Quantum chemical analysis of the structures of MgSO4 hydrates

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Quantum Chemical Analysis of the Structures of $MgSO_4$ Hydrates

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1. Introduction

Magnesium sulfate salts can form hydrated compounds with up to seven degree of hydration with an energy exchange of the order of 2.8GJ/m^3 [1]. In addition, this salt is abundant in nature and thus this material is a potential candidate for storing energy in seasonal heat storage systems. One of the main issues in using this material for seasonal heat storage system is its slow kinetics and low extent of water take-up under normal atmospheric conditions [2]. In addition, the salt undergoes considerable changes in its crystalline structure during hydration and dehydration, and often they encounter the formation of cracks and pores in the crystal structure [3]. This significantly affects the efficiency of the salt in storing energy and also reusability of the material.

A molecular level investigation is necessary to understand the process of hydration and dehydration in detail. Presence of an extensive network of hydrogen bonds in $MgSO_4.7H_2O$ crystal is identified by Allan Zalkin et al [4]. Significant delocalization of hydrogen atoms within the hydrogen bonds are reported in the study. The 7^{th} water molecule in a hepta-hydrate crystal is captured in the interstitial space within the crystals due to coulombic forces and they are very easily removable. Thus modeling a stable molecule of magnesium sulfate hepta hydrate is difficult. So we undertake the hexa hydrated magnesium sulfate to study the equilibrium molecular structure. The hydrogen bonds present in the structure, which stabilizes the molecule, is a focus of attention in this study. In addition, we report Natural Bond Orbital (NBO) [5] charges of Mg and S as a function of degree of hydration in this study. The NBO analysis gives information about electronic occupations in the molecule. In addition, the variation of the natural charges give information about the nature of inters atomic interactions involved in the hydration process of magnesium sulfates.

The hydration process is accompanied by a considerable amount of energy exchange with the surroundings. In addition, significant changes in the crystal structure are predicted to happen during hydration. The binding of a water molecule on a slab of magnesium sulfate will resemble the hydration phenomena of a real crystal. Maslyuk et al [6] have performed such an analysis on kieserite structures and found the influence of hydrogen bonds during hydration. A similar study has done towards the last part of this account, which gives important information about hydration process of magnesium sulfate crystal.

2. Methodology

Density Functional Theory (DFT) [7] is widely accepted as a reliable and accurate method for studying molecular structures and their properties. This method tries to solve the Schrödinger wave equation for a molecular system to find the ground state electronic structure distribution of the system. However, this method is computationally expensive and thus only smaller systems, consisting of few atoms, are usually studied using this method.
Optimized molecular structure of Magnesium Sulfate hexahydrate is calculated using Density Functional Method implemented in Amsterdam Density Functional (ADF) software package

[8]. In this work, we have used B3LYP functional [9] to model electronic exchange and correlation in magnesium sulfate. A doubly polarized triple zeta basis set [7] is used to construct the electronic wave functions. A spin restricted calculation is performed to find the singlet (spin paired) state of the hexa-hydrate molecule, while a spin unrestricted calculation with a spin polarization of 2 yielded the triplet state of the molecule.
The water binding on the surface of magnesium sulfate is studied by taking a slab of magnesium sulfate unit cell with a vacuum space of 10Å in x-direction of the unit cell. The geometry is periodic in the other two spatial directions. A water molecule is placed at different locations within the vacuum space at varying distances from the (100) surface of the slab. Each time, the geometry is optimized while constraining the distances between the oxygen atom in the water molecule and a magnesium atom in the crystal surface. The energy of the resulting geometry is computed using BAND [10] program implemented in ADF package.

3. Molecular structure of magnesium sulfate hexa-hydrate molecule

Magnesium sulfate hexahydrate is formed by coordinating 6 water molecules to Mg^{2+} ion to form a distorted octahedra [11] combining with an SO_4^{2-} tetrahedra through hydrogen bond interactions [12]. In a crystalline phase this structure arranges itself to form a regular order in three spatial directions. A single molecule of $MgSO_4.6H_2O$ is representative of a gaseous phase system and it does not usually exist in nature. However, for the purpose of studying the chemical interactions involved in the $MgSO_4.6H_2O$ molecules, it is worth modeling such a molecule.

3.1 Spin paired state (Singlet)

Figure.1 shows the DFT optimized structure of $MgSO_4.6H_2O$ molecule. The geometrical parameters in the structure resemble well with $MgSO_4.6H_2O$ unit in a crystalline structure [4]. The average bond lengths are compared with the literature in Table.1 and found reasonable agreement. The deviation from the literature is due to the distortion in some of the bonds because of the absence of a crystalline periodic environment for the structure.

