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Theoretical Study on Microhydration of Bisulfate Ions [HSO_4^- $(H_2O)_n$] n = 0−3,5

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Abstract - Micro-hydration studies of electropositive and electronegative ions are especially important while interpreting ionic solvation mechanisms, hydrated ground state electronic structures, and energetic properties at atomic levels. The micro-hydrated hetero-atom centered ions such as sulfur-centered HSO_4^- have always fascinated experimental and theoretical chemists due to their excessive presence in many electrolytic solutions, various day-to-day edible foods and drugs, sea water as well as in naturally occurring oligoelements. Despite their high abundances, usefulness and essentiality for the growth and survival of animal and vegetal life, in depth theoretical studies concentrated on their hydration structures and electronic stabilization in the aqueous type solutions are very limited. This research work is aimed to probe deep into the molecular-level of HSO_4^- ion hydration by employing *ab initio* type theoretical model. The noteworthy findings are that the central bisulfate H-atom always forms an H-bond to the nearest H_2O molecule, and whenever the degree of solvation $n < 3$ H_2O, the bisulfate O-atoms make two or more H-bonds with H_2O; but when $n \geq 3$ H_2O, these O-atoms form one to two H-bonds with H_2O that is further linked to another H_2O by H-bond. The significance and novelty of this study lies in illuminating most of the physicochemical properties of HSO_4^- ions in any inorganic bisulfate aqueous type solutions, as well as in modelling their hydrated systems while exploring solvation dynamics in bulk solutions.

Keywords - Micro-hydration, Hydrated bisulfate clusters, Electronic structures, and DFT optimization.

I. INTRODUCTION

A very general definition of hydration is an interaction of a substance with water. In hydration chemistry, ions-water interaction or micro-hydration of ions that is mostly referred to the number of water molecules that are coordinated to the ions and much concern is their distribution and bound state around the ions is more specifically important. Experimentally, the ionic hydration structures can be probed directly by IR [1], NMR [2], Raman spectroscopy [3], Neutron diffraction [4], Gel exclusion chromatography [5] etc. But, in theoretical/computational investigations, advanced mathematical calculations such as energy minimization techniques are used to compute the equilibrium configurations of the concerned micro-hydrated structures [6]. Such computational procedures involve calculation of the wave function and energy at a starting hydrated ionic confirmation and then proceed to search the nearest minimum energy confirmation (global minimum or ground state electronic structure) using the smallest number of calculations possible [7]. Being its scale closer to that of electrons or small molecular systems, a density functional theory (hereafter, DFT) is one of the most powerful models in electronic structure package (*Gaussian*) in terms of implementing energy minimization techniques computationally [8], [9], [10], [11], [12], [13]. It is very suitable theoretical method for the quantum mechanical study of complex multi-atomic and heteroatom-centered micro-hydrated ionic systems, as justified by the most recent publication of the same author [14].

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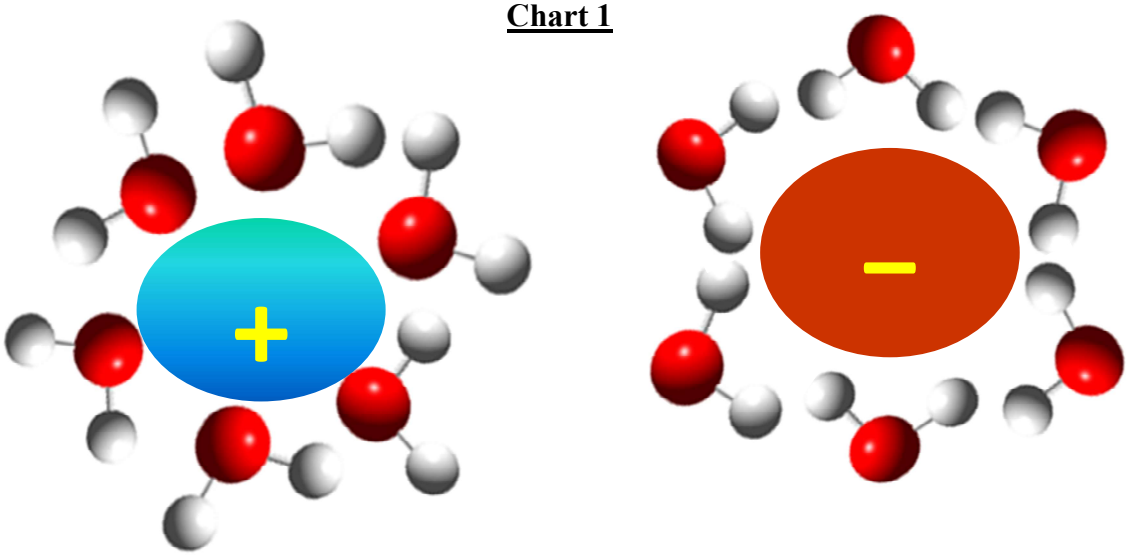
The universal solvent water plays an important role in hydration chemistry where aqueous media are desirable for processing several significant chemical and biological changes. In aqueous medium, the ionic compounds undergo ionization at first, and then respective ions form hydration shells around them (dissolution). It implies that in aqueous solutions, two or more than two components (molecules, atoms, and/or ions) are homogeneously mixed to each other and are dispersed on a molecular scale. One of the main strange features of the dissolved ions in the aqueous solution is their nearly independent existence to one another. This independency is due to the interactions between the ions (cations and anions) and the electric dipole of water molecules, as shown in chart 1. Such ion-dipole attractive force leads to ionic hydration that occurs by reorienting polar water molecules to minimize the electro-static interactions, creating the solvation shells around the immediate vicinity of the ions. Almost all types of homo- /hetero- atomic electropositive and electronegative ions undergo same type of ionic hydration but with distinct hydration structures in their aqueous solutions [14] [15]. Being Sulphur-centered bisulfate ions (hereafter, HSO_4^-) a biologically significant ionic species due to acting as a denaturing agent for the native structure of α-chymotrypsin (a digestive enzyme component of pancreatic juice) [15], their hydration structures, and structural stabilization in the aqueous type solutions have become a key area of research recently.

