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RESEARCH ARTICLE

# THE QUANTUM MECHANICAL INVESTIGATION OF THE INTERACTIONS BETWEEN $H_2SO_4$ AND $HNO_3$ MOLECULES AND WATER CLUSTERS

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## Abstract

Nitric acid and sulfuric acid can form various hydrogen bonds with each other, creating stable species with water molecules. Additionally, these acid molecules are also significant from an atmospheric perspective and play an important role in atmospheric chemistry. This theoretical study focuses on the analysis of intermolecular interactions in structures obtained by scanning the potential energy surface of clusters formed by nitric acid and sulfuric acid with two and three water molecules. In the structures obtained with three water molecules, the ionic forms of these acid molecules were observed. The most stable structures energetically are those where nitric acid acts as a proton donor to sulfuric acid. The results of all the structures obtained were analyzed structurally, energetically, and spectroscopically.

**Keywords**

$H_2SO_4$,
$HNO_3$,
Water,
Intermolecular Interaction,
Quantum Mechanical
Calculation

**Time Scale of Article**

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## 1. INTRODUCTION

Sulfuric acid, nitric acid, and water are substances abundantly found in nature and play an active role in many heterogeneous reactions, particularly those occurring in the atmosphere. Most of these reactions are associated with phenomena that affect human life, such as acid rain and the depletion of the ozone layer in the stratosphere. Specifically, it is known that many heterogeneous reactions responsible for the depletion of the ozone layer occur in Polar Stratospheric Clouds (PSC) located in the upper layers of the stratosphere [1-5]. It has been suggested that the majority of these clouds consist of supercooled ternary solutions (STS) formed by $H_2SO_4$, $HNO_3$, and $H_2O$ molecules, with a smaller portion composed of nitric acid trihydrates (NAT) and ice particles. Furthermore, sulfuric acid is considered an important compound involved in the early stages of cloud formation in the atmosphere [6] and central to new particle formation at atmospheric concentrations [7], with interactions with water, ammonia, and other species being considered as the initiation of this formation [8-10]. It is known that $H_2SO_4/H_2O$ binary aerosols play a role in the formation of $H_2SO_4/HNO_3/H_2O$ (STS) particles, which constitute a large portion of PSCs. Numerous experimental studies on $H_2SO_4/HNO_3/H_2O$ (STS) particles exist in the literature [3,11-13], but their composition and formation mechanisms are still not fully understood [5].

With the discovery of polar stratospheric clouds, interest has increased in molecules important for the atmosphere, particularly strong acid molecules (such as $HNO_3$, $H_2SO_4$, and HCl). There are numerous experimental and theoretical studies in the literature on nitric acid and its hydrates [14-19]. Additionally,

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*Corresponding Author: minebalci@sdu.edu.tr most of the heterogeneous reactions leading to the depletion of the ozone layer are catalyzed on ice surfaces. Ice surfaces contain active sites for the interactions of strong adsorbates, which are the cause of many chemical phenomena. The ability of strong acid molecules to form strong hydrogen bonds enhances the importance of intermolecular interactions in studies focused on these molecules. Specifically, the solvation and ionization of strong acid adsorbates on ice surfaces or within water molecules are among the topics actively researched in the scientific community [20-23]. Moreover, understanding how the interactions of multiple strong acids ($H_2SO_4$ and $HNO_3$) change on ice surfaces or water molecules is considered an important area of study. However, before analyzing large (bulk) systems, it is always advantageous to study smaller clusters. Therefore, this study provides a detailed analysis of the interactions of $H_2SO_4$ and $HNO_3$ molecules on clusters containing multiple water molecules.

There are studies in the literature on the binary systems of $HNO_3/H_2O$, $H_2SO_4/H_2O$, and $H_2SO_4/HNO_3$. Particularly, many studies have been conducted on the complexes formed by $HNO_3$ and $H_2SO_4$ molecules with water, which are important in atmospheric chemistry. These studies have been performed using experimental and quantum mechanical methods [17, 24-30]. It has been found that the stable $HNO_3 \cdots H_2O$ dimer has a cyclic structure, and the strong hydrogen bond is proposed to form between the acidic hydrogen of nitric acid and the oxygen of water. The interaction energy for this dimer structure has been calculated to be approximately between -7 and -10 kcal/mol in studies performed at different levels and with different basis sets [30].

Unlike $HNO_3$, $H_2SO_4$ has two protons. Potential energy surface scans for the $H_2SO_4$ monomer structure have shown that the trans conformation of sulfuric acid is more energetically stable than the cis conformation [31]. The interactions between sulfuric acid and water molecules have also been examined. In the sulfuric acid monohydrate structure, the strong hydrogen bond forms between the oxygen of water and the hydrogen of sulfuric acid. The structure in which the trans conformation of $H_2SO_4$ interacts with water has been found to be the most stable structure in the literature [32-38]. There are two studies on the $H_2SO_4 \cdots HNO_3$ dimer [38, 39]. In the most stable structure, both nitric acid and sulfuric acid act as proton donors to each other.

There are few studies in the literature regarding the interactions of $H_2SO_4$ and $HNO_3$ with water molecules. Theoretical studies have examined $H_2SO_4/HNO_3/H_2O$ ternary clusters and explored the stability of these complex structures formed through hydrogen bonds [40-42]. However, there is no existing study on the interactions of $H_2SO_4$ and $HNO_3$ with clusters containing multiple water molecules. Therefore, this study analyzes the intermolecular interactions of $H_2SO_4$ and $HNO_3$ molecules on clusters containing two and three water molecules.

## 2. MATERIALS AND METHODS

In this study, the Gaussian 09 software package was used for electronic calculations [43]. The selection of the structural parameters for the $H_2SO_4$, $HNO_3$, and $H_2O$ monomer molecules was made by comparing them with available experimental gas-phase values in the literature. Since ab initio calculations are entirely based on static computations, the results obtained are considered as gas-phase values. The Density Functional Theory (DFT) method was employed in the calculations, with the M062X functional, which is known for its reliable description of non-covalent interactions. Additionally, the aug-cc-pvdz basis set, which provides good results for hydrogen-bonded systems, was used [44].

