Hydrolysis of nitrosyl and thiosulfate anions: Structure and reactivity of water molecules in the first hydration shell

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By

Larisha Khongsit
(Roll No. CY14MSCST11006)

Under the supervision of
Dr. Bhabani Shankar Mallik

भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

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Declaration

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Signature of the Supervisor

Dr. Bhabani Shankar Mallik
Assistant Professor
Department of Chemistry
Indian Institute of Technology Hyderabad

L. Khongsit
(Signature)

Larisha Khongsit
(Student Name)

CY14MSCST11006
(Roll No)

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Dedicated to

The Almighty God, My parents and all my dear friends.

Abstract

Hydrolysis is common method to study the Hydrogen-interaction of a various molecules with water. Formation of Nitric acid in the hydrolysis of nitronium ion is an evidence of hydrogen bond interaction. The water is added is a step wise manner from n=1 to n=5. But no Nitric acid formation was seen in the first three water molecules. After addition of the fourth water molecule, one of the water molecules split up to give hydroxyl ion (OH^-) and hydrogen ion (H^+). The OH^- as a nucleophile come and combine with NO_2^+ ion to form HNO_3 molecule there by stabilizing the system, whereas the H^+ ion goes and attached with one of the water molecule to give Hydronium ion H_3O^+ via a Proton Transfer Mechanism. On further addition of five water molecule the same mechanism was follow in which one Nitric acid molecule were obtained along with a hydronium ion $nH_2O + NO_2^+ \rightarrow HNO_3 + H_3O^+ + H_2O_{n-2}$ in which this formula apply only from n=4 onwards.

Hydrolysis of Thiosulfate was examined by B3LYP method. Water molecules was added one after another starting from n=1 to n=6. Symmetric molecule along with a scissor-type of bonds was obtained in thiosulfate-water isomers. No broken of bond observed, all are H-bonding interactions. Thiosulfate has a tetrahedral geometry and when water molecule are being added it occupy all the site of the parent molecules. As a result when five water molecules are added, isomer like pentagonal kind of molecule was obtained. Similarly an octahedral kind of a shape is seen in one of the isomer when six water molecules are added. Binding energy was calculated from single point energy by considering zero point correction and thermal correction for each isomer. Frequency calculation was taken, comparison of the O-H stretching were also done based on the influence of presence of thiosulfate molecule and the surrounding water molecules.

Frequency calculation was taken for each and every isomer in both Nitronium ion and thiosulfate to obtain the thermal and zero point correction energy associated with the molecules. Therefore the total energy of the molecules includes zero point correction, the thermal correction and the single point energy.

Contents

1. Introduction

1.1 Hydrolysis

Solvolysis is a very common nucleophilic method, based on the different nucleoplilic attacks it has got different names, Hydrolysis for water, Ammonolysis for ammonia, Alcoholysis for alcohol, Glycolysis for glycols and Aminolysis for amines. Since we are using water as the nucleophile therefore Hydrolysis is our point of interest.

Hydrolysis is a process in which a water molecule is added to the substance (substrate).It comes from the Greek words for "water" and "separation. Reaction between water and substrate may lead to formation of new bond through transfer of hydrogen ion or might be just the H-bonding interaction between the two. Hydrolysis is a very important in chemistry of biomolecules. All protein molecules are linked together by H-bond, breaking and formation of new bond can be explained through H-bonding. For example glycosidic bond are the main linkage bond in polysaccharide, which can be cleaved by hydrolysis. Two or more monosaccharide can link to form disaccharide, tri-saccharide, oligosaccharides and polysaccharides. Many hydrolysis which occur in bio system required the specific enzyme to occur. Enzyme that is required to hydrolyse glycosidic bonds is called “Glycoside Hydrolases”.

Hydrolysis is not only important in the bio-chemistry but it is important in everyday life, for example, in the hydrolysis of Amides and Ester. An amide is a particular type of compound, when hydrolysis is applied, that will break down into carboxylic acid (a type of acid that gives vinegar is characteristically sour flavor) and amines (such as amino acids).

There are two types of hydrolysis, acidic hydrolysis and basic hydrolysis. Water can give both acid as well as basic hydrolysis based on Bronsted-Lowry Concept. If it acts as acid hydrolysis it will give a proton to form H_3O^+ and if it

undergoes basic hydrolysis it accepts a proton. Mechanism of an Acid hydrolysis is similar to that of acid dissociation reaction:

$HA + H_2O \rightarrow H_3O^+ + A^-$ (HA= acid)

Similarly, Base-hydrolysis mechanism is similar to base dissociation reaction

$HB + H_2O \rightarrow H_2B^+ + OH^-$ (HB= base)

Hydrolysis is very important in all aspect, in refrigerants alkyl halides was used as chemical compound in the form of CFCs (chlorofluorocarbons). When alkyl halide undergoes hydrolysis it formed into a type of alcohol, which is considered a safer compound for the environment. Cellulose is an organic compound used to make biofuels from paper. This is due to the split in the chemical bonds between cellobiose and cellulase as a result of hydrolysis. Adhesives and various types of resins (epoxies) can made from epoxide, the compound can undergo hydrolysis to produced diol. Digestion of foods in our body is a process of hydrolysis as the water help break the substance one has taken. Soap is formed through the process of hydrolysis. Hydrolysis of triglyceride or fat leads to the formation of glycerin or fatty acids, then glycerin reacts with fatty acids to turn them into specific types of salt known as soap. All these prove that hydrolysis is important in chemistry and everyday life as a whole.

1.2 Aim of the project:

Nitronium ion has a very important relation with the atmosphere and with the green chemistry [1]. Understanding the mechanism of heterogeneous condensation of water and nitric acid is a critical step in the overall comprehension of the atmospheric aerosol formation process. So theoretical study of nitronium ion was aimed to understand more about the characteristic condensation behavior of nitric acid formation into the hydrated cluster [1]. Depending on the atmosphere condition nitronium ion can react with water cluster to form nitric acid or undergo different reactions with atmospheric trace constituents [2]. Nitronium ion is also one of the common intermediate in a chemical reaction. Especially in nitration reaction, ion is

produced (in-situ) by reaction of nitric and sulphuric acid for the formation of nitro benzene. In this reaction nitronium acts as an electrophile.

Nitrosyl ions can also be obtained from thunderstorm or lightning by splitting nitrogen molecules at a high temperature. Many molecules are presence in the atmosphere where nitrogen is one of them. On formation of condensed cloud, positive and negative charges of the different molecules clashes forming a lightning and result into splitting of nitrogen, next step by combination with oxygen to formed nitrogen based oxides. Formation of nitrogen oxides in the stratosphere environment leads to the depletion of ozone layers which have adverse effects such as damage to lung tissue and reduce in lung function. Nitrogen oxides also combine with volatile organic compounds to form toxic products such nitroarenes, nitrosamines and nitrate radical which can cause biological mutation.

Thiosulfate ion is obtained by replacing one oxygen atom in sulfate ion by sulfur atom. They both have similar structure and geometry but different properties. Hydrolysis of thiosulfate helps to understand the reacting trend of the molecule and to predict more apart from the existing reactivity. Thiosulfate undergoes some different reaction for example, reactions with halogen. In acidic conditions, thiosulfate causes rapid corrosion of metals; steel and stainless steel are particularly sensitive to pitting corrosion induced by thiosulfate. Thiosulfate ($S_2O_3^{2-}$) can be used as fertilizers and are clear liquids that provide a source of sulfur (S) and can be used in a variety of situations.

Hydrolysis is a very basic and fundamental and very general reaction that one can try for any system. As water is the universal solvent, any reaction can be carried out using water as solvent. Hydrolysis method is simple but it explains many useful phenomena in chemistry. Without hydrogen bonding life would not have exist on this earth and all living organisms needs water for survival. So that is the reason study of hydrolysis of various systems is important.