Since, the dissolved and hydrated HSO_4^- ions are one of the major components in seawater that not only create alkalinity to latter (total alkalinity TA = $[HCO_3^-] + [CO_3^{2-}] + [OH^-] + [HPO_4^{2-}] + [PO_4^{3-}] + [NH_3] + [HS^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4]$---- [16]), make latter more reactive with acids (acid buffering capacity), exceed the pH value of latter, affect a total hydrogen scale (pH_T) while measuring carbonate chemistry and calculating pH_T in oceanic and estuarine systems, but their different sized hydrated clusters $[HSO_4^-(H_2O)_n]$ also affect the distillation desalination method by slowing down the osmosis process through the permeable membranes [17]. Such hydrated clusters are also found to cause excessive water flow through ion exchange membrane in redox flow battery systems [18] where aqueous H_2SO_4 acts as a supporting electrolyte. Additionally, in PbO_2/ $PbSO_4$ electrode system (lead acid battery), where concentration range of an electrolyte: aqueous H_2SO_4 used is 0.05M to 6.0M [19], the amount of $[HSO_4^-(H_2O)_n]$ present in the electrolytic solution directly affects the electrochemical activity of battery [20]. In an extracellular fluid of human body as well, naturally occurring oligoelements comprises micro-hydrated HSO_4^- ions along with many electropositive and electronegative ions [21]. The same is the reason, why HSO_4^- ions are used as one of the major additives while developing self-setting formulations of implant biomaterials (such as calcium orthophosphate) for parenteral application. Similarly, the vegetables of cruciferous family (e.g. Cauliflower, Broccoli, Chinese cabbage, Chinese broccoli and similar green leaves vegetables) and their seeds consist of substantial amount of hydrated HSO_4^- ions that can be easily extracted (along with 3D glucose) by vegetable-hydrolysis [22]. Several medicines and drugs that are aqueous in nature such as Plavix, Clopidogrel are the compounds of bisulfate into which HSO_4^-

Chart 1



ions remain stabilized by forming different sized hydrated clusters. In terms of quantity, Nair *et al.* has estimated picomolar (1 pM = 10^{-12} mol/L) level of hydrated HSO_4^- ions in various day-to-day edible plants, foods, drugs, and dog urine [23].

The HSO_4^- ion is a conjugate base of H_2SO_4 (Chart 2) which is sometimes referred to the "king of chemicals" because of its involvement in some way or the other, in the manufacture of practically everything. As aqueous H_2SO_4 produces maximum amount of HSO_4^- ions even at its 1M solution [24] (chart 2), any higher concentrated aqueous H_2SO_4 obviously contains more HSO_4^- ions (due to weak dissociating strength, pK_{HSO4^-} = 2.0) that remains deprotonation equilibrium (step **2** in chart 2) with SO_4^{2-} ions. Such equilibrium must also exist in several other HSO_4^- containing real-world samples that are predominantly aqueous in nature, and are the first of their kind. According to *ab initio* molecular dynamics studies, this deprotonation equilibrium becomes more facile and shifts to forward direction whenever HSO_4^- ions form moderate size hydrated clusters [25]. The existence of the hydrated forms (inexistence of the isolated form) of HSO_4^- in aqueous type solutions is already confirmed by IR and MS spectroscopies, more particularly with the clusters of 1 to 16 water molecules; i.e. [$HSO_4^-(H2O)_n$], n = 1−16 [26].

Chart 2

$$H_2SO_4 \overset{\mathbf{1}}{\rightleftharpoons} H^+ + HSO_4^- \overset{\mathbf{2}}{\rightleftharpoons} 2H^+ + SO_4^{2-}$$

If [H_2SO_4] = 1M;

First dissociation **1**: 100 %

Second dissociation **2**: 1.3 %

Being HSO_4^- ions a useful and an essential inorganic ions that have become an important part of our growth and survival, in-depth investigations about their stabilization by variable number of water molecules clustering around them and their mutual interactions in the aqueous type solutions are very crucial. Though, they are ionic chaotropes with low charge density (unlike ionic kosmotropes) and can interfere comparatively little in the hydrogen bonding of the surrounding water molecules [27] during hydration process, the change in total electronic energy of such microscopic interacting particle systems would be practically significant. Thus, it should be evaluated properly by some means while studying micro-hydration phenomena. The comparatively more accurate *ab initio* type computational methodology could be one of the best alternative means to compute small change in total electronic energy that arises while interacting central HSO_4^- ion with surrounding water molecules. With this major objective, a renowned DFT model is employed in this study and applied explicitly to [$HSO_4^-(H_2O)_n$], n = 0−3 and 5, (as optimizing more bigger clusters by *ab initio* type method is computationally expensive) clusters and produced their respective ground state electronic structures. They are chosen here as representative clusters among other experimentally observed bigger clusters and grouped into: (a) n = 0, (b) n < 3, and (c) n ≥ 3 for the proper identification and comparison of their electronic hydration structures and bonding patterns, and for unveiling an extensive knowledge for explaining at least a stabilization of HSO_4^- ions by variable number of water molecules and their mutual interactions in the aqueous solution. The structure of this paper is as follows. The computational methods are outlined in section 2, results and discussions are presented in section 3, and summary and conclusions are given in section 4.