Table 1 presents the calculated bond lengths and bond angles for the $H_2SO_4$, $HNO_3$, and $H_2O$ monomer molecules, along with their corresponding experimental values.

**Table 1**. Structural parameters $H_2SO_4$, $HNO_3$, and $H_2O$ molecules. Bond lengths (r) are given in Å, and bond angles (a) are given in degrees.

| Structural parameters | M062X/aug-cc-pvdz | Experimental * |
|---|---|---|
| $H_2SO_4$ (trans) | | |
| r(O-H) | 0.97 | 0.97 |
| r(HO-S) | 1.62 | 1.57 |
| r(S-O) | 1.45 | 1.42 |
| a(H-O-S) | 107.6 | 108.5 |
| a(OH-S-O) | 108.3 | 108.6 |
| a(O-S-O) | 124.8 | 123.3 |
| a(OH-S-OH) | 101.5 | 101.3 |
| $HNO_3$ | | |
| r(O-H) | 0.97 | 0.96 |
| r(N-O) | 1.37 | 1.41 |
| r(N-O4) | 1.20 | 1.21 |
| r(N-O5) | 1.19 | 1.20 |
| $H_2O$ | | |
| r(O-H) | 0.96 | 0.96 |
| a(H-O-H) | 105 | 105 |

*** references [31, 45-46].**

In this study, the potential energy surfaces of $H_2SO_4\cdots HNO_3\cdots (H_2O)_n$ (n=2,3) clusters were investigated using the ABCluster code [47,48]. The ABCluster global search method was applied in conjunction with the Gaussian 09 program. Fifty structural optimizations were performed at the B3LYP/6-31++g(d) level. At this stage, several minimum energy points were obtained, and among these, distinct and energetically more stable structures were selected. The chosen structures were further optimized at the M062X/aug-cc-pvdz level, and frequency calculations were performed to determine whether they represented true minima on the potential energy surface. The "tight convergence" criterion was employed in the optimization steps. As a result of the calculations, the binding energies and zero-point energies (ZPE) of these clusters were determined based on their configurations. The binding energies of the clusters were calculated by subtracting the energies of the monomers from the energy of the complex.

## 2.1. Description of Clusters

The systems studied are named as NSnW-m, where N, S, and W represent nitric acid ($HNO_3$), sulfuric acid ($H_2SO_4$), and water ($H_2O$) molecules, respectively. The n indicates the number of water molecules in the cluster, and m is an index representing the different structures of a specific NSnW cluster based on their energy ranking. For example; NS2W-4 refers to the fourth structure of the system containing one nitric acid molecule, one sulfuric acid molecule, and two water molecules ($H_2SO_4\cdots HNO_3\cdots H_2O)_2$) in order of energy stability.

## 3. RESULTS AND DISCUSSION

## 3.1. Results for NS2W Clusters

As a result of the potential energy surface scan, 22 minimum structures were identified for the NS2W clusters, as shown in Figure 1. The binding energies of these structures, calculated at the M062X/aug-cc-pvdz level and binding energies with zero-point energy correction (ΔZPEC) are listed in Table 2. The binding energies of the 22 structures range from -34.63 kcal/mol to -20.15 kcal/mol.

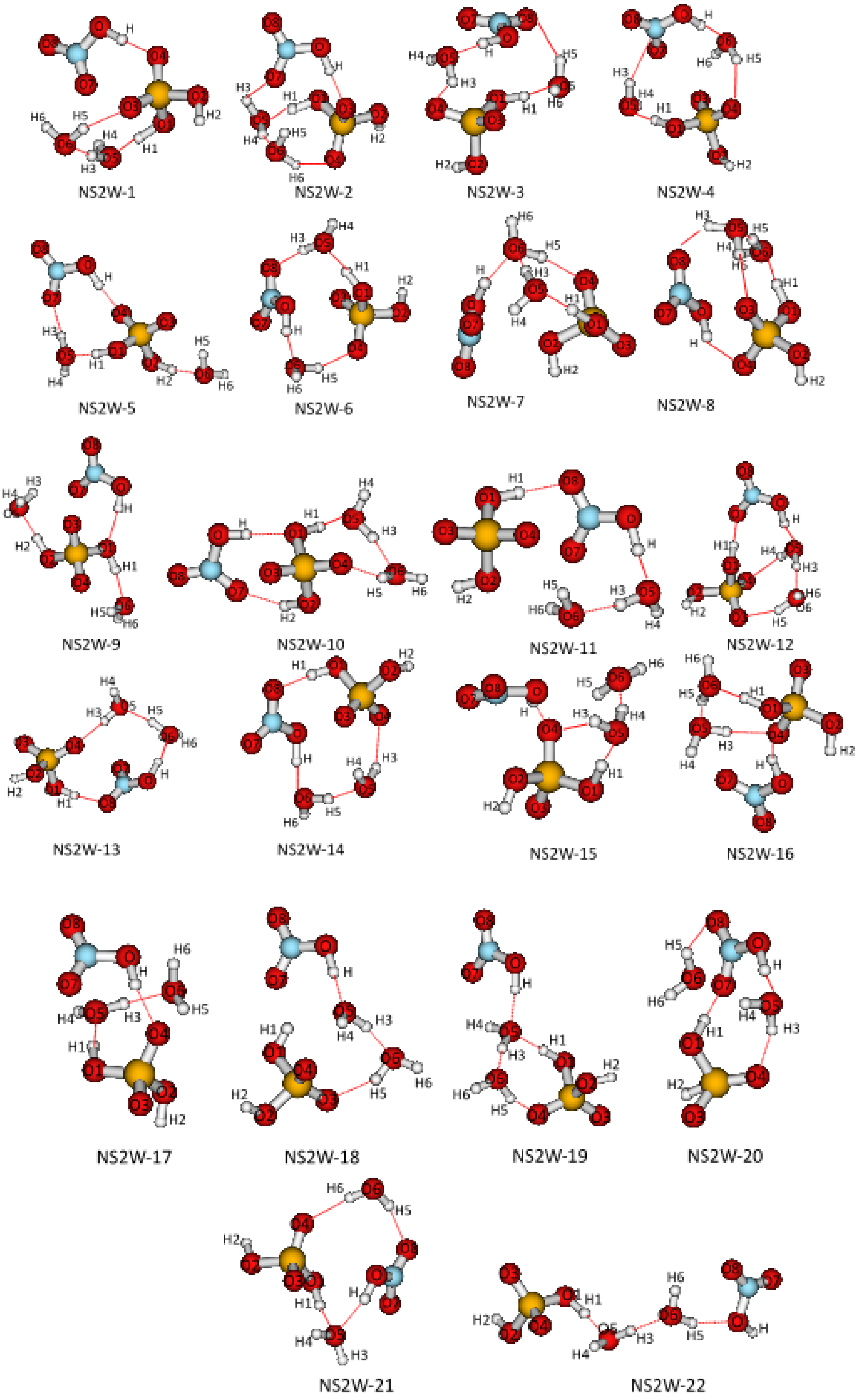
None of the structures exhibit ionic forms of nitric acid or sulfuric acid. The NS2W-1 structure was found to be the most energetically stable. In this configuration, nitric acid acts as a proton donor to sulfuric acid, while sulfuric acid serves as a proton donor to the water molecule. Water molecules interact with each other as well as with the other acid molecules. Each molecule functions both as a proton donor and a proton acceptor.