1.3 Methodology:

The theoretical foundation for computational chemistry is the time-independent Schrödinger wave equation[3]:

$$H\Psi = E\Psi$$

"Ψ" is the wave function, a function of the positions of all the fundamental particles (electrons and nuclei) in the system. "$\hat{H}$" is the Hamiltonian operator. It is the operator associated with the observable energy. "E" is the total energy of the system. It is a scalar (number). The wave equation is a postulate of quantum mechanics.

The Hamiltonian, ˆ H, is an operator. It contains all the terms that contribute to the energy of a system: $\hat{H} = T + V$, "T" is the kinetic energy operator.

The Born-Oppenheimer approximation

Electrons are much lighter than nucleus (the mass of a proton ≈ 2000 times that of an electron) and therefore travel much more faster [3]. We can say that the electrons can react instantaneously to any motion of the nuclei (think of a fly around a rhinoceros). This assumption allows us to factorize the wave equation:

$$\Psi(R,r) = \Psi n(R)\ \Psi e(r;R)$$

Where, the ';' notation indicates a parametric dependence. The potential energy surface is a direct consequence of the BO approximation.

Computable properties

Many molecular properties can be studied computationally by using different methods, these include bond energies and reaction energies, Structures of ground-, excited- and transition-states, atomic charges and electrostatic potentials, vibrational frequencies (IR and Raman), transition energies and intensities for UV and IR

spectra, NMR chemical shifts, dipole moments, polarisabilities and hyper-polarisabilities, reaction pathways and mechanisms.

Classification of methods

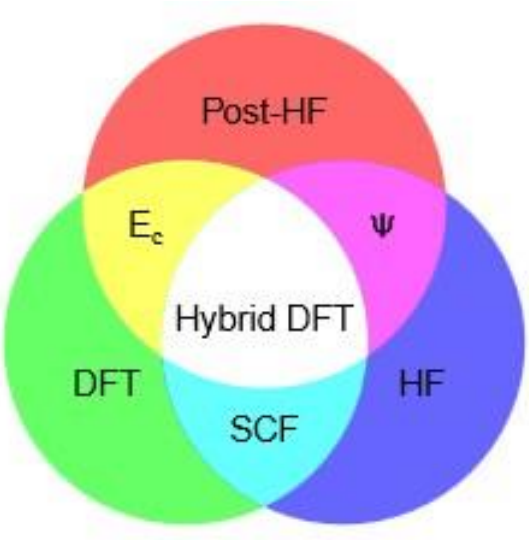

Fig1. Computational methods

Molecular structures and energy can be studied and obtained by different method in computational chemistry. Unique energy is associated with different isomers. Global minimum an isomer (local minimum) with lowest energy corresponds to the most stable isomer. The total energy is determined by approximate solution of time-dependent schrodinger equation with the help of Bohr Oppenheimer Approximation, which allow for the separation of electronic and nuclear motion. The most common and mostly method used to determined energy and structure are Density functional theory and semi-emperical. For large molecules relative total energy can be determined using molecular dynamic methods. Some of the methods are

Molecular Mechanicals Force Fields:

This method is easy to understand, quick program, extremely fasts, and has a limited interpretability and it involves no electrons.

ab- initio method.

It is a full quantum methods, only experimental fundamental constants are involves. The result produced from this method has a higher accuracy as compared to other. It

is a complete quantum method as all the interactions are involved. ab-inito requires a lot of time and as a result it is expensive. Systematic improvement is possible in this method.

Semi Empirical Method:

This is one of the quantum methods in computational chemistry to determine the structural and electronic properties of a molecules. Only valence electrons involvement are includes in this method. It is based on the Hartee-Fock formalism[3] it is a quite fast method but give a limited accuracy.

Hartree-Fock Theory

HF theory is the simplest wave function-based method in computational chemistry. It explains the basic form with more elaborate electronic structure methods. It is synonymous with the Born-Oppenheimer approximation, the Independent electron approximations and the Linear combination of atomic orbitals approximation should be considered for Hartree-Fock Theory.

Limitations of Hartree-Fock (HF) method

Correlation error motion of electrons not correlated due to independent particle model, Geometries often reliable, Energies generally not reliable. Improvements can come from Perturbation Theory, Variation Principle.

Density Functional Theory:

This is one of the advance quantum methods of ab inito used for determining the electronic molecular structure. It is based on the principle of “exactness”. This method is more reliable than the traditional ab-inito method. The method is more accurate with no systematic improvement.

Paul V. R. Schleyer in (1987) quotes “Computational chemistry is to model all aspects of chemistry by calculation rather than experiment.” "Computational

Chemistry has evolved for more than 5o years, starting from a small theoretical study of a core nucleus to a large system, becoming significant in modern research. With the help of super computers and technical system many complicated problems can be solve by incorporating basic principles of classical and quantum mechanics. Structure and behavior of complex molecular systems with more than one electrons can be in easily tackle.

With the latest advancement of computational chemistry questions arose why chemistry are being done on computers. The best answer is to improve chemical (physical) understanding, faster turnaround of new ideas, to reduce the cost and waste of chemicals, high accuracy for even very small systems.

Knowing its element is important in understand the concept of computational chemistry. The whole work is deal with simulation and it is important one should know it technical aspects and how to transfer and send the required input files like molecular structure or property, chemical reaction into the program and computers. To get the required results one has to understand and clear the concept and the method used and more importantly understanding the chemistry of the molecules is needed to get most probable results.To be more accurate and specific about the incoming results simultaneous studies between experimental and theoretical is employed.

Computational chemistry is based on three concepts

Prediction: Before the simulation firstly the prediction was being done that for example when two reactants "A" and "B" are made to react "C" product can be form sometimes with by-product "D".

Interpretation: Here after optimization, interpretation of result was done where new bond might be form through different interactions.

Validation: After interpretation, confirmation of the product formation and the final outcome are obtained. This stage gives the results of the overall studies.

In these particular optimization investigation were carried out by using DFT method of B3LYP 6-311 2d,p. HF method were considered more reliable but B3LYP method has become more defined. The energy calculation is more convincing by taken the zero point energy and thermal energy. Even in ground level

the molecules has some energy associated with them, So to get the specific energy thermal correction and zero point energy correction has to take into consideration. Heartree-Fock method does not consider electron correlation whereas B3LYP does include it.

Merit and Demerit of computational chemistry:

Advantages:

Theoretical calculations are easy to perform, whereas experiments are often difficult to get. By using the computer applications and software calculations are less costly, whereas compound and solvent are needed for experimental studies. Any system can be taken for optimized whereas experiments are limited to relatively stable molecules. Calculations are safe environmental friendly, whereas many experiments have an intrinsic danger associated with them.

Disadvantages:

Sometimes the calculation is time taken and required a lot of patient. Computational chemistry need a little bit of alertness regarding the charge you are given before optimization, improper configuration can lead to a wrong results. One needs to know the proper geometry and familiar with the system before optimizing the system.

Here three systems has been studied and analyzed using Hydrolysis method.

2. Nitronium Ion

2.1 Introduction

The nitronium ion or sometimes the nitryl ion (NO_2^+) has a vital role in stratospheric chemistry [4]. Stratosphere contains important trace components of NO_2^+ and HNO_3. When these species reacts with chlorine-containing species on polar stratospheric cloud particles, they contributed in the polar ozone destruction cycle. NO_2^+ who is produced from N_2O_5 also combine with water molecules to form nitric acid molecule, as a result acid rain has been generated. It can produce by the removal of an electron from the paramagnetic nitrogen dioxide molecule or by protonation of nitric acid.

Nitronium ion has been studied theoretically (spectroscopic studies of intracluster ydration reaction of (NO_2^+) and experimentally [1]. It can exist in normal conditions. It has been used widely as an electrophile (strong) in the nitration of benzene other substances. The ion is generated in situ for this purpose by mixing concentrated sulphuric acid and concentrated nitric acid according to the equilibrium. Nitronium ion is Raman active but Infrared inactive. It was detected by Raman Spectroscopy. (The nitronium ion is linear like carbon dioxide and their vibrational spectra are similar).