II. COMPUTATIONAL METHODS

At first, a trial structure of the monovalent HSO_4^- radical with four oxygen atoms, one hydrogen atom and a central sulfur atom in three dimensional axis was built by using GaussView visualization application software [28] and then $n$$H_2O$ molecules (n = 1, 2, 3, and 5) were added to its immediate vicinity one molecule at a time to construct the trial structures of [$HSO_4^-(H_2O)$] and its isomer, [$HSO_4^-(H_2O)_2$], [$HSO_4^-(H_2O)_3$], and [$HSO_4^-(H_2O)_5$]. While modeling the trial structures, the IR spectral patterns [26] of the concerned hydrated cluster were kept in mind so that $n$$H_2O$ molecules can be placed around the central HSO_4^- ion in the correct position. An 'n' = 0, 1, 2, 3, and 5 indicates unhydrated, monohydrated (1 molecule equivalent of water),

dihydrated (2 molecules equivalent of water), trihydrated (3 molecules equivalent of water), and pentahydrated (5 molecules equivalent of water) HSO_4^- ions (chart 3). These six different trial structures (including two isomers of monohydrated HSO_4^-) have central HSO_4^- unit with each S=O bond length 1.8Å, each S−O bond length 1.38Å, each O−H bond length 0.99Å, each O−S−O bond angle 110°, and each H−O bond length and H−O−H bond angle in H_2O is 0.99Å and 99° respectively. The oxygen and hydrogen atoms of the HSO_4^- unit in each trial structure were left unbound to surrounding H_2O molecule/s in order to realize latter as the free water molecules computationally. The initial atomic Cartesian coordinates for each cluster were extracted from the respective trial structures and concerned *x*, *y*, and *z* coordinates were explicitly used while preparing *Gaussian* input files manually for computing low energy electronic structures. All the *Gaussian* keywords and methodologies were selected as instructed in *Gaussian* 09 manual [29]. The hybrid functional based DFT methodology known as B3LYP with the basis set of this type: *6−31G* (*d, p*) was used i.e. DFT: *B3LYP/ 6−31G* (*d, p*). In order to solve the electronic Schrodinger equation iteratively, the self-consistent field (SCF) with both default SCF procedure (*SCF=Tight*) and Berny algorithm for optimizations to a local minimum were selected in *Gaussian* 09 [30]. The *Gaussian* output files such as *log*, checkpoint (*.chk*), and formatted checkpoint (*.fchk*) files were read by using the *Gaussian* graphical interface i.e. GaussView and various chemical data displayed in three dimensions were extracted. Finally, the optimized ground state electronic structures, and the respective optimized parameters for each hydrated bisulfate cluster were analyzed thoroughly.

III. Result and Discussion

3.1. Ground state electronic structures

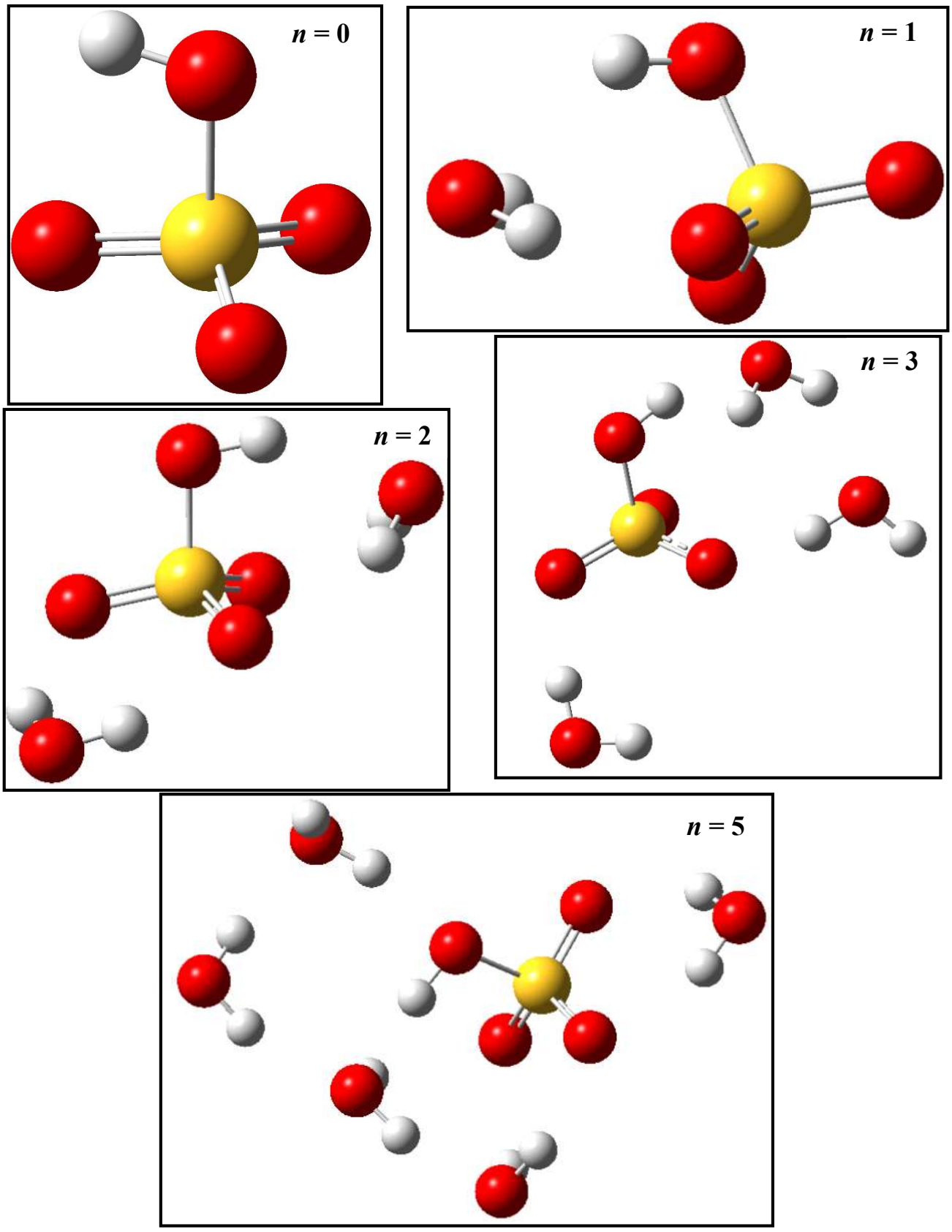
3.1.1 Naked HSO_4^- ion $[HSO_4^-(H_2O)_n]$, $n = 0$

