | -489.16243     | -489.20714     | -11.894        | -9.507           | -10.349        | -0.696         |
| HIO₄·H₂O(MP2)         | -486.55877           | -486.51161       | -486.50197     | -486.54742     | **-13.449**    | **-11.017**      | **-11.850**    | **-2.733**     |
| HIO₄·H₂O(i''1U11)     | -489.21846           | -489.17216       | -489.16244     | -489.20718     | **-11.895**    | **-9.513**       | **-10.351**    | **-0.717**     |
| HIO₄·H₂O(MP2)         | -486.55877           | -486.51160       | -486.50197     | -486.54731     |                | -                | -              |                |
| HIO₄·H₂O(i''1U11)     | -489.21846           | -489.17216       | -489.16244     | -489.20718     | -11.895        | -9.513           | -10.351        | -0.717         |
| HIO₄·H₂O(MP2)         | -486.55877           | -486.51160       | -486.50197     | -486.54731     |                | -                | -              |                |
| HIO₄·H₂O(i''1U11)     | -489.21846           | -489.17216       | -489.16244     | -489.20718     | -11.895        | -9.513           | -10.351        | -0.717         |

* – the energy difference in kcal/mol between the isomers.

[1] S. Re, Y. Osamura, K. Morokuma, "" Journal of Physical Chemistry A 103(18) 3535-3547 (1999).
[2] H. Arstila, K. Laasonen, A. Laaksonen, "" Journal of Chemical Physics 108(3) 1031 – 1039 (1998).
[3] P. Beichert, O. Schrems, "" Journal of Physical Chemistry A 102(51) 10540 – 10544 (1998).
[4] C.-H. Pak, H. M. Lee, J. C. Kim, D.-W. Kim, K. S. Kim, Structural Chemistry 16(3) 187 – 202 (2005).
[5] T. Malaspina, E. E. Fileti, J. M. Riveros, S. Canuto, "" Journal of Physical Chemistry A 110(34) 10303 – 10308 (2006).
Table 2. The frequencies [cm\(^{-1}\)] for the supermolecular isomers of water-coupled Sulfurous acid \(\text{H}_2\text{SO}_3\), using B3LYP-DFT/Aug-cc-\(p\)VDZ level of theory. In the parentheses are given the optimized structure labels given in Table 1 for the \(\text{H}_2\text{SO}_3\) supermolecular isomers.

| \(\text{H}_2\text{SO}_3\) (1U'11sp) | \(\text{H}_2\text{SO}_3\) (1U02sp) | \(\text{H}_2\text{SO}_3\) (1U12sp) | \(\text{H}_2\text{SO}_3\) (1U01sp) | \(\text{H}_2\text{SO}_3\) (1U00sp) | \(\text{H}_2\text{SO}_3\) (1U11sp) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 49              | 29.5            | 37              | 17              | 18              | 47              |
| 163             | 29.9            | 45              | 21              | 27              | 172             |
| 194             | 92              | 98              | 39              | 108             |
| 343             | 277             | 399             | 319             | 154             | 371             |
| 409             | 334             | 429             | 361             | 314             | 415             |
| 476             | 392             | 474             | 405             | 379             | 477             |
| 795             | 713             | 738             | 728             | 727             | 794             |
| 1046            | 1074            | 1077            | 1075            | 1077            | 1050            |
| 1133            | 1098            | 1157            | 1095            | 1092            | 1136            |
| 3639            | 3700            | 3582            | 3700            | 3698            | 3622            |
| 3707            | 3785            | 3627            | 3749            | 3788            | 3701            |
| 1046            | 3885            | 3871            | 3882            | 3896            | 3860            |
**Figure 1.** The system configurations for optimized geometries (B3LYP/aug-cc-pVDZ). The label under each (super)molecular structure corresponds to that in the first column of Table 1.
Figure 1. (continue) The system configurations for optimized geometries (B3LYP/aug-cc-pVDZ). The label under each (super)molecular structure corresponds to that in the first column of Table 1.
Figure 2. The system configurations for optimized geometries (B3LYP/aug-cc-pVDZ). The CRENBL ECP effective core potential was used for the heavy iodine atom. The label under each (super)molecular structure corresponds to that in the first column of Table 1.

| Acid | Label | Diagram |
|------|-------|---------|
| HClO (hypochlorous acid) | c1U00 | ![Diagram](image1) |
| | c1U01 | ![Diagram](image2) |
| | c1U'01 | ![Diagram](image3) |
| | c1U''01 | ![Diagram](image4) |
| | (lowest) | ![Diagram](image5) |
| HClO₂ (chlorous acid) | c'1U11 | ![Diagram](image6) |
| | c'1U01 | ![Diagram](image7) |
| | c'1U10 | ![Diagram](image8) |
| | c''1U10 | ![Diagram](image9) |
| | (lowest) | ![Diagram](image10) |
| HClO₃ (chloric acid) | c1U20 | ![Diagram](image11) |
| | c1U11 | ![Diagram](image12) |
| | c'1U'01 | ![Diagram](image13) |
| | c'1U'10 | ![Diagram](image14) |
| HClO₄ (perchloric acid) | 1Uc11 | ![Diagram](image15) |
| | 1Uc11 | ![Diagram](image16) |
| | 1Uc10 | ![Diagram](image17) |
| HBrO (hypobromous acid) | b1U00 | ![Diagram](image18) |
| | b1U01 | ![Diagram](image19) |
| | b1U'01 | ![Diagram](image20) |
| | b1U''01 | ![Diagram](image21) |
| | (lowest) | ![Diagram](image22) |
| HBrO₂ (bromous acid) | b'1U11 | ![Diagram](image23) |
| | b'1U01 | ![Diagram](image24) |
| | b'1U10 | ![Diagram](image25) |
| | b''1U10 | ![Diagram](image26) |
| | (lowest) | ![Diagram](image27) |
| HBrO₃ (bromic acid) | b1U20 | ![Diagram](image28) |
| | b1U11 | ![Diagram](image29) |
| | b'1U11 | ![Diagram](image30) |
| HBrO₄ (perbromic acid) | 1U'b11 | ![Diagram](image31) |
| | 1Ub11 | ![Diagram](image32) |
| | (lowest) | ![Diagram](image33) |
Figure 2. (continue) The system configurations for optimized geometries (B3LYP/aug-cc-pVDZ). The CRENBL ECP effective core potential was used for the heavy iodine atom. The label under each (super)molecular structure corresponds to that in the first column of Table 1.

| HIO  | HIO₂ | HIO₃ | HIO₄  |
|------|------|------|-------|
| (hypo-iodous acid) | (iodous acid) | (iodic acid) | (per-iodic acid) |
| (i1U00) | (i'1U11) | (i1U20) | (1Ui11) |
| (i1U01) | (i'1U01) | (i1U11) | (1Ui1) |
| (i1U'01) | (i'1U10) | (i'1U'01) | (iU'i1) |
| (i1U''01) | (i''1U10) | | |