In the NS2W-2 structure, a similar molecular interaction was observed, but the orientation of hydrogen atoms not involved in bond formation was different. The energy difference between this structure and NS2W-1 is only 0.05 kcal/mol. The structural difference between these two configurations arises from the water molecule containing the O5 atom in the NS2W-2 structure. While this water molecule accepts a proton, it simultaneously acts as a proton donor both to another water molecule and to one of the oxygen atoms of nitric acid. In the N2W-1 structure, both water molecules accept and donate a proton. This situation makes the structure more stable due to the cooperative effect in hydrogen-bonded systems. A similar situation has been observed in other studies in the literature [30,40]. In the structures NS2W-5, NS2W-8, NS2W-9, NS2W-10, NS2W-15, NS2W-16, and NS2W-17, where nitric acid acts as a proton donor to sulfuric acid, a similar effect was not observed, resulting in these structures being obtained as energetically less stable. For instance, in NS2W-8, water molecules do not interact with each other.

Apart from NS2W-22, where nitric acid does not act as a proton donor to the water molecule, all other structures show that nitric acid donates a proton to the water molecule. NS2W-22 is the least stable structure with a binding energy of -20.15 kcal/mol, as the hydrogen atoms of nitric acid do not interact with other molecules. In the NS2W-3 and NS2W-4 structures, each molecule forms a cyclic structure by both donating and accepting a proton, with binding energies calculated as -33.93 kcal/mol and -33.81 kcal/mol, respectively. In these two minimum structures, water molecules do not interact with each other.

Structures where sulfuric acid acts as a proton donor to nitric acid, such as NS2W-10, NS2W-11, NS2W-12, NS2W-13, NS2W-14, and NS2W-20, are found to be less stable. Except for NS2W-10, in these structures, nitric acid donates a proton to the water molecule. In NS2W-10, sulfuric acid acts as a proton acceptor from nitric acid, making this structure less stable compared to NS2W-1 or NS2W-2, as nitric acid does not interact with water molecules in this case.

The results of the NS2W structures can be compared with those of the $H_2SO_4 \cdots HNO_3 \cdots H_2O$ clusters found in the literature [40]. It has been observed that the most energetically stable structures obtained in this study are similar to the results reported for ternary systems. The cyclic structure, where sulfuric acid acts as a proton donor to water and nitric acid acts as a proton donor to sulfuric acid, has been identified as the most energetically stable configuration for ternary systems. At the same time, structures in which nitric acid does not engage in any interaction were found to be energetically less stable. Unlike ternary systems, in this study, due to the larger number of water molecules, nitric acid and sulfuric acid do not interact with each other in structures like NS2W-3 and NS2W-4. However, since both acid molecules act as proton donors to water molecules and form a cyclic arrangement, these structures are energetically stable. There is an energy difference of approximately 0.07 to 0.08 kcal/mol between the NS2W-1 structure and the NS2W-3 and NS2W-4 structures, respectively.



NS2W-1 NS2W-2 NS2W-3 NS2W-4

NS2W-5 NS2W-6 NS2W-7 NS2W-8

NS2W-9 NS2W-10 NS2W-11 NS2W-12

NS2W-13 NS2W-14 NS2W-15 NS2W-16

NS2W-17 NS2W-18 NS2W-19 NS2W-20

NS2W-21 NS2W-22

**Figure 1.** Optimized NS2W Clusters at the M062X/aug-cc-pvdz level.

**Table 2.** Binding energies ($E_{binding}$) of NS2W clusters calculated at the M062X/aug-cc-pvdz level and ΔZPEC corrected binding energies ($E_{binding+\Delta ZPEC}$). Values are given in kcal/mol.

| NS2W clusters | $E_{binding}$ | $E_{binding+\Delta ZPEC}$ |
|---|---|---|
| NS2S-1 | -40.22 | -34.63 |
| NS2S-2 | -39.58 | -34.58 |
| NS2S-3 | -39.14 | -33.93 |
| NS2S-4 | -39.06 | -33.81 |
| NS2S-5 | -38.99 | -33.76 |
| NS2S-6 | -38.79 | -33.76 |
| NS2S-7 | -38.78 | -33.14 |
| NS2S-8 | -37.81 | -32.88 |
| NS2S-9 | -38.07 | -32.53 |
| NS2S-10 | -37.36 | -32.11 |
| NS2S-11 | -37.28 | -31.88 |
| NS2S-12 | -36.85 | -31.78 |
| NS2S-13 | -36.80 | -31.59 |
| NS2S-14 | -36.36 | -31.34 |
| NS2S-15 | -35.55 | -30.56 |
| NS2S-16 | -35.46 | -30.19 |
| NS2S-17 | -35.35 | -30.18 |
| NS2S-18 | -35.28 | -29.65 |
| NS2S-19 | -35.00 | -29.05 |
| NS2S-20 | -33.68 | -28.64 |
| NS2S-21 | -25.51 | -20.38 |
| NS2S-22 | -25.28 | -20.15 |

When examining the structural parameters of the NS2W clusters, it is observed that hydrogen bonds play a crucial role in the stability of the structures. Important structural parameters for the NS2W clusters are detailed in Supplementary Materials, and a summary is given in Figure 2.

