学位請求論文要約

Theoretical study of hydrogen-bonded clusters

based on the hydrogen-bonding network

(水素結合ネットワークに基づく水素結合クラスターの理論化学的研究)

2014年

広島大学大学院理学研究科

化学専攻

赤瀬 大

広島大学学位請求論文

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参考論文

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主論文

Theoretical study of hydrogen-bonded clusters based on the hydrogen-bonding network

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Acknowledgments

Contents

Chapter 1

General Introduction

1.1 Hydrogen Bond

The hydrogen bond is ubiquitous in nature and is of great importance in physical, chemical, biochemical, and biological phenomena. It is therefore essential for life on the earth. A few examples are presented to illustrate the critical role of the hydrogen bond. The crystal structures of many organic compounds and inorganic hydrates are determined by hydrogen bonds. Hydrogen bonds form the base pair in DNA and contribute to the stability of DNA double helix structure. The secondary structures in proteins, such as α-helix, β-sheet, and turn, involve interresidue hydrogen bonds, which also help to maintain the tertiary and quaternary structures of proteins. Hydrogen bonds function in the molecular recognition in biological systems as well as enzymatic catalysis.

The phenomena as a consequence of hydrogen bonding were observed before it was called hydrogen bond [1]. In the early 20th century, Werner [2,3] used $X(H\cdots NH_3)$ notation to describe the interaction in ammonium salts. He called this interaction *Nebenvalenz* (near valence or secondary valence). In 1912, Moore and Winmill [4] used the term *weak union* in discussing the difference between trimethylammonium hydroxide and tetramethylammonium hydroxide in aqueous solution. The concept of what has become known as the hydrogen bond is ascribed to Huggins and, independently, to Latimer and Rodebush. Huggins introduced the hydrogen bond concept, an extension of the Lewis theory, in his undergraduate thesis at the University of California in 1919. The publication of his idea was delayed several years [5,6]. In 1920, Latimer and Rodebush [7] proposed that *the hydrogen nucleus held between two octets constitutes a weak "bond"* to rationalize the phenomena of associated liquid such as water and hydrogen fluoride. In the paper, they referred to the Higgins's unpublished work. It is presumably in the paper by Pauling [8] in 1931 that the term hydrogen bond appeared in

publications for the first time. In that year, Huggins [9] also used the term hydrogen bond. However, he later preferred [10] the term *hydrogen bridge*, which became the Garman word *Wasserstoffbrückenbindung*.

Many experimental techniques have been used to identify the hydrogen bond, and to gain insights into the nature of hydrogen bonding. For a hydrogen bond X–H$\cdots$Y, the length of X–H bond usually increases upon the hydrogen bond formation, which results in a red shift of the X–H stretching frequency. The red shift can be observed via vibrational spectroscopy. In 1936, Hilbert et al. [11] concluded that the disappearance of infrared characteristic OH absorption correlates with the presence of the hydrogen bond. Shortly thereafter, Badger and Bauer [12,13] found that the spectroscopic evidence for the presence of the hydrogen bond is not the disappearance but the red shift of the OH absorption. Since then, IR spectroscopy has been a primary method for studying the hydrogen bonding in every phase. Other experimental methods, including X-ray and neutron diffraction, Raman, NMR, and microwave spectroscopy, have been applied to the study of the hydrogen bonding. In addition, modern experimental techniques, such as 2D-IR, double resonance spectroscopy, and mass detected IR spectroscopy, have also been employed in the investigation of hydrogen bonding systems.

