Theoretical study on the hydrogen-bond network and proton switch in ionic mixed clusters

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**THEORETICAL STUDY ON THE HYDROGEN-
BOND NETWORK AND PROTON SWITCH IN
IONIC MIXED CLUSTERS**

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**DIVISION OF PHYSICS & APPLIED PHYSICS
SCHOOL OF PHYSICAL & MATHEMATICAL SCIENCES
NANYANG TECHNOLOGICAL UNIVERSITY**

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Summary

Microsolvation structures of a proton have attracted much interest with respect to the mobility of the proton in the protic solvents. For multi-components systems, the preference of the protonated site has been the subject of extensive studies. In this work, comprehensive analysis on the structure and proton switch in protonated mixed clusters was investigated by theoretical study. There are two main parts that will be studied.

Part one: protonated methanol-water clusters

A surprising switch of the protonated site from methanol to water in protonated methanol–water mixed clusters, $\text{H}^+(\text{MeOH})_m(\text{H}_2\text{O})_1$ ($m = 1-9$), was investigated. Extensive density functional calculations on all possible structural isomers revealed that the switch of the ion core is correlated with the size dependence and structural development of the hydrogen-bond network: (1) the CH_3OH_2^+ ion core is preferred for the small-sized clusters of $m = 1$ and 2, (2) coexistence of the H_3O^+ and CH_3OH_2^+ ion cores is highly plausible for $3 \leq m \leq 7$ clusters, and (3) obvious preference of the H_3O^+ ion core appears from $m \geq 8$ with the appearance of the characteristic “tricyclic” structure of the hydrogen-bond network. The ion core switch at $m \approx 8$ is experimentally supported.

We investigate the structures of $\text{H}^+(\text{CH}_3\text{OH})_m(\text{H}_2\text{O})_n$ clusters for $m + n = 5$ and 6. An effective theoretical approach is presented to search for extensive sets of structural isomers using an empirical model and substitution schemes. Stable isomers were then reoptimized by the B3LYP level of computations with the 6-31+G* basis set. Canonical averages of these structural isomers were analyzed by harmonic superposition approximation (HSA) to study their finite temperature behavior and enable quantitative comparisons with experimental results. Thermal energy is found to have a significant effect on the structure of these clusters. Our calculations show that cyclic isomers are preferred at low temperature, while linear and tree forms become more favorable at high temperature (>200 K). Furthermore, we found that proton can reside on both water and methanol ion cores and the proton switch is associated with morphology change.

The concept of anticooperativity by successive substitution in a mixed solvation system is proposed and verified. When a solvent molecule is replaced by another molecule with larger proton affinity, the strength of all other hydrogen bonds decreases. In the present study, this concept is demonstrated in $\text{H}^+(\text{CH}_3\text{OH})_m(\text{H}_2\text{O})_n$ ($m + n = 5$ and 6) mixed clusters by a joint theoretical and infrared (IR) spectroscopic approach. The observed IR spectra of the mixed clusters exhibit two high-frequency shifts of hydrogen-bonded OH stretch bands with increasing methanol content. These trends are well reproduced by first-principle IR spectra simulated by thermal averaging over a set of configurational isomers under the quantum harmonic superposition approach. Theoretical analysis on the magnitude of charge transfer from the protonated site to the solvent molecules is found to be in agreement with the

spectroscopic measurement that the individual hydrogen bond in the mixed clusters is weakened with an increase of the mixing ratio of methanol to water.

Part two: $X-H^+-(MeOH)_m$ system ($X = (CH_3)_3N$ and $(CH_3)_2SO$)

We carried out calculation on the $X-H^+-(CH_3OH)_m$. Since the proton affinity of methanol cluster increase as cluster size increase, the proton is expected to switch from methanol site to X site at certain size. Therefore, to determine the turning point is an interesting question to address and deserves further examination. We studied $X-H^+-(MeOH)_m$ system ($X = (CH_3)_3N$ and $(CH_3)_2SO$). Although the PA of methanol clusters increases substantially beyond the threshold PA for proton transfer observed for the TMA system, no proton transfer occurs up to the bulk limit. For $X = DMSO$, proton stay on the DMSO site for $m = 1$ and 2, and transfer to methanol site at $m = 3$. Significant features of IR spectra are found to tell the excess proton location.

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Publications

1. **Bing, D.**; Hamashima, T.; Fujii, A.; Kuo, J.-L., *Anticooperative Effect Induced by Mixed Solvation in $H^+(CH_3OH)_m(H_2O)_n$ ($m + n = 5$ and 6): A Theoretical and Infrared Spectroscopic Study*. **J. Phys. Chem. A** 2010, 114, 8170.
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3. **Bing, D.**; Hamashima, T.; Nguyen, Q. C.; Fujii, A.; Kuo, J.-L. *Comprehensive Analysis on the Structure and Proton Switch in $H^+(CH_3OH)_m(H_2O)_n$ ($m + n = 6$)* **J. Phys. Chem. A** 2010, 114, 3096.
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9. **Bing, D.**; Hamashima, T.; Fujii, A.; Kuo, J.-L., *Proton Location in $H^+[(CH_3)_3N](CH_3OH)_m$: A Theoretical and Infrared Spectroscopic Study.*
(Submitted)
10. **Bing, D.**; Kuo, J.-L., *Theoretical Analyses of The Influence of Cluster Proton Affinity on Proton location in $H^+[(CH_3)_2SO](CH_3OH)_m$.* (Submitted)