In the NS2W-1 structure, the strongest hydrogen bond is between sulfuric acid and water, with a bond length of 1.33 Å. This $H_2SO_4 \cdots H_2O$ interaction is the strongest interaction observed among all structures. Literature also indicates that the $H_2SO_4 \cdots H_2O$ dimer interaction is stronger than the $HNO_3 \cdots H_2O$ interaction [40]. In the NS2W-1 structure, nitric acid acts as a proton donor to sulfuric acid, with a hydrogen bond length of 1.62 Å.

In structures such as NS2W-2, NS2W-5, NS2W-9, NS2W-10, NS2W-13, NS2W-14, NS2W-15, NS2W-16, and NS2W-17, nitric acid acts as a proton donor to one of the oxygen atoms of sulfuric acid. However, the strength of these bonds is weaker compared to the NS2W-1 structure. The literature also notes that dimer structures of $H_2SO_4 \cdots HNO_3$, where both acids act as proton donors to each other, are observed to be the most stable [38,39].

In the NS2W-1 structure, the hydrogen bond between water molecules is calculated to be 1.65 Å. Within this structure, one of the water molecules acts as a proton donor to nitric acid, with this weak hydrogen bond (H4···O7) having a length of 2.41 Å.

Similarly, in NS2W-3 and NS2W-4 structures, both nitric acid and sulfuric acid donate protons to water molecules and also receive protons from them. The hydrogen bonds formed between acid molecules and water molecules are stronger, as detailed in Supplementary Materials (e.g., H···O5, H1···O6, H···O6, and H1···O5 bonds), compared to those formed between water molecules and acid molecules, which are weaker. For example, in the NS2W-3 structure, the hydrogen bond length between H3 and O3 is 2.27 Å, while in the NS2W-4 structure, the distance between H5 and O4 is 1.89 Å.

The O-H bond lengths of acid molecules have varied from their monomer values. As shown in Table 1, the O-H bond lengths for monomeric $HNO_3$ and $H_2SO_4$ are provided. In the NS2W clusters, the O-H bond length of nitric acid ranges from 0.97 Å to 1.05 Å. It has been observed that the O-H bond length is longer in structures where nitric acid donates protons to water or sulfuric acid. Specifically, in cyclic structures where each molecule donates and receives a proton (e.g., NS2W-3, NS2W-4, NS2W-13 as shown in Figure 1), the O-H bond length is notably elongated.

In the NS2W-22 structure, since the O-H bond does not participate in any interactions, the O-H bond length remains the same as in monomeric $HNO_3$ (0.97 Å). A similar situation is observed for the O-H bonds in sulfuric acid. The O-H bond lengths involved in interactions with values ranging from 0.99 Å to 1.10 Å. The greatest elongation is observed in the NS2W-1 (O1-H1) and NS2W-2 (O1-H1) structures, where the non-interacting O-H bond length remains the same as the monomeric value (e.g., O2-H2 bond in NS2W-1).

For water molecules, the O-H bond lengths involved in interactions range from 0.97 Å to 0.99 Å. Non-interacting O-H bonds in water molecules have a length of 0.96 Å.

### 3.2. Results for NS3W Clusters

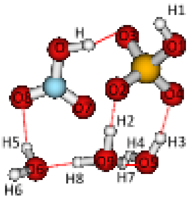
In the potential energy surface scan for the NS3W clusters, 38 minimum structures were identified, as shown in Figure 2. The binding energies calculated at the M062X/aug-cc-pvdz level and binding energies with zero-point energy correction (ΔZPEC) for these structures are presented in Table 3.

Unlike the NS2W clusters, among the 38 NS3W clusters obtained after optimization, 10 structures feature either sulfuric acid or nitric acid in an ionic state. The binding energies for these structures range from -48.14 kcal/mol to -36.14 kcal/mol. The most stable structure, according to the energy ranking, is NS3W-1, which resembles the arrangement of molecules in NS2W-1. In this structure, nitric acid acts as a proton donor to sulfuric acid, sulfuric acid donates protons to water, and the water molecules act as proton donors both to each other and to the acid molecules. The binding energy is calculated to be -48.14 kcal/mol, and sulfuric acid is found to be ionic in this minimum structure.

Sulfuric acid is also observed to be ionic in NS3W-2, NS3W-3, NS3W-10, NS3W-12, NS3W-13, NS3W-15, and NS3W-22 structures. In general, sulfuric acid in these structures is observed to be three-coordinated. The binding energies for these structures are -46.29 kcal/mol, -46.13 kcal/mol, -43.98 kcal/mol, -43.27 kcal/mol, -43.26 kcal/mol, -42.90 kcal/mol, and -41.11 kcal/mol, respectively.

Nitric acid is found to be ionic only in NS3W-8 and NS3W-32, where it is observed to be three-coordinated. The literature contains various studies on the ionization of acid molecules [17, 29, 49-51]. For instance, it has been noted that at least four water molecules are needed for the ionization of HCl [49]. Additionally, the interaction of nitric acid with HCl in water clusters has been studied, and structures where nitric acid is three-coordinated were also found to be ionic [52]. For ionization to occur, the water molecule accepting the proton must also be three-coordinated. For example, in the NS3W-4 structure, even though sulfuric acid is three-coordinated, one of the hydrogen atoms of the water molecule that donates a proton is free (H4 atom).