The unhydrated HSO_4^- ion i.e. $[HSO_4^-(H_2O)_n]$, $n = 0$ can be called naked HSO_4^- ion due to the absence of water molecules in its immediate vicinity. Despite its inexistence in nature in an isolated and unhydrated form, its ground state electronic structure is presented here in order to explore the effect of hydration on its geometry and electronic stability. The DFT optimized geometry of unhydrated bisulfate ion is shown in Figure 1, where yellow spheroid represents Sulphur (S) atom, red spheroids represent Oxygen (O) atoms, and ash grey spheroid represents Hydrogen (H) atom. As the optimized geometry is specified mostly in terms of the three parameters namely bond length: an average distance between the nuclei of two atoms bonded together in any given molecule; bond angle: angle formed between three atoms across the two bonds; and torsional angle: angle between the plane formed by the first three atoms and the plane formed by the last three atoms, the explicitly measured theoretically calculated values of the first two parameters are listed as: each S−O bond length is 1.7 Å, each S=O bond length is 1.4 Å, each O−H bond length is 0.96 Å, and each O−S−O bond angle is 110°. As HSO_4^- has altogether 6 atoms with 6 valence electrons to each O and S (6 valence electrons ×5), 1 valence electron to each H, and 1 negative charge, there are total 32 electrons i.e. 16 electron pairs that are to be distributed over 6 centers. The least electronegative H atom forms a single bond with any one O atom (duplet rule), the same O atom should form single bond with centrally located S atom (octet rule). This S atom should form two double bonds with remaining any two O atoms to satisfy octet to each O atom and finally it must form a single bond with the last O atom. There are 8 electrons around the doubly bound oxygen atoms, 6 valence electrons, and 2 inner core electrons, and thus these oxygens are neutral, because they got 8 protons in their nuclear core. Around sulfur, there are 6 valence electrons, and 10 inner core electrons, and thus for atomic number (Z) = 16, the sulfur atom is neutral. But around the singly bound oxygen atom having no connection with H atom, there are 9 electrons, i.e. 2 inner core, one from the S−O single bond, and 6 from the oxygen valance electrons and given these 9 electrons and a $Z = 8$ nuclear charge, this oxygen is formal anion, as shown in Figure 2. In order to minimize the ground state electronic energy, this monovalent HSO_4^- ion delocalizes its electron density (Figure 2), and such way of spreading out electron density is usually represented by its resonance hybrid structure as shown in Figure 1. As a rule, the more resonance forms there are, the greater the delocalization of the electrons, so the more stable the anions become. As shown in Figure 2, the negative charge of HSO_4^- ion is delocalized only on three oxygen atoms, makes it more stable than HSO_3^- ion (delocalization occur only on two O atoms) and hence, it is a reasonable factor in the greater acidity of H_2SO_4 than H_2SO_3.

It is obvious that the bond lengths in the resonance hybrid should be an average of the bond lengths in the separate resonating contributors, the DFT derived resonance hybrid structure shown in Figure 1 has all three O=S bonds equal in length i.e. 1.4 Å. While looking at the molecular shape of this structure with respect to the central S-atom, it has a tetrahedral molecular geometry. If we refer to the assumption of valence shell electron pair repulsion (VSEPR) theory and AX_nN notation, where A = central S atom, X = O atom, $n = 4$ (S is bonded to 4 O atoms) and N= 0 (number of nonbonding

electron pairs around the S), the tetrahedral geometry assumed by the HSO_4^- ion (AX_4 type) is acceptable. Similarly, according to valence bond theory (VBT), the tetrahedral geometry of HSO_4^- ion is due to the presence of SP^3 hybridized S atom at the center.