To understand the reactivity and behaviour of water- nitronium ion cluster a computational study were conducted by using DFT method, b3lyp/6311+G(2d, p). Okumura and co-workers have reported the study of water-nitric acid cluster by spectroscopic method using IR spectrum[1]. This study supported well with the DFT results which found that with $n \leq 3$(n= Number of water molecules) there is no sign of formation of nitric acid. But as they start increase the number of water (n) from three to four they observed the formation of nitric acid and hydronium along with water cluster $H_3O^+(H_2O)_2$ (HNO_3). As they go from fourth to fifth water the hydronium ion was further stabilized by completion of the first hydration shell with the formation of $H_3O^+(H_2O)_3(HNO_3)$.

$NO_2^+(H_2O)_{m-1} + H_2O \rightarrow HNO_3 + H_3O^+(H_2O)_{m-2}$

2.2 Earlier studies:

In 1994 **Yibin Cao, Jong-Ho Choi, Bernd-Michael Haas, and Mitchio Okumura** tried to study the nitronium ion through spectroscopic analysis [1]. Infrared spectra of $NO_2^+(H_2O)_n$ cluster formed through mixture of nitric acid (HNO_3) and water $(H_2O)_n$ in a pulse discharged tube were taken using Vibrational Dissociation Spectroscopy with respect to cluster size. From the studies experimentally, starting with one water molecule and so on increases they have found a unique change after they reach four water molecules. With n<= 3 nitric acid-water cluster possessed red-shifted H_2O bands and dissociate primarily by losing H_2O molecule. Till n=3 water molecules ligands bound and surrounded to the nitronium core. At n=4 they found evidence the occurrence of an intra-cluster hydration reaction $NO_2^+ + (H_2O)_n \rightarrow HNO_3 + H_3O^+$[1]. From the studies they found that vibrational excitation of the cluster led to loss of HNO_3 as the major channel, as well as loss of H_2O. New vibrational bands were observed and were that of solvated H_3O^+ and to HNO_3 ligands. By replacing H_3O^+ as a charge transfer the new arrangement were produced to form $H_3O^+(H_2O)_n(HNO_3)$. Upon addition of a five water molecule, the hydronium ion was further stabilized by completion of the first hydration shell, leaving HNO_3 in the second shell. From the spectroscopic studies here we see that experiment results agree well with the theoretical studies.

From the theoretical studies it was found that when one water molecule is added no change was observed. Similarly, there was no change observed with two and three water molecules, only the H-bond interaction can be seen. After four water was added there is a proton shift from one of the water molecule to another water to form H_3O^+ and OH^- as a nucleophile went and combine with NO_2^+ to form HNO_3 resulting in $\{HNO_3, H_3O^+, (H_2O)_2\}$ cluster. Similarly, with five molecules of water same trend were follow. So the general formula of formation of cluster is $\{HNO_3, H_3O^+,(H_2O)_{n-2}\}$.

In 2004 **Raffaella D'Auria* and Richard P. Turco** from the Department of Atmospheric, Oceanic and Environmental Sciences, University of California study the " Effects of Hydration on the Properties of Protonated-Water-Nitric Acid Cluster"[2]. Here they have taken the water molecule from n=0 to n=9. The uptake of nitric acid by protonated water (H_3O^+) and the characteristics structure of the mixture $H^+.(H_2O)_n.(HNO_3)_m$. They found that attachment reaction of nitric acid to hydronium ion-water cluster is exothermic across the spectrum of sizes considered. They was observed that isomeric configurations exist and that, depending on the degree of hydration of the ionic clusters [2]. The optimized geometry of the structure shows that the depending on the arrangement of the cluster the nitric acid molecule can dissociate into NO^{3-} and H_3O^+ when the number of water as ligand is greater than about seven onward.

2.3 Results and Discussions:

2.3.1. Monohydrates:

In mono-solvation of nitronium ion with one water molecule "a1" is the most stable among two others arrangements "a2" and "a3". The distant between oxygen and hydrogen in "a1" and "a2" even though at almost 2.4 Å but the arrangement of water molecule toward parent ion is more symmetric in "a1", that the reason "a1" is more stable than "a2" by +3.1 Kcal/mol. H-bond between Oxygen and Hydrogen which measures at an average of about 3Å indicate that there is no H-bond interaction between water molecule and parent ion. "a3" is the least stable with the energy raised by a number + 22.8 Kcal/mol from the most stable isomer.

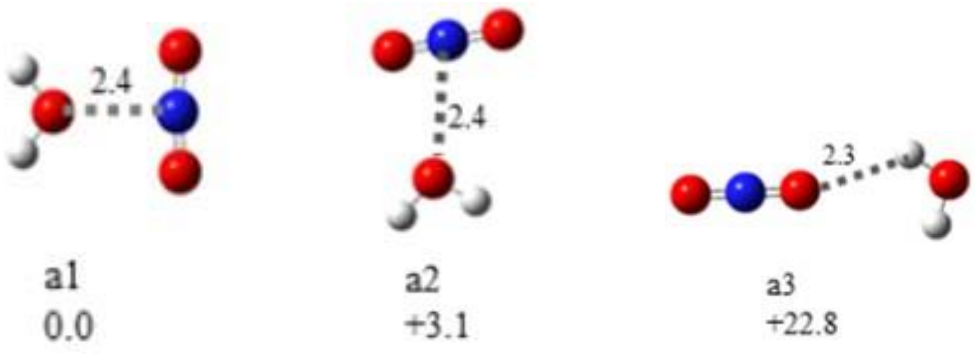

Fig 2: One water molecules isomers

2.3.2. Dihydrates:

The energy reduces in going from one water molecule to two water molecules. The distant reduces to 1.9 Å in "b2", this implies that there is interaction between oxygen of water and nitrogen of nitronium ion, in the first structure "b1" the two water molecules are symmetrically arranged just opposite to the parent molecules at distance of 2.4 Å each, it is the symmetric factor which play a role and make this molecule the most stable among the other two isomers "b2" and "b3", in the second isomer "b2" there is one H-Bond formation at a distant 1.5 Å which stabilized the molecule, however there is no much different between "b1" and "b2" with just an energy difference of just +0.35 Kcal/mol. Henceforth we can say that "b1" and "b2" are equally stable . But when we look at the third structure "b3" there is no way the water to interact with parent ion and plus there is 2.4 Å distance between oxygen and nitrogen of parent ion. This is the reason the molecule is destabilized by +4.7Kcal/mol as compared to "b1".

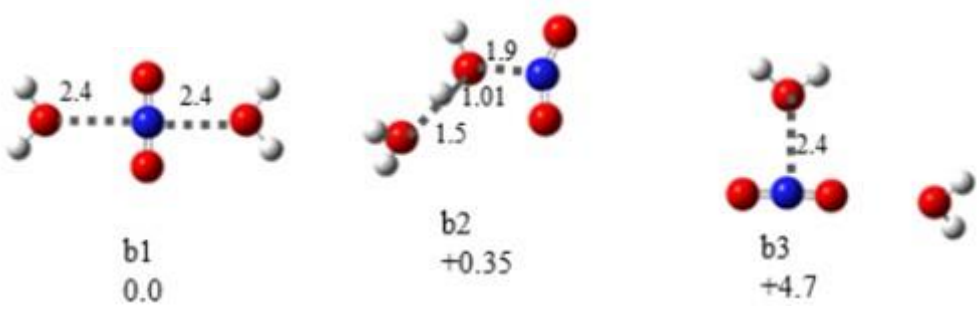

Fig 3: Two water molecules isomers.