Among the NS3W clusters, the top three energy-stable structures are in an ionic state (NS3W-1, NS3W-2, NS3W-3). The subsequent NS3W-4 structure does not feature ionic acid molecules and has a binding energy of -45.37 kcal/mol. In this structure, nitric acid acts as a proton donor to sulfuric acid, and sulfuric acid acts as a proton donor to a water molecule, resulting in a cyclic structure. This arrangement is identical to both the most energetically stable NS2W-1 structure and the most stable configuration found for ternary systems [40].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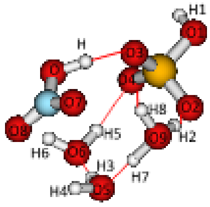
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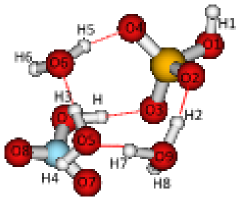
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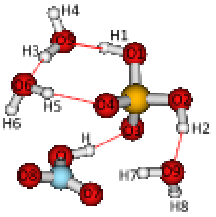
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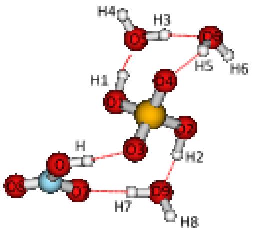
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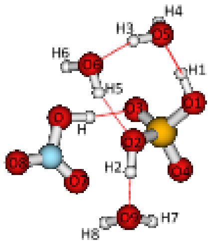
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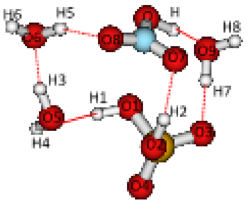
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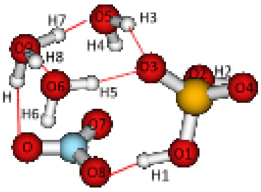
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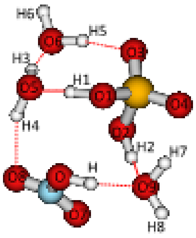
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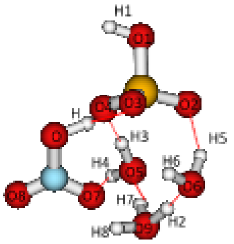
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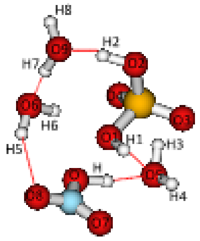
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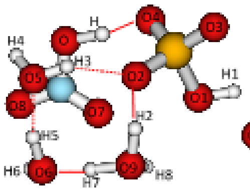
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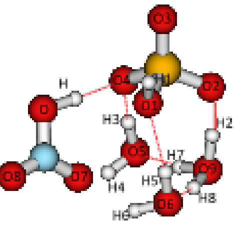
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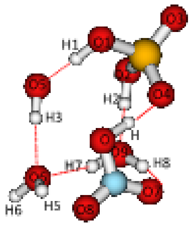
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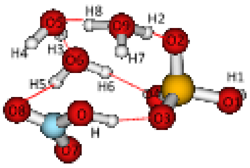
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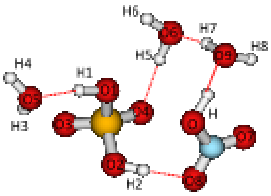
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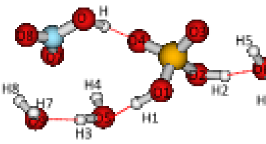
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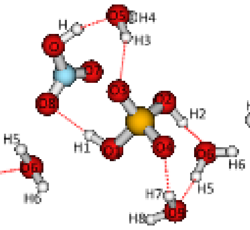
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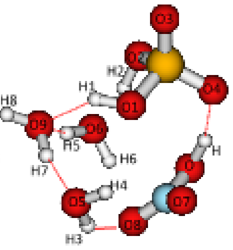
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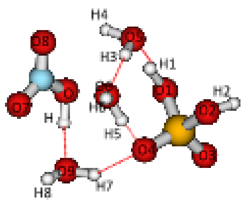
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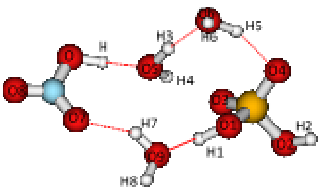
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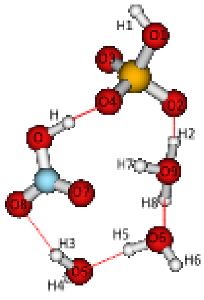
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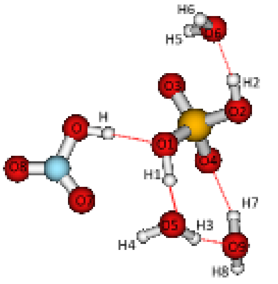
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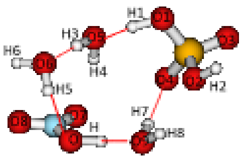
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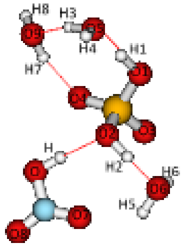
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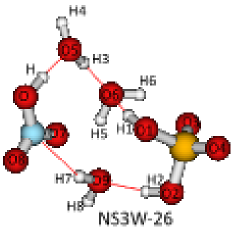
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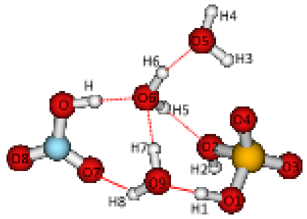
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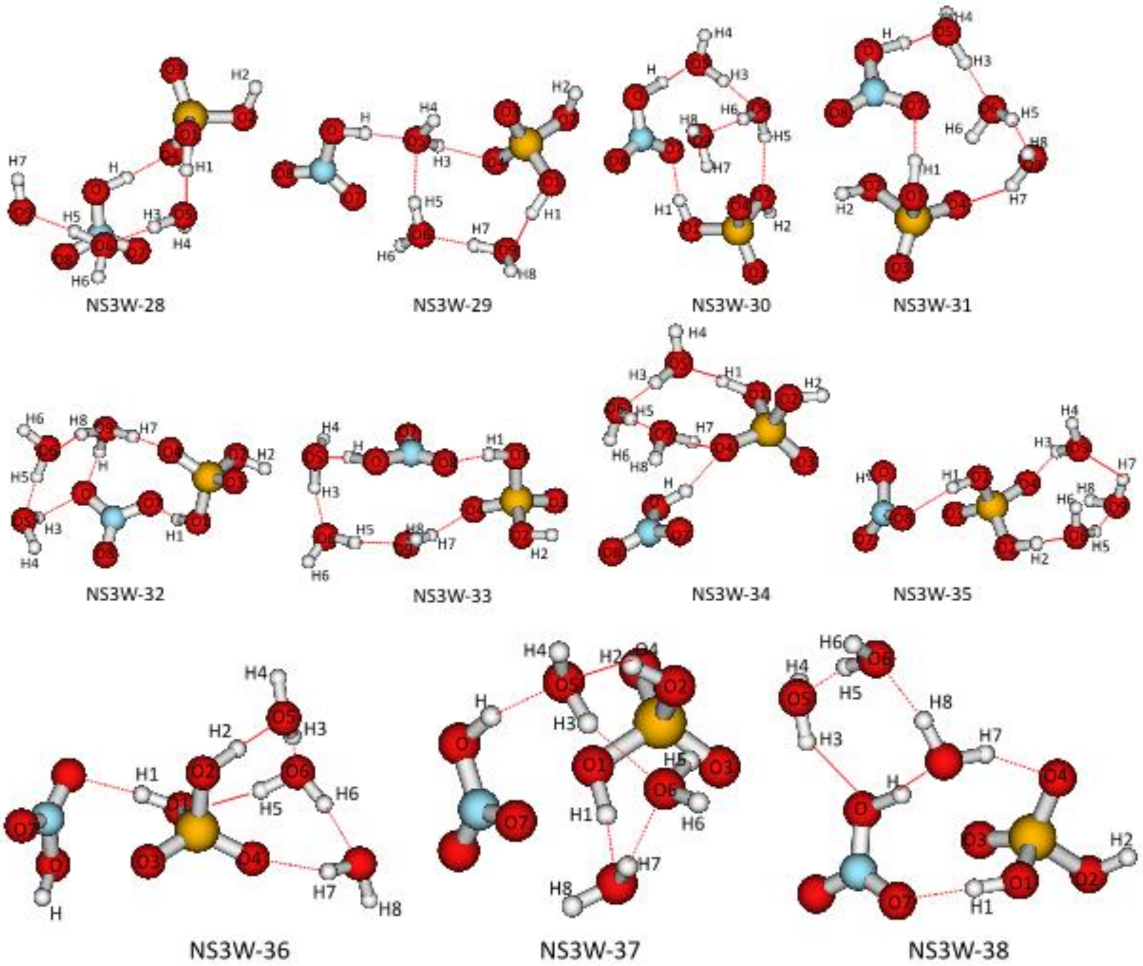