Chart 3: Trial structures of hydrated bisulfate $[HSO_4^-(H_2O)_n]$, n = 0-3, 5



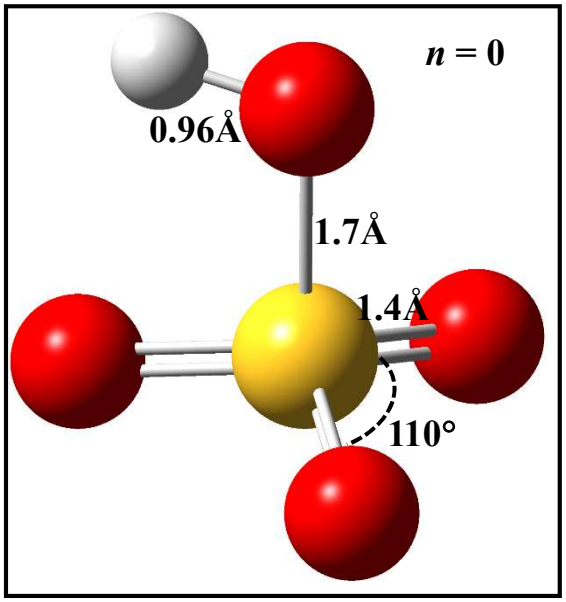


Figure 1. A DFT optimized geometry of naked HSO_4^- ion $[HSO_4^-(H_2O)_n]$,n = 0. For simplicity, formal charge of HSO_4^- ion is not shown.

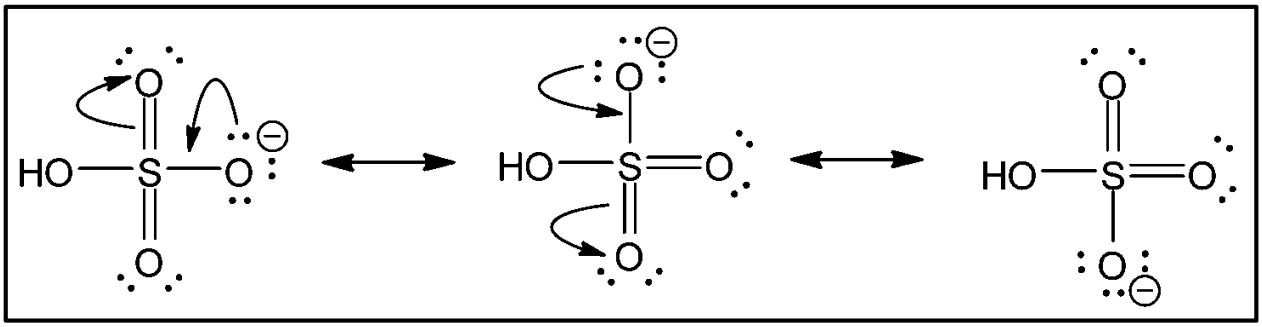


Figure 2. Delocalization of electron density on three oxygen atoms of HSO_4^- ion.

This is dictated by the fact that S needs to form bonds to four O atoms in a molecule of tetrahedral symmetry. In addition to this, π bonds that are formed by the electrons in the non-bonding *p* atomic orbitals on oxygen with the sulfur atom's empty *d* orbitals are interchanged by resonance and the net result is similar to previously depicted DFT derived Lewis resonating hybrid structure of Figure 1. Instead, the molecular shape of this structure with respect to the O-atom holding H-atom is different. This time, the AXN notation becomes AX_2N_2 type and hence, the molecular shape is bent due to the repulsive effect of non-bonding electron or lone pairs present on O-atom.

3.1.2 HSO_4^- ion $[HSO_4^-(H_2O)_n]$, $n < 3$

The mono-, and di- hydrated HSO_4^- ions i.e. $[HSO_4^-(H_2O)_n]$, n = 1,2 has one, and two molecules equivalent of water respectively in the immediate vicinity of the HSO_4^- ion. The DFT derived geometries of them are shown in Figure 3, where yellow spheroid represents Sulphur (S) atom, red spheroids represent Oxygen (O) atoms, and ash grey spheroids represent Hydrogen (H) atoms. The explicitly measured theoretically calculated dimension of the bond lengths of monohydrated cluster $[HSO_4^-(H_2O)_n]$, n = 1 are listed as: each S=O and S−O bond length is 1.4 Å and 1.6 Å respectively (naked bisulfate ion: S=O bond length is 1.4 Å and S−O bond length is 1.7 Å), an O−H bond length is 0.98 Å (naked sulfate ion: each O−H bond length is 0.96 Å) and

each H-----O hydrogen bond (hereafter, H-bond) length is 2.0 Å. It indicates no significant changes in S=O and S−O bond lengths occur while hydrating HSO_4^- ion with one molecule equivalent of water even though two of the four O and one H atoms are linked with the H atoms of H_2O molecule by comparatively weaker H−bond, as shown in Figure 3a. The experimentally observed isomer structure of Figure 3a (Yacovitch *et al.* [26] has mentioned that the isomerization barrier of these two structures is very small) is also fully optimized and presented in Figure 3b. Interestingly, not much deviations in the bond angles, bond lengths, and H-bond lengths are observed except their difference in degree of stability at room temperature. Energetically, the ground state electronic energy of first structural orientation (Figure 3a) is theoretically found to be lower than the second (Figure 3b) by 3.93 kcal/mol. It suggests that the former structural isomer is more stable than latter. Moreover, the DFT optimized geometry of dihydrated cluster $[HSO_4^-(H_2O)_2]$ (Figure 3c) has each S=O and S−O bond length 1.5 Å and 1.7 Å respectively (monohydrated bisulfate ion: each S=O and S−O bond length is 1.4 Å and 1.6 Å respectively), and O−H bond length and H−bond length equal to monohydrated cluster i.e. 0.98 Å and 2.0 Å respectively (naked sulfate ion: each O−H bond length is 0.96 Å). It signifies that no significant changes in S=O and S−O bond lengths occur while hydrating HSO_4^- ion with two molecules equivalent of water even though all the three O and one H atoms are involved in H-bond formation with the four separate H atoms of two H_2O molecules, as can be seen in Figure 3c. More interestingly, lengths of the both H−bonds and O−H bonds of both structural isomers of $[HSO_4^-(H_2O)]$ (Figure 3a and Figure 3b) as well as $[HSO_4^-(H_2O)_2]$ (Figure 3c) cluster are as equal as the H−bond length exists in between the water molecules i.e. equal to intermolecular space, and the two O−H bond lengths of each H_2O molecule in bulk water system respectively as shown in Figure 3d.