The hydrogen bond and hydrogen bonding interaction has been the subject of great interest in computational chemistry. Molecular mechanical and quantum mechanical approaches have been utilized to study hydrogen-bonded systems. The molecular mechanics (MM) uses a potential function for calculating potential energy of the system, and hence has advantage in computational cost. The efficiency of MM enables us to perform long time simulations and to treat large systems. Ab initio molecular orbital (MO) theory, one of the quantum mechanical approaches, is a powerful tool to investigate intermolecular interaction such as the hydrogen bond. Although ab initio MO calculation is time consuming, continuous development of

computers and program suites has extended the range of application of the ab initio method. Nowadays, it is a kind of a routine work with highly accurate ab initio MO method to obtain local minimum structures of small hydrogen-boned clusters on the potential energy surface and to evaluate the interaction energy at each of the points.

The definition of the hydrogen bond has been slightly altered through the extensive studies both experimentally and theoretically for a century. Considering the recent experimental and theoretical advance, the IUPAC task group [14,15] recommended in 2011 the definition of the hydrogen bond: *the hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation*. The recommendation also list six criteria useful as evidence for hydrogen bonding, because the recommended definition requires the evidence of hydrogen bond formation.

1.2   Water and Its Hydrogen Bonding

Water is one of the most important molecules that form the hydrogen bond. The importance of water cannot be overemphasized. Ancient philosophers considered water as the first principle of existing things. Water is the most abundant molecule on the earth's surface and constitutes over 60 percent of the human body. There are many anomalous macroscopic properties of water like the density maximum of liquid water at 4 ºC. A water molecule, H_2O, consists of two hydrogen atoms and one oxygen atom, where the hydrogen atoms are covalently bonded to the oxygen atom. The hydrogen atoms are partially positive and the oxygen atom is partially negative, because oxygen is more electronegative than hydrogen. The water molecule commonly donates up to two hydrogens to the acceptors and accepts up to two

hydrogens from the donors in a hydrogen-bonded system. This makes the hydrogen-bonding network of water quite complicated. The non-additive nature of hydrogen bonding interaction involving the water molecule presents the importance of hydrogen-bonding network. The strength of the hydrogen bonding interaction depends on not only the number of hydrogen bonds formed but also the hydrogen-bonding network.

1.3 Water Cluster and Protonated Water Cluster

The water cluster is a molecular assembly composed of water molecules. It is formed by the hydrogen bonds between water molecules. Many local minimum structures have been reported by means of ab initio MO method. However, it is difficult to locate all the local minima on the potential energy surface. The strength of a hydrogen bond in water clusters is of the order of a few tens kJ/mol. For example, the binding energy of water dimer is 21.84 kJ/mol at the CCSD(T)/aug-cc-pVTZ level of theory [16]. The hydrogen bond dissociation and reformation readily occurs in water clusters at finite temperatures, which results in the situation that various isomers coexist and the structures are distributed far from the minima on the potential energy surface.

The topology of hydrogen-bonding network can be represented as a digraph [17]. The number of all the topologically possible hydrogen-bonding networks in a water cluster has been enumerated [17–19] by making use of graph theory. The number increases exponentially with the number of constituent molecules. The number prescribes the upper limit of the number of topologically distinct isomers of water clusters. Once the hydrogen-bonding networks of a given structure of water cluster is determined with an appropriate criterion of the hydrogen bond, we can obtain the graph representation and compare the hydrogen-bonding network with other structures by solving a graph isomorphism problem.

The addition of a proton to water clusters produces protonated water clusters. The protonated water cluster is one of the most important hydrogen-bonded clusters, because it serves as a model system for hydrated proton and proton transfer. There are two types of ion core structures, Eigen (H_3O^+) and Zundel ($H_5O_2^+$). In Eigen isomers, the proton is strongly attached to one water molecule. In Zundel isomers, the proton is shared equally by two water molecules. Such an ideal symmetric hydrogen bond is formed only in the protonated water dimer ($H_5O_2^+$). In larger clusters, the Zundel unit departs slightly from the perfect symmetry, which may be better to be called Zundel-like structure. The OH stretching frequency in the ion cores is sensitive to the hydration. The binding energy of protonated water cluster is generally much larger than that of water cluster because of the excess charge. The number of isomers coexisting at finite temperatures is small compared with the case of water cluster.