**Figure 2.** Optimized NS3W Clusters at the M062X/aug-cc-pvdz level.

**Table 3.** Binding energies ($E_{binding}$) of NS3W clusters calculated at the M062X/aug-cc-pvdz level and ΔZPEC corrected binding energies ($E_{binding+\Delta ZPEC}$). Values are given in kcal/mol.

| NS3W Clusters | $E_{binding}$ | $E_{binding+\Delta ZPEC}$ |
|---|---|---|
| NS3S-1 | -55.50 | -48.14 |
| NS3S-2 | -53.23 | -46.29 |
| NS3S-3 | -53.16 | -46.13 |
| NS3S-4 | -53.03 | -45.37 |
| NS3S-5 | -52.58 | -45.28 |
| NS3S-6 | -53.40 | -46.11 |
| NS3S-7 | -52.01 | -44.16 |
| NS3S-8 | -51.58 | -44.29 |
| NS3S-9 | -51.49 | -43.88 |
| NS3S-10 | -51.42 | -43.98 |
| NS3S-11 | -51.16 | -43.27 |
| NS3S-12 | -51.09 | -44.19 |
| NS3S-13 | -50.98 | -43.26 |
| NS3S-14 | -50.89 | -43.30 |
| NS3S-15 | -50.76 | -42.90 |
| NS3S-16 | -50.68 | -42.74 |
| NS3S-17 | -50.51 | -42.99 |
| NS3S-18 | -50.31 | -42.97 |
| NS3S-19 | -50.09 | -43.12 |
| NS3S-20 | -50.03 | -42.65 |
| NS3S-21 | -49.37 | -42.05 |
| NS3S-22 | -48.79 | -41.11 |
| NS3S-23 | -48.75 | -41.39 |
| NS3S-24 | -48.72 | -41.42 |
| NS3S-25 | -48.67 | -41.92 |
| NS3S-26 | -48.66 | -40.30 |
| NS3S-27 | -48.64 | -41.51 |
| NS3S-28 | -48.35 | -41.09 |
| NS3S-29 | -48.15 | -40.57 |
| NS3S-30 | -47.79 | -40.33 |
| NS3S-31 | -46.93 | -39.34 |
| NS3S-32 | -46.79 | -39.55 |
| NS3S-33 | -46.71 | -39.57 |
| NS3S-34 | -46.39 | -39.43 |
| NS3S-35 | -45.45 | -37.72 |
| NS3S-36 | -44.62 | -36.21 |
| NS3S-37 | -44.09 | -36.33 |
| NS3S-38 | -43.23 | -36.14 |

In the NS3W clusters, key structural parameters are provided in Supplementary Materials. The most stable structure, NS3W-1, features nitric acid donating a proton to sulfuric acid. This structure resembles the most stable NS2W-1 structure, but sulfuric acid is in an ionic state here. The strongest hydrogen bond in NS3W-1 is between nitric acid and sulfuric acid, with an O3···H bond length of 1.42 Å. Each hydrogen atom of the $H_3O^+$ ion interacts with oxygen atoms from two water molecules and one oxygen atom from sulfuric acid. The hydrogen bonds made by the $H_3O^+$ ion are calculated as follows: O2···H2: 1.50 Å, O6···H8: 1.58 Å, O5···H7: 1.48 Å. Water molecules in this structure also donate protons to the acid molecules, but these interactions are weaker compared to the other hydrogen bonds, with bond lengths of: O4···H3: 1.78 Å, O8···H5: 1.89 Å.

