



Toward understanding the role of water molecules in the uptake of nitrosyl hydride by sulfuric acid aerosols: A computational study



Mohammad Solimannejad^{a,*}, Mohaddeseh Rabbani^a, Mehdi D. Esrafil^b

^aQuantum Chemistry Group, Department of Chemistry, Faculty of Sciences, Arak University, Arak 38156-8-8349, Iran

^bLaboratory of Theoretical Chemistry, Department of Chemistry, University of Maragheh, Maragheh, Iran

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ABSTRACT

In the present study, the equilibrium structures, binding energies, and the nature of the coupling interactions in $\text{H}_2\text{SO}_4 \cdot \text{HNO} \cdot (\text{H}_2\text{O})_n$ ($n = 0-2$) clusters have been systematically investigated at the MP2/aug-cc-pVDZ level of theory in combination with the atoms in molecules (AIM) theory and many-body interaction energies. Particular attention is given to existence and magnitude of $\text{NH} \cdots \text{O}$ blue-shifting hydrogen bonds (H-bonds). It was found that the insert of one or two water molecules can efficiently enhance the interactions between H_2SO_4 and HNO, pointing the positive role of water molecules in the uptake of the HNO via sulfuric acid aerosols. Based on the energy decomposition analysis (EDA), it can be seen that the stabilities of the clusters are predicted to be attributable mainly to electrostatic and polarization effects.

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1. Introduction

Sulfuric acid (H_2SO_4) is one of the key substances controlling climate change in atmospheric chemistry. H_2SO_4 is a main component of acid rain and is an effective nucleation agent significantly enhancing the homogenous nucleation rate of water [1,2]. It is also known that sulfuric acid plays an important role in the formation of sulfate aerosols, which can catalyze heterogeneous reactions contributing to ozone depletion in the polar stratosphere [3,4].

HNO is important in processes such as pollution formation, energy release in propellants, and fuel combustion [5]. The HNO molecule with the negative intermolecular coupling that its proton donor N–H bond contracts under protonation is a typical molecule with the blue shift of N–H stretching frequency [6]. The HNO molecule is a principal example, forming a blue-shifting H-bond with such proton acceptors as HNO [7], CH_3CHO [8], HFSO_2 [9], HArF [10], BH_3NH_3 [11], H_2XNH_2 ($X = \text{B}, \text{Al}$) [12], HOX ($X = \text{F}, \text{Cl}, \text{Br}$) [13], CH_3X ($X = \text{F}, \text{Cl}, \text{Br}$) [14], H_2O_2 [15], XCHZ ($X = \text{CH}_3, \text{H}, \text{F}, \text{Cl}, \text{Br}; Z = \text{O}, \text{S}$) [16], and even when interacting with the π -electron cloud of alkynes like acetylene [17,18]. Water, as one of the most important molecules in nature, is able to form hydrogen bonded networks. Recently, structures, binding energies, and vibrational frequencies of water clusters and water complexes with other guest molecules have been explored using ab initio methods [19,20].

* Corresponding author. Tel.: +98 861 4173400; fax: +98 861 4173406.

E-mail address: m-solimannejad@araku.ac.ir (M. Solimannejad).

The mixed clusters of $\text{H}_2\text{O} \cdot \text{HNO}$ exhibit a clear evidence for the existence of hydrogen bonding (H-bonding) in this system with blue-shifting of the NH vibrational stretching mode upon H-bonding [21]. Additionally, there are also molecular interactions between $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, which had been investigated previously [22–28].

Therefore, complicated interactions could exist among H_2SO_4 , HNO, and H_2O . We expect that the interactions between H_2SO_4 and HNO may be perturbed more or less by the presence of water molecules, depending on the selected coupling modes of H_2O with H_2SO_4 and HNO. A systemic study on the interactions between H_2SO_4 and HNO in the absence or presence of water molecules is highly desirable to provide some useful information on the uptake of the HNO by H_2SO_4 aerosols under the atmospheric conditions. The role played by of water molecules in the process of the uptake of the HNO by H_2SO_4 aerosols still remains unclear. Therefore, in the present study, the possible clusters formed among H_2SO_4 , HNO, and H_2O have been explored theoretically.