Table 1. Average bonds lengths between Mg-Water and S-O bonds in $MgSO_4.6H_2O$

Type of bonds	Average distance in Å	Literature[4]
Mg-water	2.10	2.06
S-O	1.49	1.48

Three hydrogen bonds (shown in dotted lines) are identified in the structure which are connecting the $[Mg(H_2O)_6]^{2+}$ octahedral to SO_4^{2-} tetrahedra. Among the three hydrogen bonds, one among them exhibits an intra-molecular proton transfer mechanism from one of the coordinated water molecule to one of the Oxygen atom in SO_4^{2-} tetrahedra (Figure 1). Out of the three hydrogen bonds, this hydrogen bond appears to be the weakest with an O-H—O distance of 2,643Å, where as the other two hydrogen bonds have distances 2.51 Å and 2.473 Å respectively. The reasons for such proton transfer mechanisms are investigated in the literature for several other systems [13]. Proton transfers are known to exist in low barrier hydrogen bonded interactions. Also, studies report proton transfer reactions when there are significant changes in proton affinity between molecular fragments.

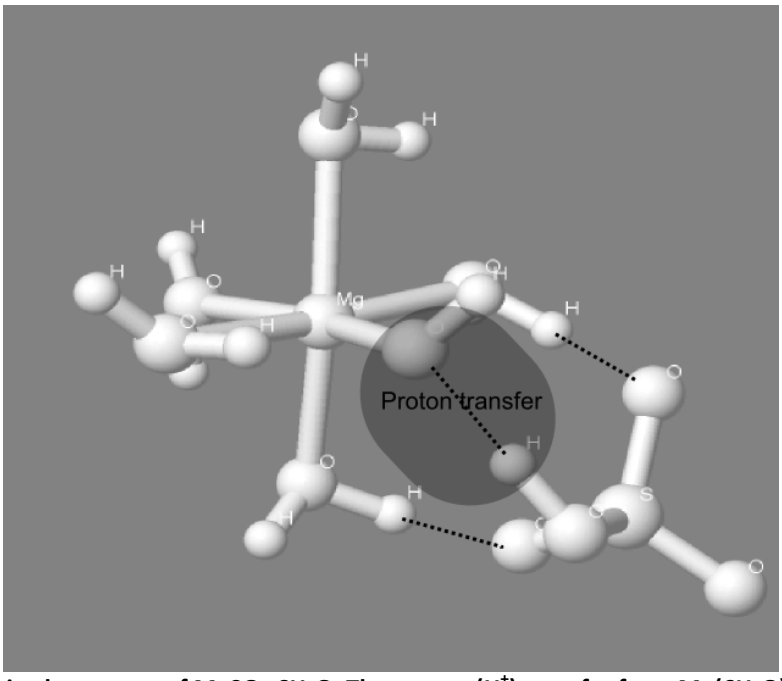

Figure 1. Optimized structure of $MgSO_4.6H_2O$. The proton (H^+) transfer from $Mg(6H_2O)^{2+}$ octahedra to SO_4^{2-} tetrahedra is shown. Three hydrogen bonds are shown with dotted lines.

3.2 Intra molecular proton transfer in $MgSO_4$ hexahydrate

The hydrogen bond interaction which involves proton transfer is further examined to study the possible reasons for such an interaction. The hydrogen atom which was moved towards the SO_4^{2-} tetrahedral is placed at various positions along the direction of the hydrogen bond interaction in the molecule.