In addition to NS3W-1, sulfuric acid is also found in an ionic state in NS3W-2, NS3W-3, NS3W-10, NS3W-12, NS3W-13, NS3W-15, and NS3W-22. In these structures, the three-coordination state of the $H_3O^+$ ion is less stable. For instance, in NS3W-2, the hydrogen bonds involving the $H_3O^+$ ion with the molecules are: O2···H2: 1.46 Å, O5···H7: 1.37 Å, O7···H8: 2.08 Å. The O7···H8 interaction is notably weaker. Similar observations are made in other structures where sulfuric acid is ionic. In NS3W-8 and NS3W-32, nitric acid is ionic. In NS3W-8, the hydrogen bonds between the $H_3O^+$ ion and water molecules are: O6···H8: 1.47 Å, O5···H7: 1.43 Å. The interaction with the nitrate ion (O···H hydrogen bond) is 1.84 Å. The strongest hydrogen bond is observed as O8···H1 at 1.34 Å. In NS3W-32, the hydrogen bonds made by the $H_3O^+$ ion are: O6···H8: 1.43 Å, O···H: 1.56 Å, O4···H7: 1.65 Å. In this structure, the nitrate ion is three-coordinated, but unlike NS3W-8, one of the oxygen atoms of the nitrate ion (O atom) is two-coordinated. In NS3W-8, all the oxygen atoms of the nitrate ion are single-coordinated.

In NS3W structures where the acid molecules are molecularly obtained, nitric acid either donates a proton to sulfuric acid or to water. In the more stable structures, nitric acid donates a proton to sulfuric acid such as in NS3W-4 and NS3W-5. However, only in NS3W-35 and NS3W-36, the hydrogen of nitric acid does not participate in any interactions. Generally, the hydrogen atom of nitric acid interacts with one of the non-proton-containing oxygen atoms of sulfuric acid. Only in NS3W-23 and NS3W-25 does the hydrogen atom of nitric acid donate a proton to one of the proton-containing oxygen atoms of sulfuric acid, which is weaker compared to interactions where nitric acid donates a proton to non-proton-containing oxygen atoms of sulfuric acid. For NS3W-23, the O1···H bond is 1.75 Å, and for NS3W-25, the O2···H bond is 1.78 Å.

In the NS3W clusters, the O-H bond lengths of nitric acid involved in interactions range from 0.98 Å to 1.09 Å. The maximum extension is observed in NS3W-31, a structure where each molecule forms a chain-like configuration by donating and accepting a proton, similar to the structure described for NS2W-13. As the number of water molecules increases, a further extension of the O-H bond lengths is observed.

A similar trend is noted for the O-H bonds of sulfuric acid and water molecules, where the bond lengths also increase with more water molecules in the system.

### 3.3. Vibrational Frequencies

Harmonic frequency analyses for the NS2W and NS3W clusters were performed at the M062X/aug-cc-pvdz level. Figure 3 shows the IR spectra of five structures with different configurations selected from these clusters (NS2W-1, NS2W-3, NS3W-9, NS3W-1, and NS3W-8); the IR spectra of all other structures are presented in Supplementary Materials. In the NS2W-1 structure, nitric acid acts as a proton donor to sulfuric acid, while in the NS2W-3 and NS3W-9 structures, nitric acid is the proton donor to water. In the NS3W-1 structure, sulfuric acid is in an ionic form, whereas in the NS3W-8 structure, nitric acid is in an ionic form.

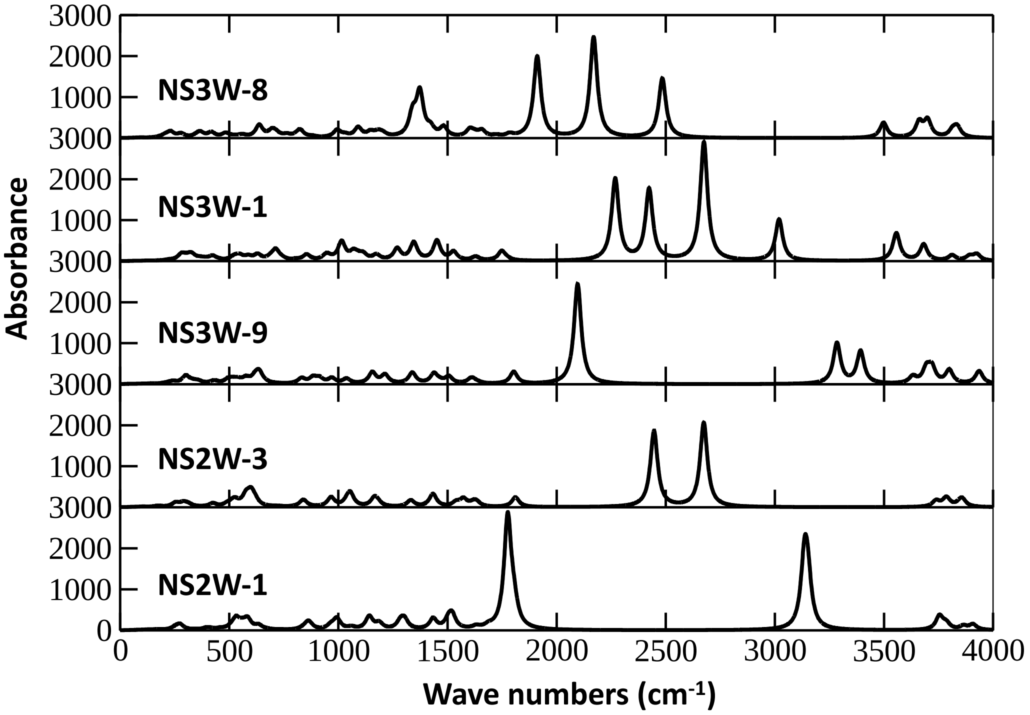

**Figure 3.** IR spectra of NS2W-1, NS2W-3, NS3W-9, NS3W-1 and NS3W-8.

Looking at the spectra of NS2W-1 and NS2W-3 structures, the vibration frequencies of the O-H bond in $HNO_3$ peak at 3136 $cm^{-1}$ and 2674 $cm^{-1}$, respectively. For the monomer $HNO_3$, the O-H bond vibration frequency is calculated to be 3769 $cm^{-1}$ at the M062X/aug-cc-pvdz level. In this case, the O-H bond is more stretched when $HNO_3$ acts as a proton donor to water. A similar situation has also been observed in ternary systems [40]. In the NS3W-9 structure, although $HNO_3$ is also a proton donor to water, the O-H bond peaks at 3284 $cm^{-1}$ in the spectrum. This structure causes less stretching of the O-H bond compared to others due to the involvement of both protons of sulfuric acid in the interaction. In the NS3W-1 structure, sulfuric acid is in an ionic state, and the O-H bond of $HNO_3$ shows the largest stretching in this structure, peaking at 2268 $cm^{-1}$ in the IR spectrum.