Chapter 1

Introduction

1.1 An overview of hydrogen-bonded clusters

Cluster science. A group of atoms bound together by interatomic forces is called an atomic cluster. As the number of atoms increases, atomic clusters acquire more and more specific properties, which make them unique physical objects different from both single molecule and solid states, and also bridge the gap between the gaseous and condensed phase. The investigation of weakly bound clusters has attracted a lot interest in recent years.¹ The advantage of clusters is the possibility to simply vary the size and to investigate the development of properties of the condensed phase step by step. In general, the structure of small clusters is quite different from that of the infinitely extended solid. There are many different types of atomic clusters, and one can distinguish between different types of clusters by the nature of the forces between atoms.

Hydrogen-bonded clusters. Of special interest is the hydrogen-bonded cluster. Polar molecules, such as water molecules, have a weak, partial negative charge at one region of the molecule (the oxygen atom in water) and a partial positive charge elsewhere (the hydrogen atoms in water). Thus, when water molecules are close, their positive and negative regions are attracted to the oppositely-charged regions of nearby molecules. The force of attraction is called a hydrogen bond. Despite this simple

concept, understanding the electronic nature of the hydrogen bond appears to be more elusive than for covalent and ionic bonds and van der Waals forces. This is because the term hydrogen bond applies to a wider range of interactions. Very strong hydrogen bonds resemble covalent bonds, while very weak hydrogen bonds are close to van der Waals forces. The majority of hydrogen bonds are distributed between these two extremes.²

These complex networks determine the usual and unusual properties of the most important solvent molecules such as alcohols and water. Hydrogen bonds are of special importance in nature. They are weaker than covalent bonds and cover a wide range of binding energies (4 – 40 kJ/mol), depending on the local geometry and the type and strength of interaction between the hydrogen donor and acceptor groups. For example, the hydrogen bond in the water dimer has $\Delta E = D_e = 22 \pm 3$ kJ/mol.³ Hydrogen bonding is strong enough to determine the structure of many molecular systems, such as water, ice, and macromolecules such as DNA or proteins.⁴

The nucleus of hydrogen bond nomenclature is the distinction between donor and acceptor. In any D–H...A bond, D–H is the hydrogen bond donor (or electron acceptor), and A is the hydrogen bond acceptor (or electron donor). The main feature that characterizes the hydrogen bond and makes it different from any other donor-accepter interaction is the sharing of the proton between the hydrogen bond donor and acceptor atoms. In other words, hydrogen bonds can always be seen as shared-proton interactions.⁵

Cooperativity. In chemistry, the concept that a particular configuration of single and multiple covalent bonds has a total energy greater than the sum of the energies of

individual bonds is familiar. This extra energy is called resonance energy in valence bond theory. The same principle applies to certain pattern of hydrogen bonds, where it is known generally as cooperativity. Cooperative effects in clusters seem to be generally associated with donor-accepter interactions where a monomer can participate both as a donor and acceptor. Formation of a hydrogen bond $D-H\cdots A$ increases both the polarity of the $D-H$ bond and the basicity of A . These changes may lead to a significant increase in the strength of additional hydrogen bonds. Cooperativity applies to all intermolecular interactions in general sense, and represents the difference between calculating energies using atom-pair potentials and many-atom potentials. In hydrogen bonding, it is of particular importance because of the diffuse nature and high polarizability of the hydrogen and lone-pair electron densities.²

There are two types of hydrogen-bond cooperativity. One involves hydrogen-bonding between molecules with conjugated multi π -bonds. This is described as Resonance-Assisted Hydrogen Bonding (RAHB).⁶ The second type of cooperativity occurs when hydrogen-bonding functional groups with both donor and acceptor properties form continuous chains or cycles. This occurs principally with hydroxyl groups and was first recognized in the crystal structures of small carbohydrate molecules.⁷ It has been described as σ -bond cooperativity, in contrast to π -bond cooperativity, since there are no multiple bonds involved.

1.2 Ionic hydrogen bond and proton switch in multicomponent cluster ions

Ionic hydrogen bonds (IHBs) are a special class which form between ions and molecules with bonds strength of 5–35 kcal/mol, up to a third of the strengths of covalent bonds.⁸ These strong interactions are critical, for example, in protonated clusters, ion solvation, and acid–base chemistry.⁹ With such wide-ranging roles, the fundamental properties of IHB interactions need to be understood. The energetic of IHB interactions cannot be isolated and quantified in the condensed phase. However, these interactions can be isolated and studied quantitatively in gas phase. These studies lead to a fundamental understanding of relations between IHB strengths and molecular structure, the solvation of ions, and acid-based phenomena and bioenergetics.