Considering the protonated water clusters as $H_3O^+(H_2O)_{n-1}$, we can represent the topology of the hydrogen-bonding network in a protonated water cluster as a rooted digraph. The number of all the possible hydrogen-bonding networks of protonated water clusters has also been enumerated [20]. The number is larger than that of the water cluster at each size, because of the excess proton. A topologically exhaustive search of local minima water clusters was performed [20] for small protonated. It is, however, impractical to apply the exhaustive search to larger cluster because of the large number of possible topology. The OH bonds in the protonated water clusters up to heptamer were classified into nine types according to the difference of the local hydrogen-bonding network [21]. It was found that the corresponding OH stretching frequency range of each type is systematically classified.

1.4   Goals and Outline

The general objective of this thesis is to obtain insights into the properties of

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hydrogen-bonded clusters employing the analysis based on the hydrogen-bonding network. To this end, we apply some analyses based on the hydrogen-bonding network to water clusters and protonated water clusters.

This Chapter provided the general background behind this thesis. In Chapter 2, water clusters at finite temperatures are investigated. We will focus on the hydrogen-bonding network of the whole cluster, because it dominates the structure, energetics, dipole moment of each cluster. The concept of hydrogen-bonding pattern, a set of configurations whose hydrogen-bonding pattern is the same, is adopted to characterize the structure distribution of the water clusters. The average dipole moment of hydrogen-bonding pattern is discussed. The constituent water molecules are classified into nine types on the basis of local hydrogen-bonding network, and the enhancement of molecular dipole moment is evaluated for each type of molecule. In Chapter 3, protonated water clusters are investigated. A comprehensive search of topologically distinct local minimum structures of protonated water octamer is conducted. Many local minimum structures, whose hydrogen-bonding networks are individually distinguishable, are presented. The population ratios of the topologically different structures as a function of temperature are computed under the harmonic oscillator approximation. The O–H bonds in the obtained structures are classified into ten topological types based on the local hydrogen-bonding network. The O–H stretching frequency of each topological type is discussed. A summary of this thesis and the general conclusion is presented in Chapter 4.

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Chapter 2

Water Cluster

Chapter 3

Protonated Water Cluster

Chapter 4

General Conclusion

In this thesis we have showed that the analysis based on the hydrogen-bonding network revealed characteristic properties of hydrogen-bonded clusters. The properties are relevant to the topology of the hydrogen-bonding network of the clusters. In Chapter 2, we investigated the structure distribution of water cluster and the influence of hydrogen bonds on the constituent water molecule in terms of dipole moment. The structures of water clusters at finite temperatures were classified into hydrogen-bonding patterns, each of which is a set of structures whose hydrogen-bonding network is the same. The hydrogen-bonding patterns not related to any local minimum structure are highly populated at finite temperatures. The molecular dipole moment of a constituent water molecule is enhanced via hydrogen bonds with surrounding water molecule. The enhancement is rationalized by the local hydrogen-bonding network of the water molecule. In Chapter 3, we investigated the energetics and harmonic frequencies of various hydrogen-bonding networks of protonated water octamers. A comprehensive search of topologically distinct local minimum structures of protonated water octamer was conducted using the Hamiltonian algorithm and the scaled hypersphere search method, independently. We obtained 134 topologically distinct local minimum structures of protonated water octamer, and estimated temperature-dependent population ratios for these structures. The O–H bonds in a protonated water cluster are classified into ten topological types of the O–H bonds on the basis of the local hydrogen-bonding network. The O–H bond stretching frequencies are transferable, and the O–H topological types can be used to distinguish the spectral signatures of the O–H stretching modes.

As shown in this thesis, the analysis based on the hydrogen-bonding network is useful for investigating hydrogen-bonded clusters, especially ones including water molecules, and is a promising approach for other hydrogen-bonded systems.

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