2.3.3. Trihydrates:

When we take a quick look at structure one "c1" and two "c2" of three water molecules there is no much different in the arrangement of water molecule with the parent ion but there is different in the arrangement of atom in which "c1" is a 3-D structure whereas "c2" is a planar. Even though both "c1" and "c2" have almost same bond length but in 3-D structure the interaction are believed to be more

effectively, that the reason why “c1” is more stable than “c2” by +12.2 Kcal/mol. whereas in the third arrangement “c3” all the three water molecules are far apart from the parent molecule making the it the least stable one with energy +21.3 Kcal/mol from the reference, stable isomer “c1”.

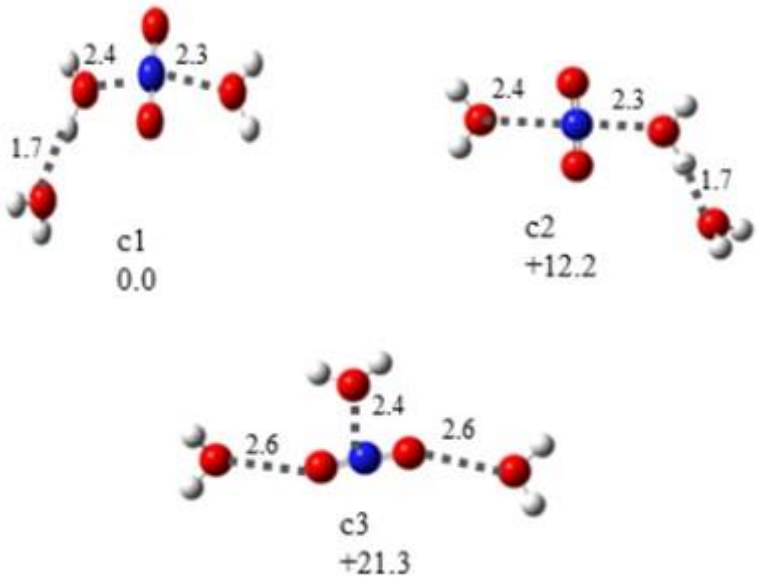

Fig 4: Three water molecules isomers

2.3.4. Tetrahydrates:

When come to four water arrangement due to the increase stabilization by H-bonding the molecule become more stable. There is a formation of nitric acid plus with hydronium ion as shown in the figure1 below. Formation of these molecules raises the stability of the overall molecule. The formation of nitric acid is evident from the compared N-OH bond length of experimental value (1.34 Å) with calculated value (1.405 Å). This happen when there is a proton transfer from one water molecule which breaks into H^+ and OH^-, where the OH^- comes and combines with NO_2 to give nitric acid(HNO_3) and the H^+ combines with water to give hydronium ion (H_3O^+) via Proton Transfer Mechanism. Among all three isomers of four water molecules “d1” is the most stable one. When we look about the structure

two “d2”, here also we can see the formation of product, but the distant between the bond lengths (N-O) here is less significant as compared to “d1”. Come to isomer “d3” there is no transfer of proton and due to a larger distance no product can be seen, molecule is destabilizes and the destabilizing energy came out to be about +20.4 Kcal/mol greater than “d1”. The only stabilizing factor here is only H-bond formation.

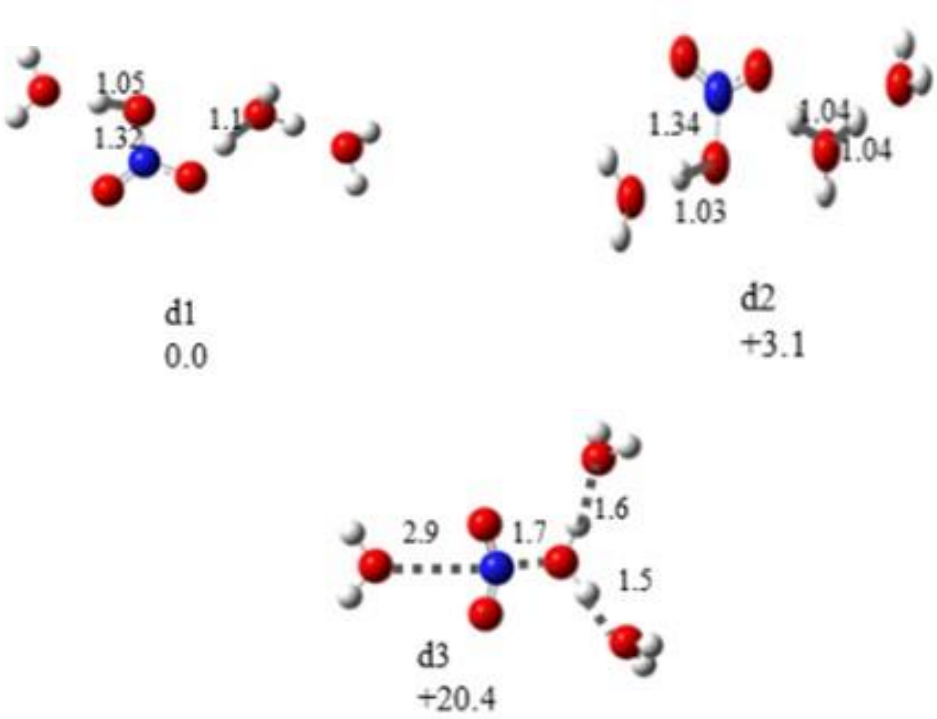

Fig 5: Four water molecules isomers

2.3.5. Pentahydrates

When come to five water molecules, they follow the same trend as in four water molecules. In “e1” there is bond formation showing formation of nitric acid, with this there is a stabilization of the whole molecule through the proton transfer from one water molecule. Hydronium ion (H_3O^+) is formed by splitting of water into H^+ and OH^- whereby OH^- as nucleophile goes and attacked parent ion and H^+ came and binds with one of the water molecule to form H_3O^+. In “e3” the molecule is hold

stable by the formation of two H-Bonding. The H-Bonding is at a distant of 1.7 Å and 1.8 Å each. However, the molecules are not that stabilized and the stabilization energy is raised by 25.4 Kcal/mol from the most stable "e1". From the structure and energy calculation "e2" has almost same stability as compared to "e1".The energy different is just 0.028 Kcal/Mol. This is due to the different arrangement of atoms around the parent ion which causes "e1" a little increase in stabilizing energy.