The formation of $D-H^+ \dots A$ bond involves partial proton transfer from the donor to the acceptor. The bond strengths correlate with the efficiency of proton transfer. Several solvent molecules can be added stepwise to ions to form clusters. The bonding energies of consecutive solvent molecules to ions approach the condensation enthalpy of the bulk solvent, usually after four to six solvent molecules. In mixed clusters of unblocked and blocked components, the protons can be transferred to the former, such as water, to form an H_3^+O ion core where the proton is stabilized by a net work of strong hydrogen bonds. The proton can remain in a water core even when it is surrounded by alkyl-blocked molecules that have higher proton affinities. This has significant biological consequences, as in membrane transport. Cluster studies show the stepwise development of solvation effects.

Proton transfer is the basis of acid-basis chemistry, of which that involving hydrogen bonds is only one component. As pointed out by Arnett and Mitchell,

hydrogen bonding and proton transfer are very different concepts, although the former may facilitate the latter.¹⁰ An interesting discussion of hydrogen bonding with and without proton transfer in the ammonium halides is presented by Legon.¹¹ The fact that hydrogen bonding facilitates proton transfer is considered to be the most important chemical property of the hydrogen bond. The facility of hydrogen bonds to transmit H^+ ions provides a catalysis mechanism for many reactions. In the field of molecular biological proton transfer has come to be recognized as a significant component of enzyme catalysis and the transmission of ions through membranes.²

Information on the properties of clusters incorporating several solvent molecules about a proton is of interest from the point of view of understanding the structure of acidic solutions. Clusters comprising several different solvent molecules are of interest because they simulate multicomponent solvent systems, and studying them can clarify the structure of hydrogen-bonded networks about a protonated solute ion. For multicomponents systems, such as methanol-water mixture, the preference of the protonated site has been the subject of extensive studies.¹²⁻¹⁹ Though the proton affinity (PA) in the gas phase is a useful index to infer the preferential protonated site, recent gas phase cluster studies, which provide us clear microscopic structures of the proton solvation, have showed that the proton migration can occur from the larger PA site to the smaller PA site with the development of the step-wise solvation. This is reasonably explained by that the greater advantage in the solvation makes compensation for the lower affinity at the bare molecule. The proton location in a multiple component system cannot be determined by a simple push-pull relation between the two molecules neighboring to the proton. The preferential location of the

proton should be understood in terms of the structural development of the whole hydrogen bond network.

1.3 Ab initio calculation and Infrared spectra of hydrogen bonding systems

Ab initio calculation, in conjunction with Infrared spectroscopy, is becoming one of the most powerful tools in characterizing neutral and ionic clusters. Precise hydrogen bond energies are difficult to determine. Hydrogen bond energies can be measured by thermodynamics from the large number of properties of associated molecules which are temperature dependent. Although individual measurements quote precision to ± 0.5 kcal/mol, the range of for a particular type of bond may vary over several kcal/mol, depending on the methods used.² Ab initio calculation has achieved a remarkable degree of success in reproducing experimental, gas-phase thermochemistry.²⁰ The accurate prediction of solution thermochemistry has yet to be achieved, and the development of quantitative solvation models continues to be a paramount goal of computational chemistry.

Brief mention should be made of the IR spectral features of hydrogen-bonded complexes, in relation to the donor-accepter model. The motion of the hydrogen atoms is greater than that of the heavier atoms to which they are covalently bonded. The formation of a hydrogen bond restricts the degree of vibrational motion, since the hydrogen atom is restrained by two bonds rather than one. A measure of the vibration of D–H bond is therefore a sensitive criterion of the formation and strength of hydrogen bonds. The formation of D–H...A hydrogen bonds decreases in frequency

(ν_{DH}) and increases in intensity.²¹⁻²³ This is the basis for the extensive use of infrared spectroscopy for studying and classifying hydrogen bonds. Changes in the H...A hydrogen bond and acceptor frequencies are less dramatic and more difficult to interpret.²

Infra-red spectroscopy played a major role in the hydrogen bond research. The OH stretching band represents the most easily recognizable signature of hydrogen bonding, and its properties have been examined in much detail. It was rapidly understood that spectral effects strongly depend on the OH...O bond distance.²⁴ Hydrogen bonds have been distinguished on the OH...O distance into weak (2.8 to 3.0 Å), medium-strong (2.6 to 2.8 Å) and strong (≤ 2.6 Å) hydrogen bonds. Formation of the hydrogen bond D-H...A causes a red shift of the fundamental D-H stretching vibration. The shift is more than 100 cm^{-1} and is associated with a lengthening of the D-H bond and a large increase in the infrared intensity of the fundamental D-H stretching vibration. The fundamental infrared D-H stretching vibration is normally broadened by hydrogen bonding. This arises from coupling to the low-frequency intermolecular modes.²⁵

1.4 The motivation and organization of this thesis

Motivation

To better understand the nature of ion hydration, experimental and theoretical investigations of cluster ions in the gas phase have been performed over the past few decades. However, the number of spectroscopic measurements is limited owing to experimental difficulties. Theoretical calculations offer an alternative approach in increasing our understanding of ion-solvent interactions. Recent advances in *ab initio*

calculations have allowed the structures, binding energies, and vibrational frequencies of molecular clusters to be fairly accurately predicted. The calculations not only serve as a useful reference for comparison with experiments but also furnish a complete picture of the structures and dynamics of the clusters of interest.