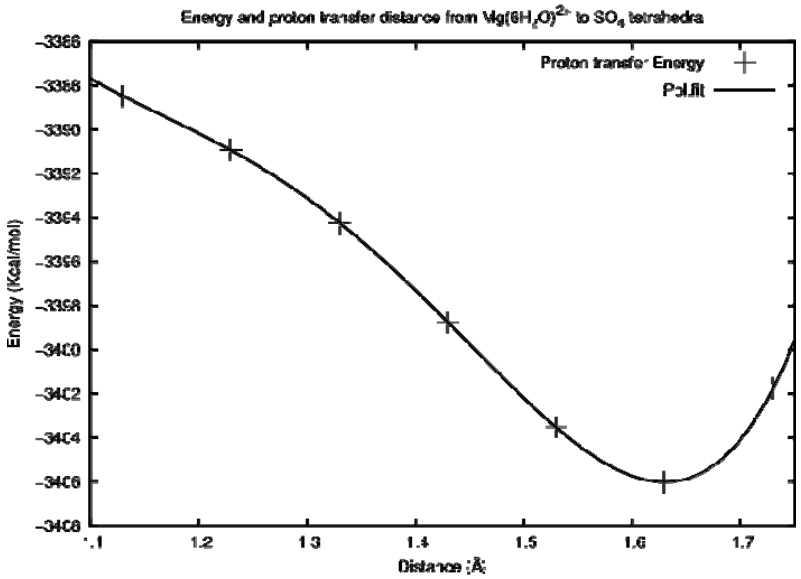

Figure 2. This figure shows the energy as a function of the proton movement from the $Mg(6H_2O)$ to SO_4 tetrahedra. The distance in x-axis is the distance from the (nearest) Oxygen atom in the $Mg(6H_2O)$ fragment.

The energy is computed at each positions and Figure.2 shows the energy as a function of distance as the hydrogen atom moves away from $[Mg(H_2O)_6]^{2+}$ fragment. Clearly there is no barrier in the potential and this rule out the possibility of the presence of a low barrier hydrogen bond interaction. The energy difference as the proton moves from left to right in Figure.3 is

approximately 21kcal/mol which is more than the energy involved in the formation of strong hydrogen bonds (10-15kcal/mol) [14]. This suggests that one of the possible reasons for this proton transfer is the increased proton affinity of SO_4^{2-} fragment. This increased proton affinity and the possible motion of hydrogen atom through the hydrogen bonds might potentially dissociate the water molecule during hydration. This has been confirmed in our binding energy analysis reported in section 5.

3.3 Spin unpaired (triplet)

When two electrons tend to pair each other, they form either a singlet state or a triplet state. The triplet molecules do exhibit paramagnetism. We have done a spin unpaired calculation on $MgSO_4.6H_2O$ molecule to find the triplet state. The resulting structure is shown in Figure 3. Unlike in Figure 1, there is no proton transfer in the triplet state of the molecule. The result shows that the proton transfer disappears when the material is polarized. However, this triplet configuration has an energy 84.16 kcal/mol higher than the singlet state and thus the latter is energetically favorable in terms of its electronic state. In addition, there is no paramagnetic $MgSO_4$ molecule reported in the literature. Nevertheless, a comparison of both the states will give insights into the reasons for the proton transfer mechanism exhibited by singlet $MgSO_4$.

A triplet state demands the presence of unpaired electrons in the molecule. This requires that the spatial part of the wave function to be antisymmetric and they are spatially farther away from that of paired electrons [15]. Thus it can be concluded that the proton transfer in $MgSO_4.6H_2O$ is a direct result of stabilizing the molecule by pairing the electrons.

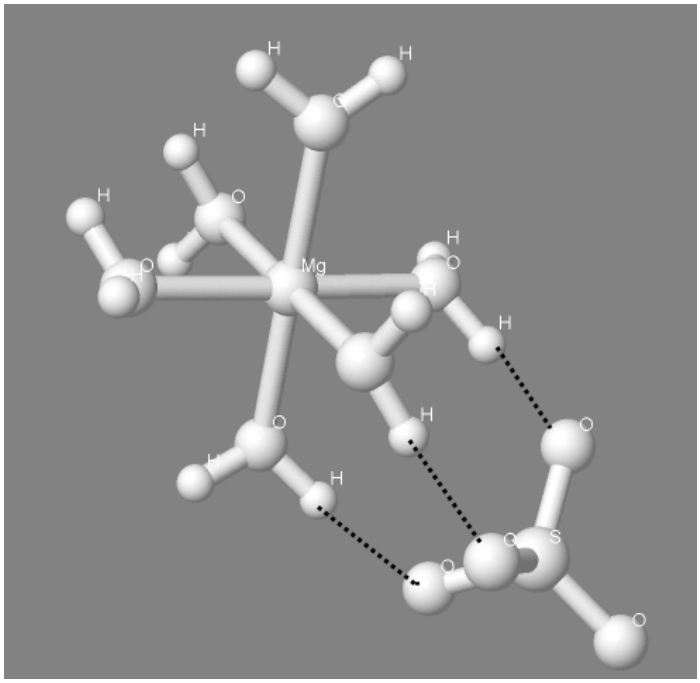

Figure 3. The optimized structure of $MgSO_4.6H_2O$ in the triplet state. This state do not show a proton transfer and the $Mg(6H_2O)$ and SO_4 fragments are connected via three hydrogen bonds which is shown with the dotted lines.