2. Computational details

In the present study, the geometries of the isolated HNO, H_2O and H_2SO_4 molecules and their clusters were fully optimized at the MP2/aug-cc-pVDZ computational level [29]. Subsequently, harmonic vibrational frequency analysis has also been carried out at the same level of theory in order to identify whether the optimized structures correspond to a true local minimum or not.

The stabilization energy (SE) has been calculated as the difference of the total energy of the complexes and the sum of

the isolated monomers in their minima configuration. The full counterpoise (CP) method [30,31] was used to correct the interaction energy from the inherent basis set superposition error (BSSE).

The atoms in molecules (AIM) methodology [32] has been used to analyze the electron density of the systems considered at the MP2/aug-cc-pVDZ computational level. For atom–atom interactions such as intermolecular contacts, electron density (ρ_{BCP}) and its Laplacian ($\nabla^2\rho_{\text{BCP}}$) provide a description of characteristics of the corresponding bond critical point (BCP). The energetic properties of BCPs are often considered as the electron energy density at BCP (H_C) and its components: the kinetic electron energy density (G_C) and the potential electron energy density (V_C). There is a relation between these energetic characteristics, $H_C = G_C + V_C$. It is also known from the virial theorem that $1/4\nabla^2\rho_{\text{BCP}} = 2G_C + V_C$. The negative value of the Laplacian of the electron density at BCP designates the concentration of the electron charge among the nuclei of interacting atoms and is typical for covalent bonds (shared interactions). In some studies [33,34] it is also stated that for $\nabla^2\rho_{\text{BCP}} > 0$, $-G_C/V_C < 1$ and $H_C < 0$, the interaction may be considered as partly covalent in nature. For positive values of $\nabla^2\rho_{\text{BCP}}$, there is a depletion of electron charge between the atoms, indicating an interaction of closed-shell systems: ions, van der Waals interactions or HBs. The topological analysis has been carried out with the AIM2000 program [35].

To gain a deeper insight into the nature of intermolecular interactions in terms of meaningful physical components, interaction energies were decomposed using the following partitioning scheme [36]:

$$E_{\text{int}} = E_{\text{elst}} + E_{\text{exch-rep}} + E_{\text{pol}} + E_{\text{disp}} \quad (1)$$

where E_{elst} is the first-order electrostatic term describing the classical Coulomb interaction of the occupied orbitals of one monomer with those of another monomer, $E_{\text{exch-rep}}$ is the repulsive exchange component resulting from the Pauli exclusion principle, E_{pol} and E_{disp} correspond to polarization and dispersion terms. The polarization term contains all classical induction, exchange-induction, etc., from the second order up to infinity. All geometry optimizations, interaction energies and energy components were calculated using GAMESS suite of programs [37].

3. Results and discussion

3.1. $\text{H}_2\text{SO}_4 \cdots \text{HNO}$ cluster

Optimization of different 1:1 complexes of $\text{HNO} \cdots \text{H}_2\text{SO}_4$ leads to one local minimum named R at the MP2/aug-cc-pVDZ level of theory as displayed in Fig. 1. R cluster is characterized by the double intermolecular H-bonds with the distances varying from

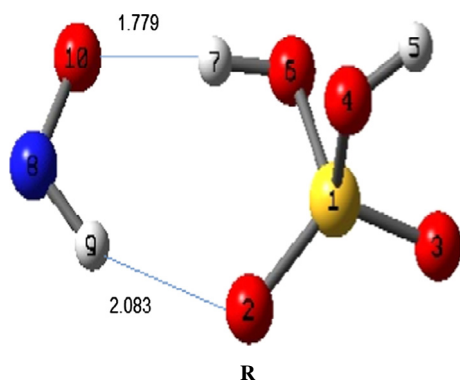


Fig. 1. The optimized $\text{H}_2\text{SO}_4 \cdots \text{HNO}$ binary cluster as well as the selected parameters. The H-bond distances are given in angstroms.

1.779 Å for $\text{O}10 \cdots \text{H}7$ and 2.083 Å for $\text{O}2 \cdots \text{H}9$ contacts, where both the HNO and H_2SO_4 molecules acts as an H-bond donor and acceptor simultaneously.