Mixed clusters have a lot of isomers, which make it difficult to do calculations. In this work, we studied two systems, $\text{H}^+(\text{CH}_3\text{OH})_m(\text{H}_2\text{O})_n$ and $\text{X-H}^+(\text{CH}_3\text{OH})_m$ (X =Trimethylamine and Dimethylsulfoxide). First, all isomers of the protonated water and methanol clusters are generated. Then, the initial structures of mixed clusters are constructed based on these pure clusters, which reduced the difficulty. With the use of *ab initio* computations, we attempt in this work to focus on following studies:

- (1) Theoretical analyses of the morphological development of the hydrogen-bond network.
- (2) The preference of the ion core depending on size, stoichiometry, and proton affinity differences in the mixed clusters.
- (3) Calculation of IR spectra which help to distinguish between various low-energy isomers when compared with experimental data.

Organization

In this thesis, we systematically studied the hydrogen bond network in mixed cluster ions, and which of the species present in the ion cluster is preferentially bound to the proton. The organization is as follows. This thesis starts with the introduction of theoretical methods in chapter 2. In chapter 3, 4, and 5, we present our study on protonated methanol-water clusters $\text{H}^+(\text{CH}_3\text{OH})_m(\text{H}_2\text{O})_n$ by increasing cluster size and

changing the mixing ratio of the two components. Chapter 3 studies the mixed clusters by fixing the number of water molecule ($n = 1$) and increasing cluster size. Chapter 4 investigates the clusters by fixing the total number of molecules, $m + n = 5$ and 6, and changing the mole concentration. Chapter 5 proposes and verifies the anticooperativity induced by mixed solvation, based on the results of Chapter 4. In chapter 6, we use protonated methanol cluster as a probe to study proton transfer in $X-H^+-(CH_3OH)_m$ (X =Trimethylamine and Dimethylsulfoxide). In chapter 7, we give the conclusions and future work.

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Chapter 2

Theoretical Methodology

2.1 Density functional theory

The ultimate goal of most quantum chemical approaches is the approximate-solution of the time-independent, non-relativistic Schrödinger equation

$$\hat{H}\Psi = \left[\hat{T} + \hat{V} + \hat{U} \right] \Psi = \left[\sum_i^N -\frac{\hbar^2}{2m} \Delta_i^2 + \sum_i^N V(\vec{r}_i) + \sum_{i<j}^N U(\vec{r}_i, \vec{r}_j) \right] \Psi = E\Psi \quad (2.1)$$

Where $\hat{H}$ is the electronic molecular Hamiltonian, N is the number of electrons, $\hat{T}$ is the N -electron kinetic energy, $\hat{V}$ is the N -electron potential energy from the external field, and $\hat{U}$ is the electron interaction energy for the N -electron systems.

It is impossible to solve equation (2.1) by searching through all acceptable N -electron wave functions. In the Hartree-Fock scheme, it consists of approximating the N -electron wave function by an antisymmetrized product of N one-electron wave functions. This product is usually referred to as Slater determinant

$$\Psi(x_1, x_2, \dots, x_N) = (N!)^{-1/2} \begin{vmatrix} \psi_1(x_1) & \psi_2(x_1) & \cdots & \psi_N(x_1) \\ \psi_1(x_2) & \psi_2(x_2) & \cdots & \psi_N(x_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(x_N) & \psi_2(x_N) & \cdots & \psi_N(x_N) \end{vmatrix}. \quad (2.2)$$

Density functional theory is a successful approach for the description of ground state properties of many-electron system, in particular atoms, molecules, and the condensed phases. The ultimate goal of the DFT method is the calculation of the total energy of the system and the ground-state electron density distribution without using the wave function of the system. The DFT calculations are not expensive. Their cost is comparable with that of the Hartree-Fock method. Therefore, the same computer power allows us to explore much larger molecules.

2.1.1 The electron density

We begin from the Born-Oppenheimer approximation, which allows us to obtain the electronic wave function corresponding to fixed positions of the nuclei. To describe the ground-state instead of the N electron wave function $\Psi(1,2,\dots,N)$, we need only the electron density distribution defined as,

$$\rho(r) = N \sum_{\sigma_1=-\frac{1}{2}, \frac{1}{2}} \int d\tau_2 d\tau_3 \dots d\tau_N |\Psi(r, \sigma_1, r_2, \sigma_2, \dots, r_N, \sigma_N)|^2. \quad (2.3)$$

It is seen that we obtain ρ by carrying out the integration of $|\Psi|^2$ over the coordinates of all the electrons except one and in addition the summation over its spin coordinate (σ_1).