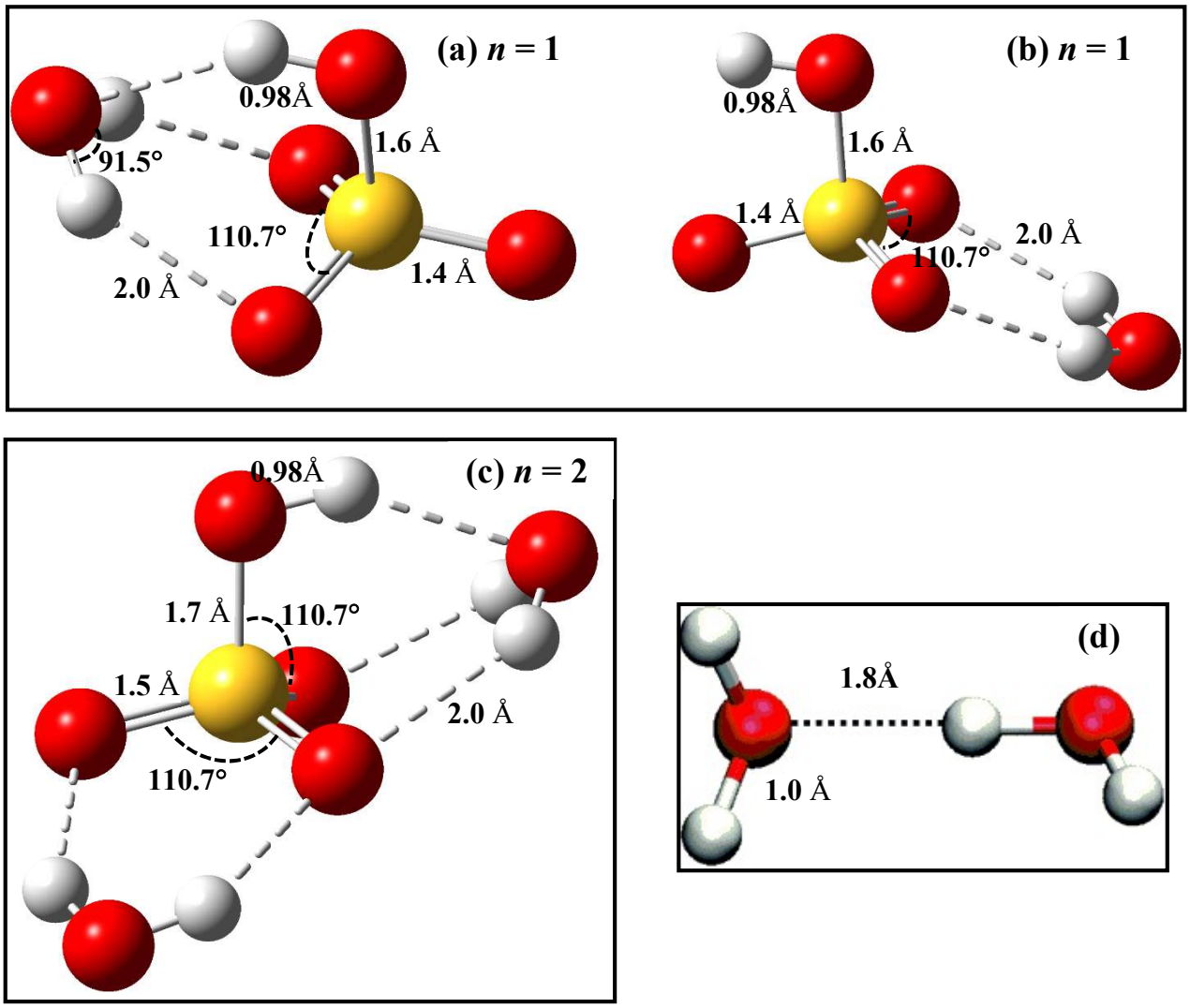


Figure 3. A DFT optimized geometries of hydrated HSO_4^- ions: (a) and (b) isomers of $[HSO_4^-(H_2O)]$; (c) $[HSO_4^-(H_2O)_2]$; (d) Intermolecular space in bulk water. For simplicity, formal charge of the HSO_4^- ion is not shown.