Looking at the O-H bonds of sulfuric acid; in the NS2W-1 and NS2W-3 structures, the interacting O-H bonds peak at 1775 $cm^{-1}$ and 2446 $cm^{-1}$, respectively. The vibration frequencies of the O-H bonds for the monomer $H_2SO_4$ are calculated to be 3783 $cm^{-1}$ and 3788 $cm^{-1}$. Accordingly, the largest shift in the spectrum is observed in the NS2W-1 structure. In this structure, sulfuric acid acts as a proton acceptor from nitric acid and also shows three-coordinations of sulfuric acid.

In the NS3W-9 structure, both O-H bonds of sulfuric acid are involved in interactions. The interacting O-H bonds peak at 2096 $cm^{-1}$ (O1-H1) and 3632 $cm^{-1}$ (O2-H2). In the NS3W-1 structure, sulfuric acid donates one proton to water to form an $H_3O^+$ ion, while the other O-H bond does not participate in any interaction. The vibration frequency of this O-H bond is 3812 $cm^{-1}$. In the NS3W-8 structure, the O-H bond of sulfuric acid interacting with the nitrate ion peaks at 1911 $cm^{-1}$, while the free O-H bond peaks at 3814 $cm^{-1}$. In both NS3W-1 and NS3W-8 structures, the peaks associated with the $H_3O^+$ ion appear in the spectrum approximately between 2100 $cm^{-1}$ and 2600 $cm^{-1}$.

When examining the O-H bonds of water molecules, it has been observed that the interacting O-H bonds show larger shifts in the spectrum compared to their monomer values (3867 $cm^{-1}$ and 3976 $cm^{-1}$). Additionally, it has been noted that the interaction of O-H bonds with acids or water alters the stretching of these bonds. When water molecules interact with each other, their O-H bonds peak in the region of 3000 $cm^{-1}$ to 3400 $cm^{-1}$, whereas they peak between 3600 $cm^{-1}$ and 3750 $cm^{-1}$ when they act as proton donors to acid molecules. Peaks of free O-H bonds not involved in any interactions are found between 3850 $cm^{-1}$ and 3950 $cm^{-1}$.

## 4. CONCLUSION

Nitric acid and sulfuric acid can form stable species with water molecules by creating various hydrogen bonds. These acid molecules are significant from an atmospheric perspective and play an important role in atmospheric chemistry. In this theoretical study, interactions in clusters of these acids with two and three water molecules were analyzed at the M062X/aug-cc-pvdz level. The potential energy surfaces for $HNO_3\cdots H_2SO_4\cdots(H_2O)_2$ and $HNO_3\cdots H_2SO_4\cdots(H_2O)_3$ clusters were initially scanned using the ABCluster program. On the potential energy surface, 22 minimum energy points were obtained for $HNO_3\cdots H_2SO_4\cdots (H_2O)_2$ clusters and 38 minimum energy points for $HNO_3\cdots H_2SO_4\cdots(H_2O)_3$ clusters. In the NS2W clusters, neither sulfuric acid nor nitric acid was ionized. By adding one more water molecule to the system, ionic forms of sulfuric acid or nitric acid were obtained in the NS3W clusters. Literature studies exist on the number of water molecules required for acid molecules to ionize [49-51]. For example, it has been noted that ionization of HCl requires at least four water molecules. There are also studies examining $HNO_3$ with HCl in water clusters [52]. When $HNO_3$ replaces one water molecule, it was observed that HCl ionizes with three water molecules. The same study reported that $HNO_3$ ionizes in clusters containing four water molecules and HCl. In this study, sulfuric acid or nitric acid did not ionize in the NS2W clusters, where $H_2SO_4$ was examined with two water molecules and nitric acid. By adding a water molecule to the system, both ionic forms of nitric acid and sulfuric acid were obtained. The literature mentions only one study where sulfuric acid's ionic form is stable in a structure containing five water molecules with $HNO_3$ and $H_2SO_4$ [42]. However, no studies have been conducted on clusters with fewer water molecules.

When examining the binding energies of the clusters, it was found that both NS2W and NS3W clusters exhibit the most stable structures, with nitric acid acting as a proton donor to sulfuric acid. This result is consistent with previous studies on $HNO_3\cdots H_2SO_4\cdots H_2O$ ternary clusters [40]. Generally, hydrogen bonds are found to enhance the stability of the clusters, and cyclic structures in which each molecule in the cluster donates and accepts a proton are more energetically stable. Structural and spectroscopic analyses have shown that the strength of hydrogen bonds varies according to the proton donation and acceptance states of the molecules within the cluster. For example, in the NS2W-1 structure, sulfuric acid interacts with three oxygen atoms, forming a three-coordinated structure. In this structure, the hydrogen bond between sulfuric acid and water has a length of 1.33 Å, and the O-H bond of sulfuric acid peaks at 1775 $cm^{-1}$. In the NS2W-3 structure, sulfuric acid is two-coordinated and does not interact with nitric acid. The hydrogen bond between sulfuric acid and the water molecule is 1.47 Å, and the O-H bond peaks at 2446 $cm^{-1}$. Therefore, in the NS2W-1 structure, where a strong hydrogen bond is formed, the O-H bond is more stretched. In another structure, NS3W-9, both protons of sulfuric acid participate in hydrogen bonding. The hydrogen bond distances for O5···H1 and O9···H2 are 1.39 Å and 2.04 Å, respectively, and their vibration frequencies are observed to be 2096 $cm^{-1}$ (O1-H1) and 3632 $cm^{-1}$ (O2-H2), respectively. A similar situation is also true for nitric acid. The stretching of the O-H bond changes depending on the strength of the hydrogen bond it forms. Another significant point of the study is that the hydrogen bonds between water molecules themselves are observed to be stronger than in cases where they act as proton donors to acid molecules.

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## CONFLICT OF INTEREST

The author stated that there are no conflicts of interest regarding the publication of this article.

## CRediT AUTHOR STATEMENT

**Fatime Mine Balcı:** Conceptualization, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Methodology.

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