4. NBO charges in various hydrates of magnesium sulfate

Natural Bond Orbital (NBO) [5] method is widely applied to compute the charges from the electron density of a molecule. NBO charges of Mg and S as a function of degree of hydration in $MgSO_4$ hydrates is plotted in Figure 4. The values are compared with a similar study in the literature for upto four hydrates.

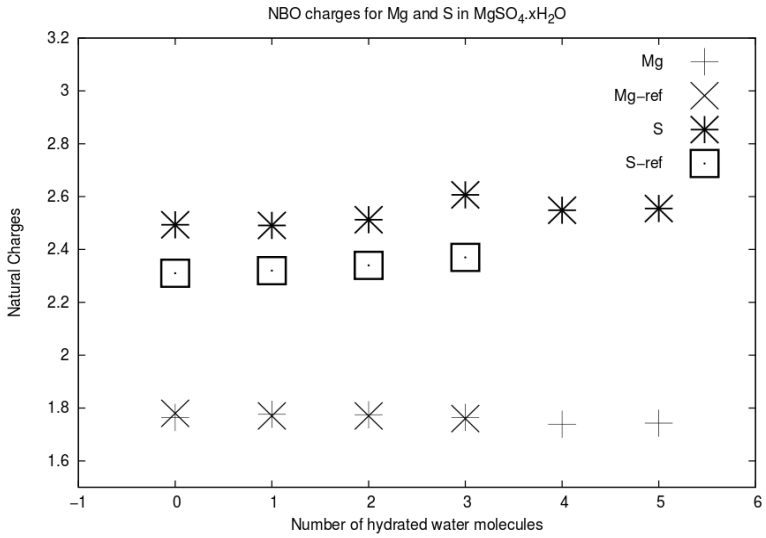

Figure 4. Natural Bond Orbital (NBO) charges of Mg ans S in various hydrates of $MgSO_4$. They are compared with literature [16].

The NBO charges in Mg show excellent agreement with the literature [16], whereas S shows fairly good match with the literature. What reveals from Figure 4 is that the charge transfer (variation in the charge as a function of degree of hydration) from water to Mg is comparatively less prominent in $MgSO_4$ hydrates. Thus the water coordination effect seems to play a less significant role in the hydration process compared to coulombic interaction and hydrogen bond interaction. In addition, an ample possibility for the formation of hydrogen bonds in magnesium sulfate hydrates crystal explains the slow kinetics [2] of $MgSO_4$ hydration process. The strong hydrogen bonds, which potentially distorts the octahedral coordination of water around the magnesium atom, thus, possibly dissociates water molecule during hydration. This has been investigated in the next section.

5. Water binding at magnesium sulfate surface

Water binding at the surface of $MgSO_4$ slab gives insights into the hydration process of magnesium sulfate. Masyluk[6] has performed a similar study on keiserite (magnesium sulfate monohydrate) to find the minima in the potential energy surface when water is close to (100) surface. The study reveals that the minima is found when the water molecule is directly above the Mg atom sitting on the surface. The study gives insights about the formation of hydrogen bonds between water and oxygen atoms on the surface.

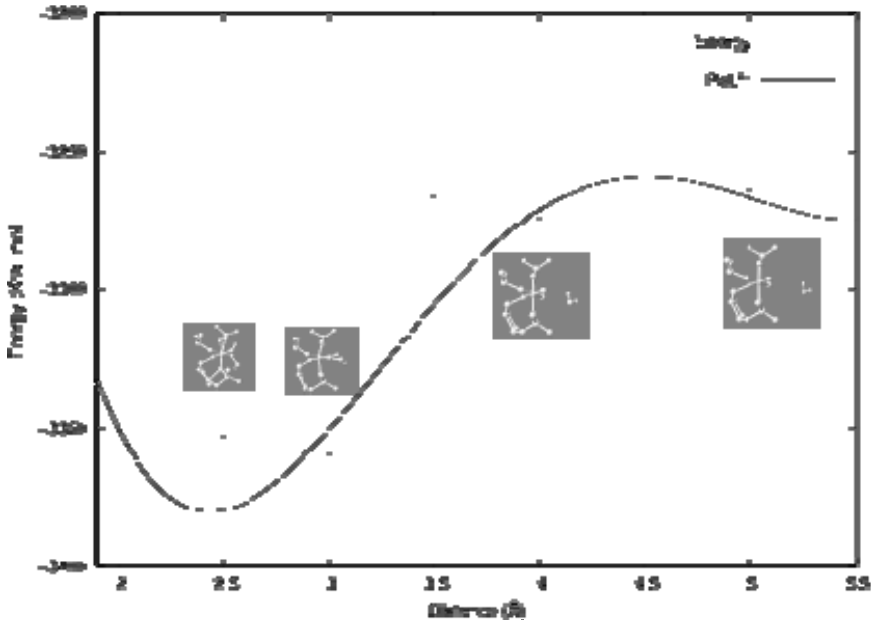

Figure 5. Energy as a function of distance between $MgSO_4$ slab and water molecule. The minima in the curve shows the equilibrium distance between Mg and O in the water. Extreme left geometry shows the dissociation of the incoming water molecule.