Thus we obtain a function of the position of electron 1 in space $\rho(\mathbf{r})$. The wave function Ψ is antisymmetric with respect to the exchange of the coordinates of any two electrons. Therefore, $|\Psi|^2$ is symmetric with respect to such an exchange. The definition of ρ is independent of the label of the electron we do not integrate over. According to this definition, ρ represents nothing else but the density of the electron cloud carrying N electrons.¹

2.1.2 Total energy expression

A general expression for the electronic ground-state energy includes kinetic energy of electrons, their interaction with the nuclei and their repulsion among themselves. However, in the DFT approach it can be written as

$$E = T_0 + \int v(r)\rho(r)d^3r + J[\rho] + E_{xc}[\rho], \quad (2.4)$$

where the electronic kinetic energy of the fictitious Kohn-Sham system of electrons

T_0

$$T_0 = -\frac{1}{2} \sum_{i=1}^N (\phi_i | \Delta \phi_i). \quad (2.5)$$

There is a correct electron-nuclei interaction term

$$\int v(r)\rho(r)d^3r \quad (2.6)$$

Then, there is a self-interaction of electron cloud with it self

$$E^J = \frac{1}{2} \iint \rho(\vec{r}_1) (\Delta r_{12})^{-1} \rho(\vec{r}_2) d\vec{r}_1 d\vec{r}_2 \quad (2.7)$$

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} d^3r_1 d^3r_2 \quad (2.8)$$

Two electrons repel each other electrostatically and therefore around each of them there has to exist a kind of no-parking zone for the other one. That's the exchange-correlation energy.

2.1.3 Exchange-correlation energy

The DFT exchange energy (E_x) is calculated in the same way as in the Hartree-Fock methods, but with the Kohn-Sham determinant, the exchange-correlation energy can be further split into exchange and correlation contributions

$$E_{xc} = E_x + E_c \quad (2.9)$$

The electron density distribution in a molecule is inhomogeneous, but locally (within a small volume) we may assume its homogeneity. To a good approximation, the exchange-correlation energy contribution could be calculated as a product of the small volume and the exchange-correlation energy density from the homogeneous gas theory (calculated inside the small volume). The analytical form is not known, so there are several approximations, such as Local density approximation (LDA) and Perdew-Wang functional (PW91).

In this thesis, we use the famous B3LYP (Becke, three-parameter, Lee-Yang-Parr) hybrid functional. The B3LYP approach belongs to the hybrid approximations for the exchange-correlation functional. Semiempirical coefficients were introduced to determine the weights of the various components². The B3LYP exchange-correlation functional is constructed as a linear combination of the LDA, Hartree-Fock (HF), Becke in 1988 (B88), Lee-Yang-Parr (LYP), and Vosko-Wilk-Nusair (VWN) exact exchange functional,

$$E_{B3LYP}^{XC} = E_{LDA}^X + c_0(E_{HF}^X - E_{LDA}^X) + c_X \Delta E_{B88}^X + E_{VWN3}^C + c_C(E_{LYP}^C - E_{VWN3}^C) \quad (2.10)$$

Where c_0 , c_X , and c_C are the three empirical parameters determined by fitting the predicted values to a set of atomization energies, ionization potentials, proton affinities, and total atomic energies. The amount of exact exchange in the functional is determined through the parameters by controlling the contributions of exchange and correlation gradient corrections to the local density approximation.³⁻⁵

Density functional theory is an extremely successful approach for description of ground state properties of bulk and clusters. In the following section, we focus on the calculation of natural bond orbital analysis, harmonic vibrational frequencies, and

thermodynamic quantities, which are applied to study our systems.

2.2 Natural bond orbital analysis

Atomic charge is not a measurable property of a molecule, because molecules do not consist of atoms but nuclei and electrons. Some arbitrary decisions have to be taken on how to divide up calculated electron density between atoms. In Mulliken population analysis, the overlap population is divided equally between the two partner atoms. Most electron modeling programs calculate charges by Mulliken method, because it is simple to do so.

Natural bond orbital (NBO) analysis originated as a technique for studying hybridization and covalence effects in polyatomic wave functions, based on local block eigenvectors of the one-particle density matrix.^{6,7} NBOs were conceived as a “chemist’s basis set” that would correspond closely to the picture of localized bonds and lone pairs as basic units of molecular structure.⁸ NBO analysis comprised a sequence of transformations from the input basis set $[\chi_i]$ to various localized basis sets [natural atomic orbitals (NAOs), hybrid orbitals (NHOs), bond orbitals (NBO), and localized molecular orbitals (NLMOs)]

$$\text{Input basis} \rightarrow \text{NAOs} \rightarrow \text{NHOs} \rightarrow \text{NBOs} \rightarrow \text{NLMOs} \quad (2.11)$$

These steps are automated by the NBO computer program,⁹ which has been attached to ab initio and semiempirical electronic structure packages, such as GAUSSIAN.¹⁰ Natural population analysis has been applied to a variety of chemical systems and has been shown to exhibit good numerical stability and agreement with other theoretical and experimental measures of charge distribution.^{11,12} In the present work, it is used to

access the intermolecular charge transfer that accompanies formation of a hydrogen bond.