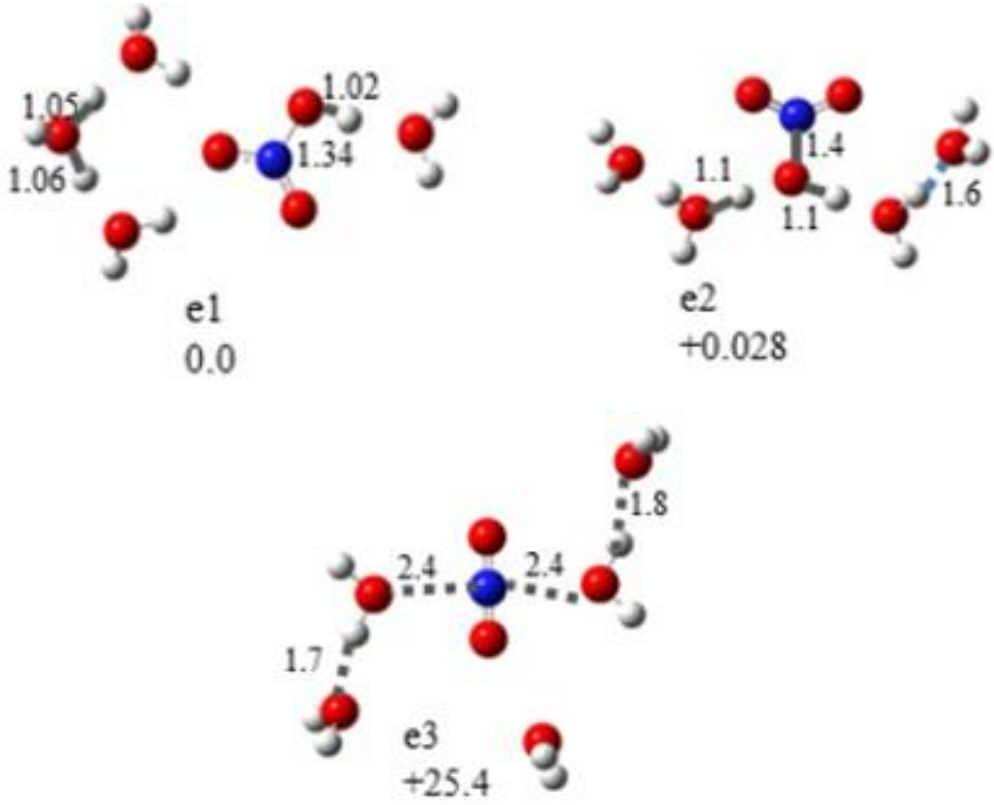

Fig 6: Five water molecules isomers

2.4 Conclusions:

The reaction was performed in aqueous medium by using (b3lyp/6-311 +G/2d, p). The same parent molecule was being examined by using HF/3-21 method but b3lyp is more accurate than HF method. There is no reaction taking place with one, two

and even in three water molecules. The reaction started when fours water molecules are added (surrounding the parent nitronium ion). The electron transfer results into the formation of nitric and hydronium ion. One proton was being transferred from one water molecule leave OH^- ion which was then combined with NO_2^+ to form the corresponding product.

The reaction does not occur with lesser water molecule due to the required high activation energy which cannot be achieved, however with increase in water molecules the solvolysis increases as a result stabilization energy further increases leading to the formation of products. We also noticed that as the number of water molecules increases the stabilization factor increases with one water having the lowest energy(-6 Kcal/mol) and then goes on increasing till five water being the highest energy(-39.9 Kcal/mol). This comparison is made by taken the most stable molecule among the three isomers from all the five arrangements. From this observation we can say that the stability of a molecule is directly proportional to the numbers of water molecules associated with it. More the number of water molecules greater is the stabilization energy.

3. Thiosulfate

3.1 Introduction

Thiosulfate is an oxyanion of sulfur. It derives from a sulfate ion in which one of the oxygen is replaced by sulphur.it can be made from by reacting elemental sulfur and sulphite ion.

$$S(s) + SO_3^{2-}(aq) \rightarrow S_2O_3^{-2}(aq)$$

Thiosulfate is not stable in acidic medium where as it can be stable in aqueous or basic medium. In acidic medium it dissociates to sulphite and sulfur, it is a versatile compound. Many fundamental reactions of chemistry for example gas formation (GF), precipitate formation(PF), complex formation(CF), acid-base interaction(ABI), redox interaction(RI) can be explained in aqueous solution of thiosulfate [5] etc.

Thiosulfate can also found in nature, naturally it is found in hot spring and geysers. It is also produced by certain biochemical processes. Thiosulfate converts cyanide in a small amount in our body to a harmless product. Thiosulfate has an important role in biosynthesized of cysteine, an amino acid containing Sulfur which helps protein to lock in their correct three-dimensional shapes. Thiosulfate is found in small quantity in nature. Thiosulfate has a distorted tetrahedral geometry with C_{v3} symmetry, similar to that of a sulfate ion with a central and a peripheral sulfur [6]. Sulfur is larger atom as compared to oxygen so the pi bond of S-S in thiosulfate is weaker with a longer bond distant than that of S-O in sulfate ion.

Thiosulfate can be used mainly as reducing agent. It is used as titrant in determining the concentration, for example in the titration of iodine. It converts iodine into iodide anion during the process. Thiosulfate can also be also used as an anti-chlorinating agent in the pool, it is ant used as bleaching agent for example to stop bleaching in paper industry and instantly de-chlorinate water. Thiosulfate formed water-soluble complexes with metal which as a result very useful in photo-processing by dissolving excess silver bromide on the surfaced of an exposed film

preventing excessive darkening. It also can be employed in the metal extraction, like silver from silver ore. Leather industry and textiles industry uses thiosulfate during the process.

Common thiosulfate are obtained from different compounds such as Ammonium thiosulfate ($NH_4S_2O_3$), Barium thiosulfate (BaS_2O_3), Calcium thiosulfate (CaS_2O_3), Sodium thiosulfate (NaS_2O_3), gold(1) Sodium thiosulfate di-hydrate ($AuNa_3(S_2O_3).2H_2O$, Potassium thiosulfate ($K_2S_2O_3$). Because of different properties each of these thiosulfate salts has got its different uses. Commonly it can be used as metal lubricants, fungicide and metal cleaning agent. It also found important in agricultural treatments whitening agents, in matches and explosive etc.

Thiosulfate plays an important role in both living and the surrounding environment. It acts as an antidote for cyanide poisoning, sulphite and thiocyanite ions was produced when thiosulfate react with cyanide. The reaction occur through an enzyme catalyst, small quantities of ingested cyanide was neutralized by cell mitochondria produced (occur naturally in cassava roots, lima beans and almonds). Thiosulfate is an intermediate in various biochemical pathways.

$$CN^- + S_2O_3^{2-} \rightarrow SCN^- + SO_3^{2-}$$

Raman and IR spectra are one of the important tools to identify and characterized qualitatively and quantitatively the structure and dynamics of a compound[7]. One important application of optimization by using B3LYP is the study of frequency. Absorption frequency of each and every bond can be obtained and characterized. By study of these absorptions one can compare the theoretical frequency and obtained frequency based in different conditions. The value obtained has a high accuracy. The density functional theory (DFT) including some correlation is often the best compromise between accuracy and computer sources available. The B3LYP functional is a very common choice providing sufficiently high accuracy for a wide range of molecular systems.

Published in 2012 Małgorzata A. Brodaa, Aneta Buczeka, Teobald Kupkaa, Jakub Kaminsky in their paper "Anharmonic vibrational frequency calculations for solvated molecules in the B3LYP Kohn–Sham basis set limit" [7] explained about the solvent dependency of harmonic and anharmonic vibrational wave numbers of water, formamide and formaldehyde was studies using B3LYP method.

3.2 Earlier studies

In 2003 Richard A. Bryce, John M. Charnock, Richard A. D. Pattrick and Alistair R. Lennie studied the EXAFS (X-Ray Absorption And Fine Structure Spectroscopy) and Density Functional Study of Gold(I) Thiosulfate $Au(S_2O_3)_2^{3-}$ Complex in Aqueous Solution[8]. They also study high level quantum mechanical calculations, which include the effect of aqueous solvent via a dielectric continuum model. EXAFS measurements on Au $(S_2O_3)_2^{3-}$ show gold coordinated by two sulfurs at 2.29 Å. Density functional calculations, incorporating the effect of solvent using the COSMO method, show the 2-fold S coordination of Au to be linear in geometry. This computational approach is further employed to examine the conformational potential energy surface of the complex in aqueous solution.

In this study, they explore aspects of Au-S aqueous chemistry[8]. A number of experimental and theoretical studies have addressed the nature of aqueous Au-S transport. Calculation predicts a rotational barrier in solution of less than 3 kcal/mol. Calculated Au-S bond dissociation energies indicate a strong metal-S bond in aqueous solution. Lower solution stability of Au $(S_2O_3)_2^{3-}$ with respect to another thio gold complex, $Au(SH)^{2-}$, is predicted in accord with measured overall stability constants. These calculations, together with our experimental observation that $Au(S_2O_3)_2^{3-}$ decomposes at 393 K, support the view that gold transport by the thiosulfate complex of Au(I) may be restricted to ambient and moderate temperatures. This contrasts with the Au (I) thiolate complex which can mobilize gold at elevated temperature and pressure.