We have done a similar investigation by bringing a water molecule closer to the (100) surface of an MgSO4 slab containing four molecules periodically aligned in y and z-directions with a perfectly crystalline structure. Figure 5 shows the variation of energy as the water comes closer to the $MgSO_4$ slab. The polynomial fit shows that the energy decreases as the water comes closer to the surface (right to left in the figure). Besides, there are no energy barriers for the water binding (hydration) and thus this process is spontaneous. In addition, the energy exchange in this process is approximately 100kcal/mol.

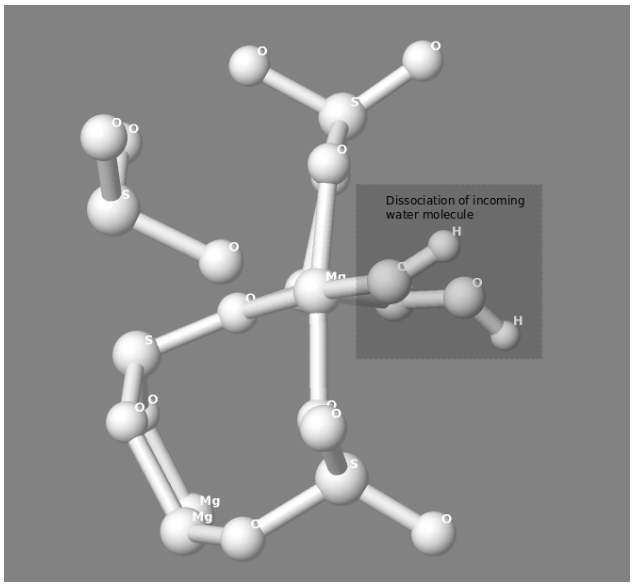

Figure 6. Dissociation of water during the binding of water molecule to $MgSO_4$ slab.

An important feature observed in this process is that as the water molecule comes closer to the slab, the hydrogen bond interactions between water and the electronegative Oxygen atoms come into play resulting in the dissociation of the incoming water molecule. This is shown in figure 6. However, such an observation was not found for kieserite [6] and the reason could possibly be the lesser number of oxygen atoms present on the (100) surface of the crystal. This observation strengthens the argument that the hydrogen bond interaction in $MgSO_4$ is strong enough to dissociate some of the O-H bonds in the system. This account gives an insight into

the process of hydration of $MgSO_4$ as being highly influenced by the presence of strong hydrogen bonds.

6. Conclusion

Molecular structure of magnesium sulfate hexa hydrate molecule is optimized using Density Functional Theory method. The singlet state of the molecule is energetically stable compared to the triplet state of magnesium sulfate hexa hydrate. This singlet state exhibits intra-molecular proton transfer from one of the coordinated water molecule towards the SO_4^{2-} fragment. This proton transfer is attributed to the relatively high proton affinity of SO_4^{2-} fragment.

The NBO charge analysis shows little variation in the charge of Mg and S as a function of degree of hydration. This shows that the hydration process involves mostly coulombic interaction between water molecule and magnesium atom. In addition proton transfer mechanism gives evidence to the presence of strong hydrogen bonds in the system. Both these observations together reveals that the hydrogen bonds present in the system can significantly influence the process of hydration and potentially affecting the kinetics of the reaction.

A binding energy analysis on an magnesium sulfate slab containing 4 molecules with periodic boundary conditions in two spatial direction reveals the possibility of dissociation of water molecule during hydration. It appears that the hydrogen bond interaction involved in the system between the oxygen atoms in $MgSO_4$ and water is strong enough to split the water molecule while it comes in contact with the surface. Purely from a geometrical point of view, it can be understood that for water molecule to penetrate through the crystal, either the crystal has to disintegrate or the water molecule has to dissociate. Thus dissociation of water appears to be inevitable in the hydration process of $MgSO_4$. However, such dissociation was not observed during a similar study conducted on kieserite structure. This suggests that the dissociation of water is not always necessary and several other factors play important roles in the hydration of magnesium sulfate to make it a rather complex process. A detailed account about the hydration reaction needs further analysis.

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