2.3 Harmonic vibrational frequencies

Calculated normal-mode vibrational frequencies play important roles in the use of theory as a means of characterizing molecular potential surface. First of all, they may be used to characterize stationary points on the surface. Local minima have all real frequencies, while saddle points have a single imaginary frequency. Secondly, for stable but highly reactive or short-lived molecules, they provide a means of identification. The appearance of only a single infrared line may be the only indication that a new molecule has actually been formed. Any theory capable of calculating vibrational frequencies with sufficient high accuracy would obviously be of great value for assignment of spectra. Finally, calculated normal-mode vibrational frequencies provide thermodynamic properties of molecules by way of statistical mechanics. Thus, reaction entropies and equilibrium isotope effects, which are widely used to probe the structures of reactive intermediates in experiment, can be calculated from first principles. In addition, the corresponding quantities may also be obtained for reaction transition structures. Theoretical vibration frequencies may also be employed to correct experimental thermochemical data to 0 K and to evaluate zero-point vibrational energies.¹³

The total energy of a molecule comprising N atoms near its equilibrium structure may be written as

$$E = T + V = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2 + V_{\text{eq}} + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_{\text{eq}} q_i q_j. \quad (2.12)$$

Here, the mass-weighted Cartesian displacements, q_i , are defined in terms of the locations x_i of the nuclear relative to their equilibrium $x_{i, \text{eq}}$ and their masses M_i ,

$$q_i = M_i^{1/2} (x_i - x_{i, \text{eq}}). \quad (2.13)$$

V_{eq} is the potential energy at the equilibrium nuclear configuration, and the expansion (2.1) of the vibrational energy in terms of a power series is truncated at a second order.¹⁴ For such a system, the classical-mechanical equations of motion take the form

$$\ddot{q}_j = - \sum_{i=1}^{3N} f_{ij} q_i \quad j = 1, 2, \dots, 3N. \quad (2.14)$$

The f_{ij} , termed quadratic force constants, are the second derivatives of the potential energy with respect to mass-weighted Cartesian displacements, evaluated at the equilibrium nuclear configuration, that is,

$$f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_{\text{eq}}. \quad (2.15)$$

The f_{ij} may be evaluated by numerical second differentiation,

$$\frac{\partial^2 V}{\partial q_i \partial q_j} \square \frac{\Delta(\Delta V)}{\Delta q_i \Delta q_j}, \quad (2.16)$$

by numerical first differentiation of analytical first derivatives,

$$\frac{\partial^2 V}{\partial q_i \partial q_j} \square \frac{\Delta(\partial V / \partial q_i)}{\Delta q_j}, \quad (2.17)$$

or by direct analytical second differentiation, Equation (2.15). The choice of procedure depends on the quantum mechanical model employed and practical matters such as the size of the system.

Equation (2.14) may be solved by standard methods to yield a set of $3N$ normal-mode vibrational frequencies. Six of these (five for linear molecules) will be zero as they correspond to translational, and rotational (rather than vibrational) degrees of freedom.

2.4 Thermodynamic quantities

The partition function from any component can be used to determine the entropy contribution S from that component, using the relation:

$$S = Nk_B + Nk_B \ln\left(\frac{q(V, T)}{N}\right) + Nk_B T \left(\frac{\partial \ln q}{\partial T}\right)_V \quad (2.18)$$

In Gaussian, molar values are given, so we can divide $n = N/N_A$, and substitute $N_A k_B = R$. We can also move the first term in to the logarithm, which leaves (with $N = 1$):

$$\begin{aligned} S &= R + R \ln(q(V, T)) + RT \left(\frac{\partial \ln q}{\partial T}\right)_V \\ &= R \ln(q(V, T)e) + RT \left(\frac{\partial \ln q}{\partial T}\right)_V \\ &= R \left(\ln(q_t q_e q_r q_v e) + T \left(\frac{\partial \ln q}{\partial T}\right)_V \right) \end{aligned} \quad (2.19)$$

Contributions from translation. The translational partition function is,

$$q_t = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{k_B T}{P}. \quad (2.20)$$

The partial derivative of q_t with respect to T is,

$$\left(\frac{\partial \ln q_t}{\partial T}\right)_V = \frac{3}{2T} \quad (2.21)$$

which will be used to calculate both the internal energy E_t and the third term in Equation (2.19). The translational entropy

$$S_t = R \left(\ln(q_t e) + T \left(\frac{3}{2T} \right) \right) = R(\ln q_t + 1 + 3/2). \quad (2.22)$$

The contribution to the internal thermal energy due to translation is,

$$E_t = N_A k_B T^2 \left(\frac{\partial \ln q_t}{\partial T} \right)_V = RT^2 \left(\frac{3}{2T} \right) = \frac{3}{2} RT. \quad (2.23)$$

Contributions from electronic motion. The usual electronic partition function is,

$$q_e = \omega_0 e^{-\varepsilon_1/k_B T} + \omega_1 e^{-\varepsilon_1/k_B T} + \omega_2 e^{-\varepsilon_2/k_B T} + \dots, \quad (2.24)$$

where ω is the degeneracy of the energy level, ε_n is the energy of n -th level. Gaussian assumes that the first electronic excitation energy is much greater than $k_B T$. Therefore, the first and higher excited states are assumed to be inaccessible at any temperature. Further, the energy of the ground state is set to zero. These assumptions simplify the electron partition function to, $q_e = \omega_0$, which is simply the electronic spin multiplicity of the molecule. The entropy due to electronic motion is,

$$S_e = R \left(\ln q_e + T \left(\frac{\partial \ln q_e}{\partial T} \right)_V \right) = R(\ln q_e + 0). \quad (2.25)$$

Since there are no temperature dependent terms in the partition function, the electronic heat capacity and the internal thermal energy due to electronic motion are both zero.