3.3 Results and Discussions:

The system was systematically studied by hydrolysis process. From the results observed water molecules was added symmetrically to the parent molecule (thiosulfate). Both the hydrogen of the water would arrange to get a minimum stable structure thus by facing to both oxygen atoms or toward oxygen atom and sulfur atom respectively.

One water molecule was added in two different isomers. As we can see from the diagram 7(A) below, both the isomers have almost same structural identification. As a result the isomer "1a" has an energy difference of just 0.062 Kcal/mol as compared to the stable isomer "1b". Different kind of arrangements of one water molecule is limited as all the isomer will get into stable isomer just by only a point difference in energy. In another word, this means that the one water arrangement had a very less isomers (configuration). As a result only two isomers "1a" and "1b" are observed with one water molecule. In both "1a" and "1b" the water molecule bind to parent thiosulfate from below that means water molecule are facing both the oxygen as seen in the fig 7(A).

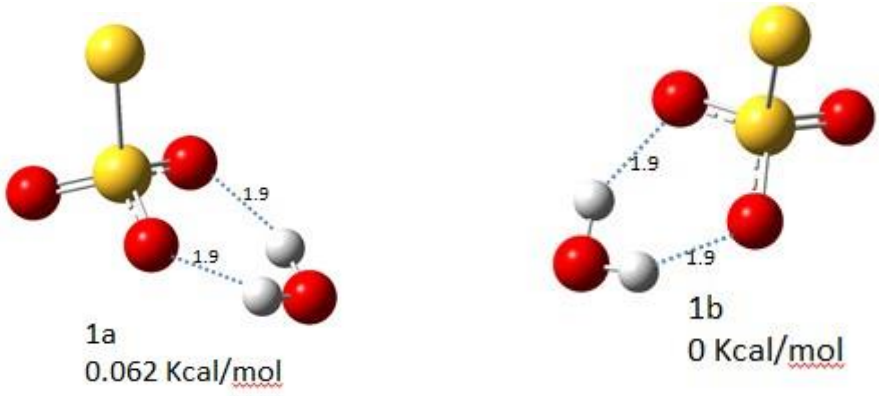

Fig: 7(A) Thiosulfate with one water molecule

Similarly, with two water molecule both the isomers are stabilized by formation of a scissor bonds. Isomers "2a" and "2b" are shown in fig 7(B) where two water

molecules are being added. In both the arrangement one water is added from the top position facing sulfur and oxygen while one is added from the bottom position facing the two oxygen of the thiosulfate molecule. One oxygen atom interact commonly to both the water molecules. The interaction is within the H-bonding for example with a bond distance of within 2 Å from the bottom face whereas the upper face has a bond distance greater than that. This implies that the interaction is more favorable from the lower face. As we see from the fig 7(B) below both the isomer have almost similar stability with just "2a" greater than "2b" by just 0.00055Kcal/mol.

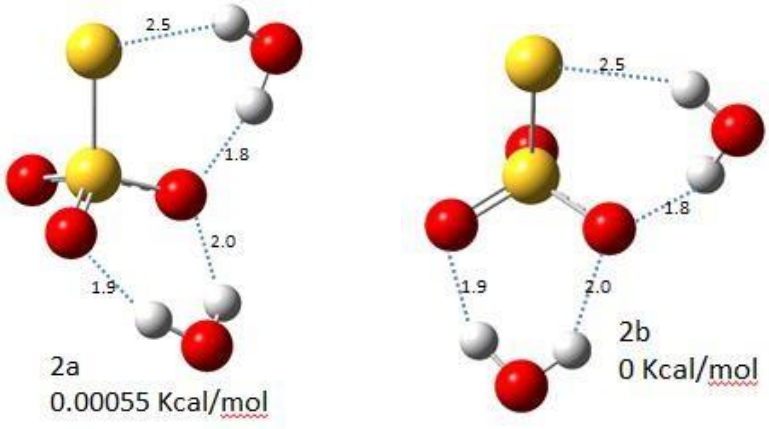

Fig: 7(B) Thiosulfate with two water molecules

On further going on by adding one more water molecules, three isomers was observed "3a", "3b" and "3c". Here again there is breaking of bond but the molecules are stabilized by formation of a scissor bonds. As we can see all the three water molecules are arranged in such a way that all the sides of the parent thiosulfate are occupy by the water molecules. As we can see from the diagram 8 isomer "3a" and "3b" have almost same stability with an energy range of 0.74 Kcal/mol. This mean that in three water also only two isomers can be seen in which both of the isomers two water molecules are being added from the upper face. All the interactions are H-bonding and Ion-Dipole. Isomer "3c" comes up to be the most

stable among all the isomer. Here two of the water molecules are added from the upper face.

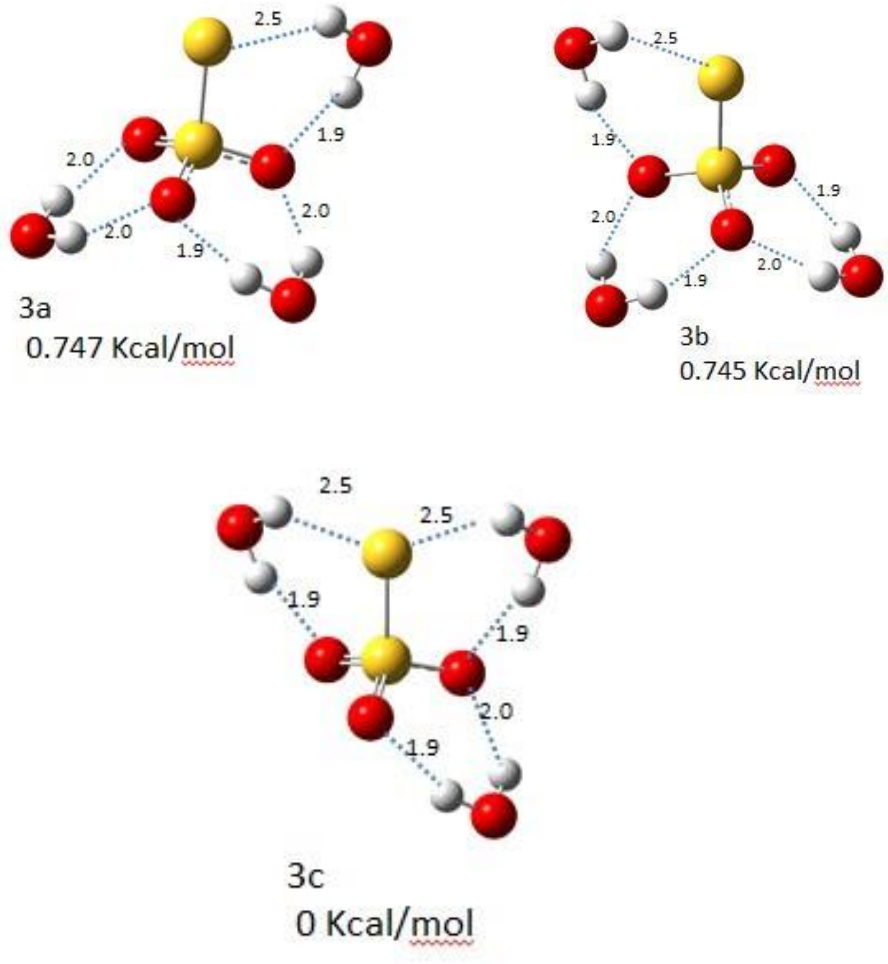

Fig: 8 Thiosulfate with three water molecules

When come to four water molecules, here some of the bonds have scissor type whereas some are not. As we see from the fig 9 below "4a" three of the four water arranged in a scissor form whereas the fourth water is out of the box. In this way we can conclude that to get a scissor bond formation at the most three water molecules are required to add in and around the parent molecule. As every rules has exception, similar here we saw that one of the isomer "4b" has acquired a symmetric structure in which all the water molecules are occupying the site of thiosulfate ion. This is due to the reason that somehow the fourth water manage to go within the first solvation sphere. But in "4c" only two of the water molecules have a scissor bonding with the parent thiosulfate whereas the other two are arranged randomly quite far from the

thiosulfate molecule. Energetically also as obtained from the experimental calculation, we can convinced that "4b" has the highest stability with all the bonds arranged symmetrically in a scissor form thereby having a lowest energy. After that followed "4a" with three waters being arranged symmetrically. The least stable is "4c" with an addition of 2.045 Kcal/mol of energy as compared to that of "4b". All the interactions are of H-bonding with similar bond distance for all the isomers.