However, the original O–S–O bond angle (110°) of naked bisulfate ion is slightly changed to 110.7° in average; and an H–O–H bond angle in H_2O is reduced to 91.5° from its original value 99.0° after hydration as indicated in Figure 3. Maximum difference (~1°) in the angular value is observed in the O–S–O angle facing towards hydrated water molecule/s. This is simply due to the bound state of the two O atoms through the hydrogen bonds (the negative charge on HSO_4^- attracts H_2O molecule/s closer towards itself in such a way that two or more H–bonds are formed to each other) that may fix their positions in the three dimensional space and hence, may restrict them at the specific position. It ultimately affects rest of the O–S–O bond angles and causes small deviation in the original tetrahedral geometry. The reverse is true for bound H_2O molecule/s which remains in the immediate vicinity of an electronegative O atom of HSO_4^- and occupies its/their specific position/s fixed by the two or more H–bonds. That is why, the O–S–O angle/s of HSO_4^- facing towards immediate H_2O molecule/s may also play an important role to reduce the H–O–H angle/s and vice versa. Except these consequences, no drastic change in overall geometry of the central HSO_4^- ion is observed while hydrating it with one and two molecule equivalent of water separately, though the little delocalization of charge from former to latter species occur, that may be further responsible to bind them each other. A brief overview of the above results and discussions is: the bisulfate H-atom is always found to be involved in H-bond formation process with the water network, and degree of hydration $n < 3$ is insufficient condition to develop inter-H_2O-molecular H-bond due to unfavorable spatial orientation of H_2O molecules in three dimensional (hereafter, 3D) space.

3.1.3 HSO_4^- ion $[HSO_4^-(H_2O)_n]$, $n \geq 3$

The tri-, and penta- hydrated HSO_4^- ions i.e. $[HSO_4^-(H_2O)_n]$, n = 3,5 have three, and five molecules equivalent of water respectively in the immediate vicinity of the central HSO_4^- ion. The DFT optimized geometries of them are shown in Figure 4 and Figure 5 respectively, where yellow, red, and ash grey spheroids represent S, O, and H atoms respectively. The explicitly measured theoretically calculated dimension of the bond lengths in either of these two hydrated structures are listed as: each S=O and S–O bond length is 1.5 Å and 1.7 Å respectively (naked bisulfate ion: S=O bond length is 1.4 Å and S–O bond length is 1.7 Å), an O–H bond length is 0.9 Å (naked sulfate ion: O–H bond length is 0.96 Å) and the H–bond length is 2.0 Å in average. It indicates no significant changes in S=O and S–O bond lengths take place while hydrating HSO_4^- ion with three and five molecule equivalent of water even though all three O and one H atoms are linked with the three separate H atoms of the H_2O molecules and one O atom of nearby H_2O molecule respectively by comparatively weaker H–bond, as shown in Figure 4 and Figure 5. In these tri- and penta- hydrated structures, average lengths of the H–bonds and O–H bond lengths are also as equal as the H–bond length exists in between the water molecules i.e. equal to intermolecular space and the two O–H bond lengths of each H_2O molecule in bulk water system respectively (Figure 3d). However, the original O–S–O bond angle (110°) of naked bisulfate ion is changed to 111° in average; and an H–O–H bond angle in H_2O is reduced to 91.5° from its original value 99.0°.

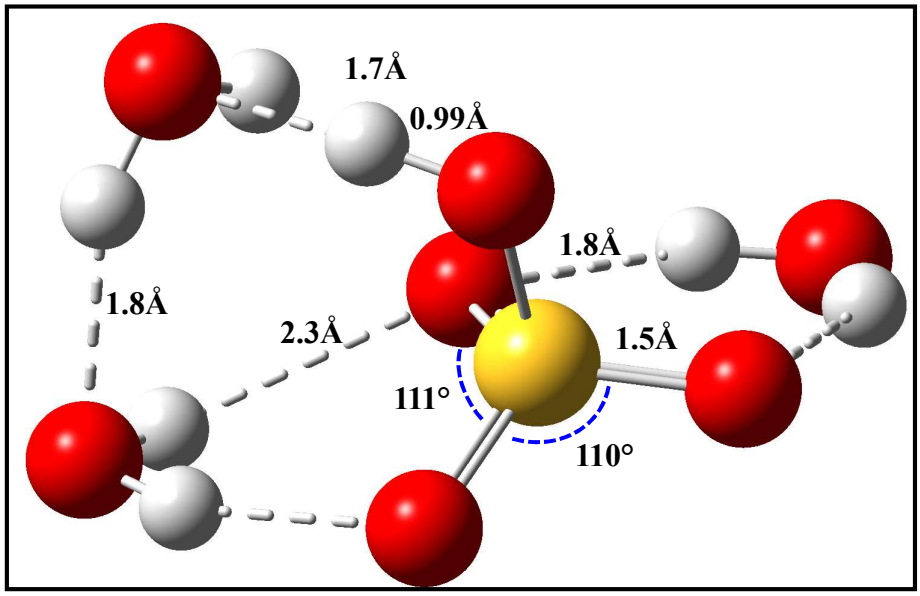


Figure 4. A DFT optimized geometry of tri-hydrated HSO_4^- ion: $[HSO_4^-(H_2O)_3]$. For simplicity, formal charge of the HSO_4^- ion is not shown.