As displayed in Fig. S1 (Supplementary data), the formations of the H-bonds have been further verified by the locations of the BCPs between proton donors and proton acceptors. As presented in Table S1, the calculated electron density and its Laplacian at the BCPs all fulfill the criteria of the existence of intermolecular H-bonds proposed by Koch and Popelier [38,39]. For some of the interactions in Table S1, $\nabla^2\rho_{\text{BCP}} > 0$ and $H_C < 0$ with $-G_C/V_C > 1$, so they are closed-shell interactions. As displayed in Table S1, double intermolecular H-bonds in R are closed-shell interactions. Thus, the effect of water molecules on the coupling interactions between H_2SO_4 and HNO are mainly discussed below based on R structure.

3.2. $\text{H}_2\text{SO}_4 \cdots \text{HNO} \cdots \text{H}_2\text{O}$ clusters

As the first step toward understanding the influences of the water molecules on the uptake of the HNO by H_2SO_4 aerosols, one water molecule has been considered firstly based on the geometry of R. As displayed in Fig. 2, five ternary clusters have been located. Qualitatively, they can be divided into two groups in terms of the coupling modes of water molecules adopted in ternary clusters. Namely, in the first group, the water molecule only interacts with one of the H_2SO_4 and HNO fragments through the formation of new intermolecular H-bonds, such as N1, N2, and N3. In the N1 cluster, the water molecule interacts with the other hydroxyl and sulfonyl groups of H_2SO_4 via double intermolecular H-bonds on the other side of HNO , resulting in the formation of an additional six-membered ring structure.

For clusters N2 and N3, the water molecule interacts with the oxygen and nitrogen atoms of HNO on the side of HNO , resulting in the formation of a single intermolecular H-bond, respectively. In the second group, the introduced water molecule interacts with both H_2SO_4 and HNO simultaneously, such as B1 and B2 clusters. In other words, the water molecule has been inserted into the original seven-membered ring to form a nine-membered ring structure, resulting in the breaking of one of the original double intermolecular H-bonds in R. As displayed in Fig. S2, the formation of the intermolecular H-bonds can be further verified by the locations of the BCPs between the proton donors and proton acceptors. Therefore, all the $\text{H}_2\text{SO}_4 \cdots \text{HNO} \cdots \text{H}_2\text{O}$ clusters are characterized by multiple intermolecular H-bonds.

Moreover, the existences of the ring critical points (RCPs) suggest that all the formed clusters possess ring structure characteristics. For example, the ring structure of N1 cluster is similar to the spiro ring (Fig. S2). Only one ring exists in the other clusters, where the nine-membered ring structure has been observed in B1 and B2 structures. As presented in Table S1, in the N1, N2, and N3 clusters, the closed-shell interaction characters of intermolecular H-bonds between H_2SO_4 and HNO still remain. Similarly, the same is also true for the newly formed $\text{O}11 \cdots \text{H}5$ H-bond between the H_2O and H_2SO_4 in N1 structure.

For the other newly formed $\text{O}3 \cdots \text{H}13$ in N1 with H-bond distances 2.193 Å, it is dominated by the partially covalent reflected in $\nabla^2\rho_{\text{BCP}} > 0$ and $H_C > 0$ and $-G_C/V_C < 1$ at the BCPs of the H-bonds. As for B1 cluster, the newly formed $\text{O}11 \cdots \text{H}7$ H-bond is partially covalent, however, $\text{O}10 \cdots \text{H}12$ and $\text{O}2 \cdots \text{H}9$ H-bonds are closed-shell interactions. For B2 cluster, all the intermolecular H-bonds are closed-shell in terms of AIM analyses as presented in Table S1.

Compared with the binary cluster R, the $\text{O}10 \cdots \text{H}7$ and $\text{O}2 \cdots \text{H}9$ intermolecular H-bonds in N1, N2, and N3 clusters have been elongated and contracted, respectively. Therefore, both intermolecular H-bonds have been weakened and strengthened if one water molecule is inserted without breaking the original double H-bonds. In B1 structure, $\text{O}2 \cdots \text{H}9$ H-bond has been strengthened when one

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