Contributions from rotational motion. For the general case for a nonlinear polyatomic molecule, the rotational partition function is,

$$q_r = \frac{\pi^{1/2}}{\sigma_r} \left(\frac{T^{3/2}}{(\Theta_{r,x} \Theta_{r,y} \Theta_{r,z})^{1/2}} \right), \quad (2.26)$$

where $\Theta_r = h^2 / 8\pi^2 I k_B$ and I is the moment of inertia. The translational entropy and internal thermal energy are,

$$S_r = R \left(\ln q_r + T \left(\frac{\partial \ln q_r}{\partial T} \right)_V \right) = R(\ln q_r + \frac{3}{2}) \quad (2.27)$$

$$E_r = RT^2 \left(\frac{\partial \ln q_r}{\partial T} \right)_V = RT^2 \left(\frac{3}{2T} \right) = \frac{3}{2} RT \quad (2.28)$$

Contributions from vibrational motion. The contributions from vibrational motions are composed of a sum of the contributions from each vibrational mode, K . Only the real modes are considered, while modes with imaginary frequencies are ignored. Each of the $3N-6$ (or $3N-5$ for linear molecules) modes has a characteristic vibrational temperature, $\Theta_{v,K} = h\nu_K / k_B$. There are two ways to calculate the partition function, depending on where you choose the zero of energy to be: either the bottom of the internuclear potential energy well, or the first vibrational level. If zero-point energy is computed separately, then you should use the bottom of the well as your reference point, and the overall vibrational partition function is,

$$q_v = \prod_K \frac{e^{-\Theta_{v,K}/2T}}{1 - e^{-\Theta_{v,K}/2T}}. \quad (2.29)$$

On the other hand, if you chose the first vibrational energy level to be the zero of energy ($V = 0$), then the overall vibrational partition function is,

$$q_v = \prod_K \frac{1}{1 - e^{-\Theta_{v,K}/2T}} \quad (2.30)$$

The translational entropy and internal thermal energy are,

$$S_v = R \sum_K \left(\frac{e^{\Theta_{v,K}/T}}{e^{\Theta_{v,K}/T} - 1} - \ln(1 - e^{-\Theta_{v,K}/T}) \right) \quad (2.31)$$

$$E_v = R \sum_K e^{\Theta_{v,K}/T} \left(\frac{e^{\Theta_{v,K}/T}}{e^{\Theta_{v,K}/T} - 1} \right)^2 \quad (2.32)$$

At the end, we can get thermal correction to Enthalpy and Gibbs free energy,

$$H_{\text{corr}} = E_{\text{tot}} + k_B T, \quad (2.33)$$

$$G_{\text{corr}} = H_{\text{corr}} - TS_{\text{tot}}, \quad (2.34)$$

where $S_{\text{tot}} = S_{\text{t}} + S_{\text{e}} + S_{\text{r}} + S_{\text{v}}$, and $E_{\text{tot}} = E_{\text{t}} + E_{\text{e}} + E_{\text{r}} + E_{\text{v}}$.

The corresponding quantities may also be obtained for reaction transition structures. Of particular interest are kinetic isotope effects and entropies of activation, which provide mechanistic information. Only equilibrium thermodynamic properties have been considered in this research. Application to non-minimum-energy forms requires the additional assumption of a transition-state model. This may lead to the discrepancies between theoretical and experimental frequencies.

2.5 References

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Chapter 3

Proton switch correlated with the morphological development of the hydrogen-bond network in

3.1 Introduction

Since the proposal of the proton-transfer (hopping) mechanism by Grotthuss,¹ microsolvation structures of a proton have attracted much interest with respect to the mobility of the proton in the protic solvents.²⁻⁹ For multicomponents systems, such as methanol–water mixture, the preference of the protonated site has been the subject of extensive studies.¹⁰⁻²⁷ Though the proton affinity (PA) in the gas phase is a useful index to infer the preferential protonated site, recent gas-phase cluster studies, which provide us clear microscopic structures of the proton solvation, have shown that proton migration can occur from the larger PA site to the smaller PA site with the development of stepwise solvation. This is reasonably explained by the fact that the greater advantage in the solvation compensates for the lower affinity at the bare molecule. For example, Chang and co-workers demonstrated that in $H^+[(CH_3)_2O]_1(H_2O)_n$ the preferential protonated site switches from $(CH_3)_2O$ to water at $n = 2$ in spite of the larger PA of $(CH_3)_2O$ (189 kcal/mol) than that of water (165

kcal/mol).²⁶ This switch of the protonated site (so-called “proton switch”) was attributed to the asymmetric solvation structure of the $(CH_3)_2O$ site. Such results strongly suggest that the proton location in a multiple-component system cannot be determined by a simple push–pull relation between the two molecules neighboring the proton. The preferential location of the proton should be understood in terms of the structural development of the whole hydrogen-bond network.