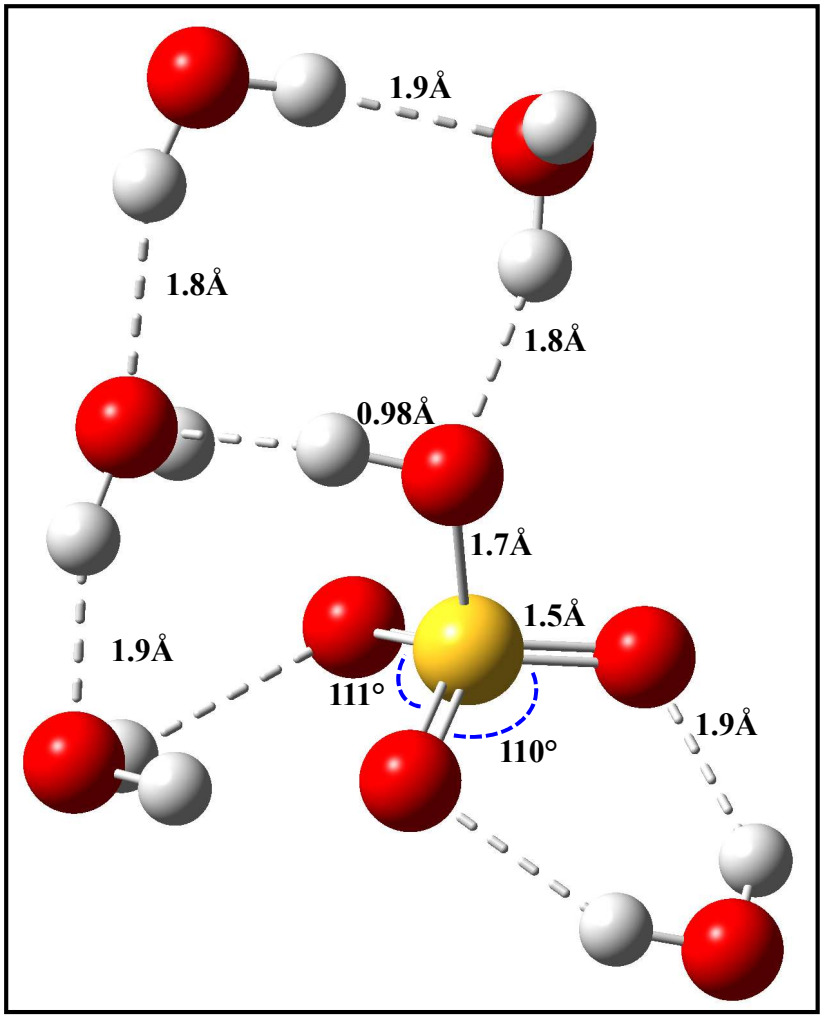


Figure 5. A DFT optimized geometry of penta-hydrated HSO_4^- ion: $[HSO_4^-(H_2O)_5]$. For simplicity, formal charge of the HSO_4^- ion is not shown.

This is simply due to the bound state of the two O atoms through the H-bonds that ultimately fix their positions in the 3D space and hence, may direct them at the specific direction, as explained already in subsection 3.1.2. As a whole, like in small hydrated clusters ($n < 3$), no drastic change in overall geometry of the central HSO_4^- ion is observed in tri- and penta- hydrated clusters as well, except some more delocalization of charge from central HSO_4^- unit to surrounding H_2O molecules occur, that may be due to binding additional H_2O molecules to central ion. A brief overview of this subsection is: like in $n < 3$ clusters, the bisulfate H-atom is found to involve in H-bond formation with the water network, and unlike in $n < 3$ clusters, the water molecules are linked to each other by H-bonds in $n \geq 3$ case. It suggests that whenever degree of hydration $n \geq 3$, the intermolecular space between the H_2O molecules and the space between the central HSO_4^- ion and H_2O molecule is found to be so close to each other that the intermolecular H−bonds formation is a must.

IV. Conclusion

In order to get a clear picture of stepwise hydration and structural stabilization of the biologically significant monovalent HSO_4^- anion, an *ab initio* type theoretical model is applied explicitly to hydrated and unhydrated HSO_4^- ions of the form $[HSO_4^-(H_2O)_n]$, $n \geq 0 \leq 5$. The DFT derived electronic structure of the naked HSO_4^- i.e. $[HSO_4^-(H_2O)_0]$ ion is found to be tetrahedral in shape with respect to central S-atom, representing the resonance hybrid structure that results from electronic delocalization. So, the measured

values of the bond lengths are found to be an average of the bond lengths in the separate resonating contributors. Whenever a first water is added to its immediate vicinity i.e. [$HSO_4^-(H_2O)$], both of its DFT derived isomer structures are found to be bound strongly by H−bonds though they are not theoretically predicted as equally stable isomers energetically. In a similar way, while adding a second H_2O molecule, more number of H−bonds are created with the central HSO_4^- ion due to comparatively more charge delocalization from latter to former species. In addition to this, the additional inter-water H-bonds are detected while increasing solvent number n to three or more ($n \geq 3$) as in [$HSO_4^-(H_2O)_3$] and [$HSO_4^-(H_2O)_5$] clusters. Interestingly, the H-atom of HSO_4^- unit present in all of these micro-hydrated clusters is always remained bound by H-bond with water network. In such sequential hydrations, no any significant differences in the O−S−O bond angles, S−O/S=O/O−H bond lengths of the central HSO_4^- unit are observed. As a whole, the noteworthy points are: whenever the solvent number $n \geq 1 < 3$, the unit negative charge on HSO_4^- attracts water closely enough that two or multiple H-bonds are formed with each water, and whenever the solvent number exceeded three ($n \geq 3$), the negative charge on HSO_4^- may be sufficiently screened so that H_2O-H_2O interactions are favored and hence, inter-water H-bonds are developed.

Even though it was desired to study bigger hydrated HSO_4^- clusters ($n > 5$) theoretically, due to lack of enough budget and time factor, the smaller clusters of the size $n \leq 5$ became the subject of research interest this time. More consistently accurate quantum mechanical model can be applied to the same hydrated clusters to further galvanize the results obtained in this study. Despite these technicalities, this contribution will definitely ease to understand most of the physicochemical properties of HSO_4^- ions in any inorganic bisulfate solutions (including in human body fluids, drugs, sea water, battery systems etc.) and hence, can simplify to model sequential HSO_4^- ions hydrations while exploring their solvation dynamics in bulk aqueous type solutions.

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