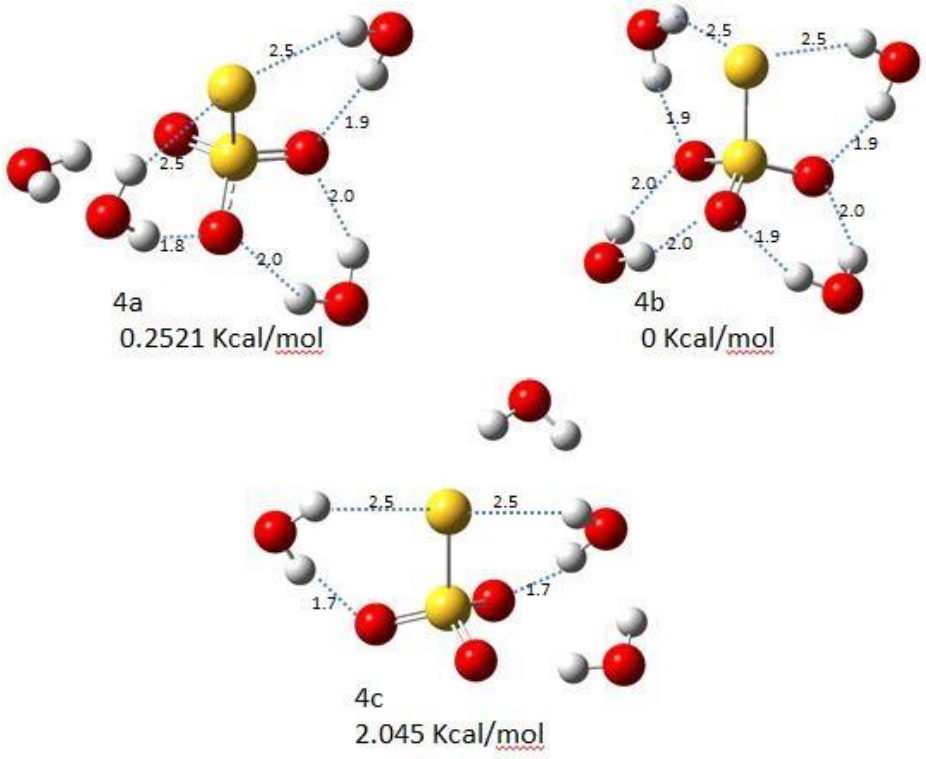

Fig: 9 Thiosulfate with four water molecules

With five water molecules many arrangements was tried out, however only three isomers were taken for analysis. Among these two arrangements two of the isomers were found to be of comparable stability and similar structural orientation. Looking at "5a" the position of some of the water molecules were not proper and not symmetrically arranged toward the parent ion. As we can see from the diagram 10 below only two out of five waters were symmetrically positioned, the rest were randomly arranged. But when we look at "5b" and "5c" it is surprising to see that all the water are symmetrically arranged toward the parent molecule. At one click we can think that how this is possible, how oxygen molecule have more than two bonds.

But as we have seen right from one water molecule, all the interaction is just via H-bonding and not a real bond, the formation of "5b" and "5c" can be justify. Both "5b" and "5c" are comparable but in "5b" three of the waters are added from the lower face which we can say is more crowded as we compared to "5c" in which three water molecules are added from the upper face and the rest two are added from the lower face. Because of this reason "5c" is the more stable than "5b" by just 0.627 Kcal/mol. Energetically, when we compare, "5a' is the least stable with energy raised of 3.6 Kcal/mol from the most stable isomer. "5b" and "5c" are in a distorted pentagonal shape.

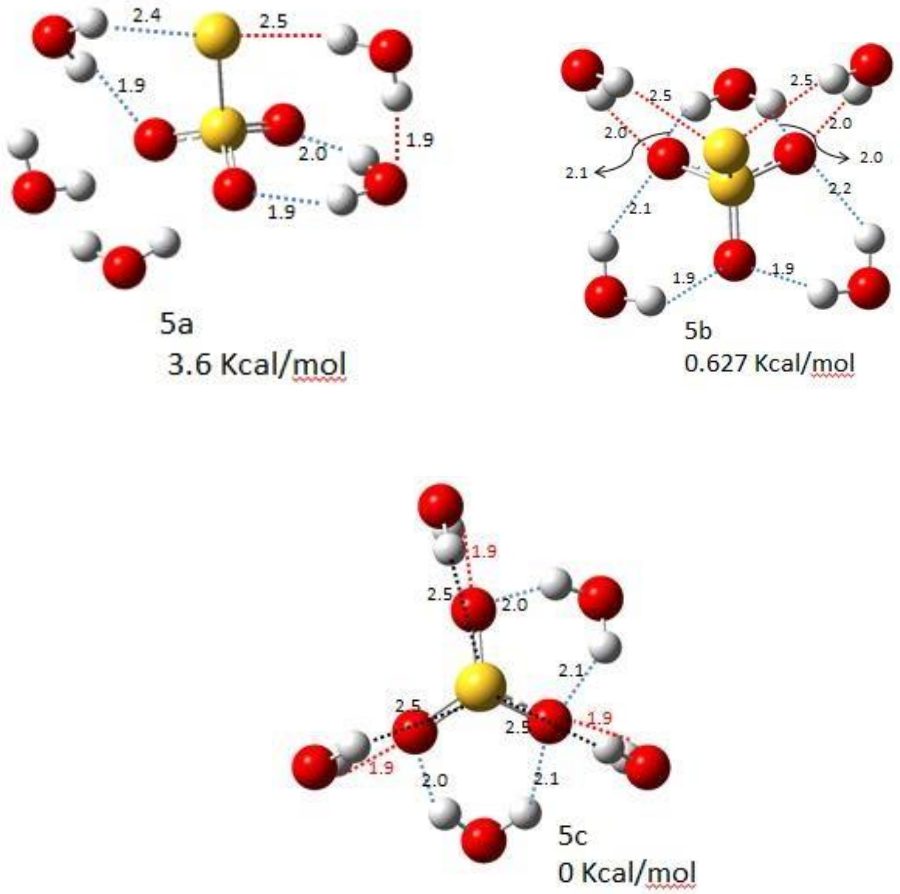

Fig: 9 Thiosulfate with five water molecules

The optimization was extended till six water molecules. To a surprise we found that thiosulfate with six water molecules still have one symmetric system. The system is such a way that all the site of thiosulfate is connected to water molecule via a H-

bonding thereby obtaining a distorted octahedral shape. This can be found from the fig (10) “6c” below, this system has a highly symmetrical orientation. The symmetry is followed only in “6c” whereas the other two isomers “6a” and “6b” the symmetry is destroyed and the water are oriented randomly. In “6a” only two water molecules are oriented symmetrical to the parent ion, in”6b” three water molecules were arranged in a symmetrical way whereas the rest three waters are arranged randomly around the ion. So from the water arrangement we can easily predict the stable isomer. “6c” being a symmetric system has the highest stability. “6b” comes second with its energy raise of 0.111 Kcal/mol from “6c”. “6a” having the least stability with energy raised of about 2.7Kcal/mol from the most stable isomer “6c”.

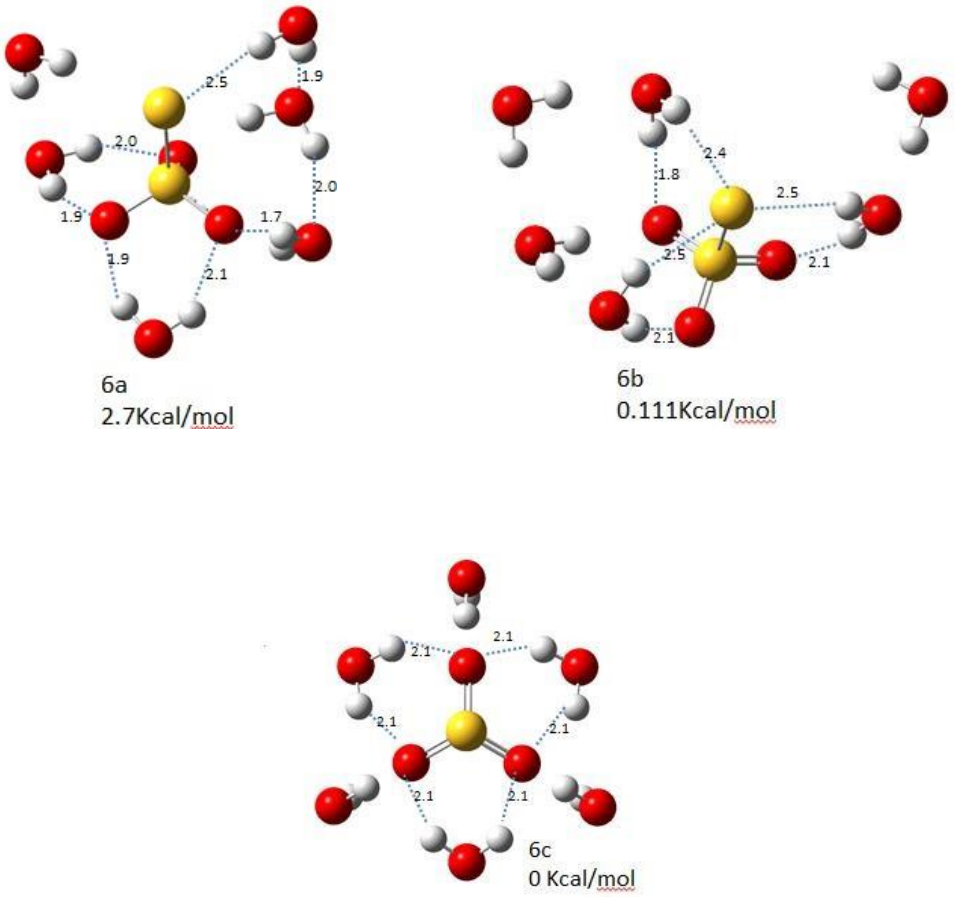

Fig:10 Thiosulfate with six water molecules

3.4 Frequency analysis

The frequency calculation was also studied, only some of the isomers frequency has been reported to avoid the complexity problem. From the observation we found that O-H stretching frequency increases with increase in water molecules. This can be explained from the theory below;

As we know,

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Where, “v” is the the wavenumber of absorbance

“k” is the force constant

“μ" is the reduce mass

As the reduced mass remains the same so the change in frequency is only dependent on the force constant according to the equation above. But force constant depends on the bond length and the strength of the bond. In isomer 1b we can say the interaction with the parent thiosulfate ion is 1:1 because one water molecule is present, the frequency obtained is (3587.96 cm^{-1}). In isomer “2b” the interaction with the parent ion is contributed by two water molecules and as a result the mentioned O-H stretch bond is stronger and absorb at a higher frequency (3659.71 cm^{-1}) as compared to isomer “1b”. Similarly as we move to three water molecules, now the contribution is from three water molecules. O-H bond become strong with shorter bond distant within the water molecule itself and stretch at frequency of about (3681.66 cm^{-1}). The stretching is maximum with four water molecule (3699.52 cm^{-1}) as the mentioned O-H bond contribution is least resulting in a strongest bond due to shorter bond distant. Due to this it required more energy to stretch and as result the frequency is high. Frequency comparison has shown below in a table.1 and the mentioned O-H symmetric stretching is shown in the figure 11 below.

Table1: Frequency comparison of all the stable isomers.

SL. No	System	Mode of stretching (O-H stretching)	Frequency (cm^{-1})
1	One water (1b)	Symmetric stretching	3587.96
2	Two water (2b)	Symmetric stretching	3659.71
3	Three water (3c)	Symmetric stretching	3681.66
4	Four water (4b)	Symmetric stretching	3699.52

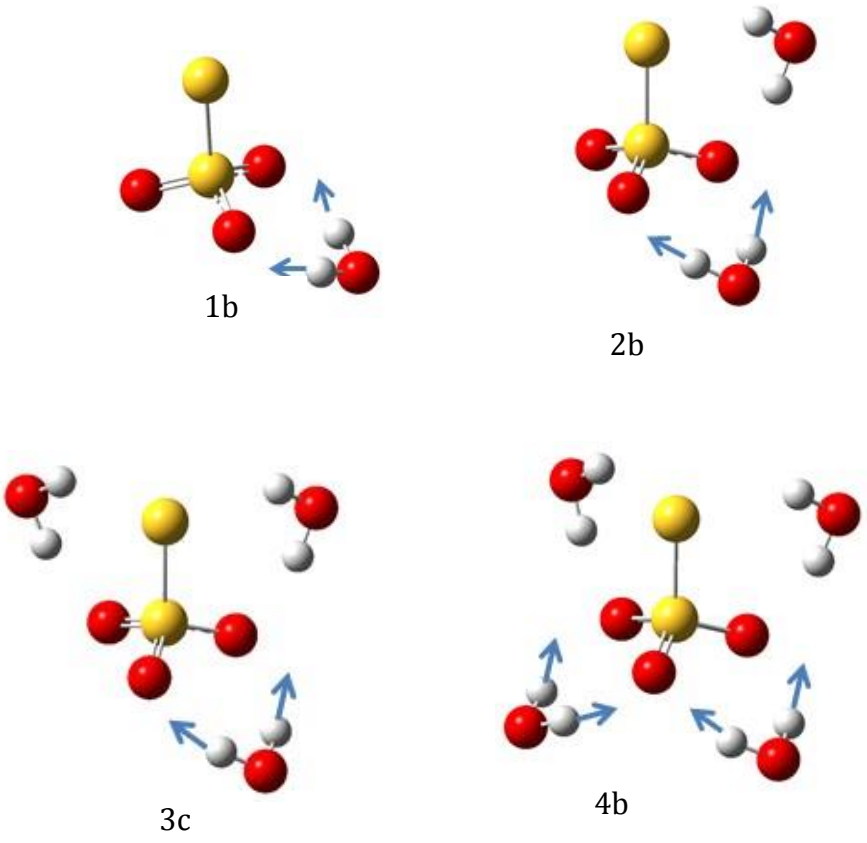

Fig: 11 Molecules having highest mentioned O-H stretching

However, the due to the complexity of the system it is very difficult to clearly predicts the stretching of all the vibrations as more than one stretching will have the same value. This is due to the reason that two or more stretching are equivalent as they experience the same chemical environment.

3.5 Conclusion:

From the above studies we found that the thiosulfate-water has a scissor-type of bonds and some isomers attained the symmetric geometry in the first solvation sphere. However, the symmetry pattern is broken when the water molecule entered the second solvation sphere. There were no products formation, all was just H-bonding interaction. Due to formation of scissor bonds the system is stabilized, five and six stable isomers had a symmetric arrangement of distorted pentagonal and octahedral respectively. Frequency prediction has become complicated due to the equivalent stretching. However, some fundamental stretching can be predicted and found to be increases with increase in water molecules.

4. References:

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