Protonated methanol–water mixed clusters, $H^+(MeOH)_m(H_2O)_n$ (hereafter abbreviated to $H^+M_mW_n$), are very attractive systems to elucidate the correlation between the preferential proton location and the hydrogen-bond network structure. The PA of methanol (180 kcal/mol) is larger than that of water, but the difference between the magnitudes is much smaller than the cases between water and ketones or amines; therefore, the proton location is expected to be more sensitive to the hydrogen-bond network structure.²⁸ It has been shown that protonated water clusters (H^+W_n) and protonated methanol clusters (H^+M_m) have very different types of hydrogen-bond network structures (“morphologies”), reflecting the different coordination nature of water and methanol.^{29–45} While complicated three-dimensional cage structures are finally favored in H^+W_n , much simpler “bicyclic” structures are the terminal of the “morphological” development in H^+M_m . Mixing of these two components would result in different hydrogen-bond network structures depending on the relative concentration between the two components.

The proton location in $H^+M_mW_n$ has been mainly studied in the two extreme cases, $m \ll n$ (water-rich clusters) and $m \gg n$ (methanol-rich clusters), except the small-sized

clusters ($m + n = 4$).^{17-19,22-24} Chang and co-workers carried out the pioneering infrared (IR) spectroscopic and theoretical studies of the water-rich clusters ($m = 1, n = 1-6$) as well as the small-sized $m + n = 4$ clusters to elucidate their detailed hydrogen-bond structures.^{17,24} They identified the existence of the $CH_3OH_2^+$ (abbreviated to $MeOH_2^+$), H_3O^+ , and $CH_3OH-H^+-(H_2O)_2$ ion cores. The preferential protonated site sensitively depends on the cluster size and hydrogen-bond structure. Coexistence of the $MeOH_2^+$ and H_3O^+ ion cores was observed in the small-sized clusters ($m + n \leq 4$) at the finite temperature. We also recently reported the correlation between the proton location and hydrogen-bond network morphology in the water-rich clusters of the relatively larger sizes ($m = 1, n = 1-9$, and 21).^{20,46} Because of the difference of the preferential coordination numbers of the ion cores (2 for $MeOH_2^+$ but 3 for H_3O^+), the development of the hydrogen-bond network into the 3-D cage structures in the water-rich clusters induces the exclusive location of the proton on the water site.

In contrast to the extensive spectroscopic and theoretical studies in the water-rich clusters, the proton location in the methanol-rich clusters has been mainly discussed only on the basis of mass spectrometric and thermochemical studies.^{14-16,21-23,47} Kebarle et al. first carried out the mass spectrometric study of $H^+M_mW_n$.¹⁴ On the basis of the cluster size distribution, the preferential solvation of the proton by water was predicted for the larger-sized clusters, while coexistence of both ion cores was suggested for the smaller-sized clusters ($m + n \leq 6$). Stace and co-workers measured the metastable decay of $H^+M_mW_1$ and found the switch of the preferential fragmentation channel with the cluster size. While at the $m < 9$ clusters water loss is

the dominant fragmentation channel, the methanol loss becomes dominant at $m \geq 10$.^{15,16} These results were interpreted as the proton switch occurring from the $MeOH_2^+$ ion core to the H_3O^+ ion core at $m \approx 9$ because of the lower evaporation possibility for the protonated site. On the other hand, Meot-Ner measured the enthalpy change in the stepwise replacement of water by methanol. In every step from H^+W_7 to H^+M_7 , the replacement was exoenergetic, and preferential solvation of the proton by methanol was concluded up to $m = 7$.²¹ Garvey and co-workers observed the magic number behavior of $H^+M_mW_1$ and $H^+M_mW_2$ at $m = 9$ and 10 , respectively, and proposed the formation of a characteristic “inclusion” structure at the magic number, where the H_3O^+ (or $H_5O_2^+$) ion core is surrounded by a methanol ring. They also measured the collision-induced dissociation of $H^+M_mW_1$ and reported the change of the preferential dissociation channel from the water loss at $m \leq 8$ to the methanol loss at $m \geq 9$.²³ This was interpreted as evidence for the proton switch from $MeOH_2^+$ to H_3O^+ . Jackson recently reported the mass distribution of the larger-sized $H^+M_mW_n$ mixed clusters and supported the suggestion by Garvey et al.⁴⁷

All these mass spectrometric studies strongly suggested the characteristic ion core switching at $m \approx 9$. However, proton migration prior to dissociation can obscure the actual critical size of the switching. Moreover, detailed structural information on the hydrogen-bond network is hardly extracted from the mass spectrometric results. Systematic consideration of the proton switch along with the hydrogen-bond network morphology development has never been given except the qualitative assumption of the characteristic inclusion structure formation to explain the critical size for the

proton switch.^{22,23} Collaboration between theoretical calculations and infrared spectroscopy is expected to give us unequivocal structural information also for the methanol-rich clusters. However, IR spectroscopic studies on methanol-rich mixed clusters have been limited to small-sized clusters, $H^+M_4W_1$ and $H^+M_3W_1$, by Chang and co-workers.^{18,24} Recently, the IR spectroscopy and extensive theoretical calculations of H^+M_m established the fundamental process of the morphological development of the hydrogen-bond network of H^+M_m .^{30,31} The structures of H^+M_m are much simpler in comparison with those of H^+W_n because of the lower flexibility in the coordination of methanol. Mixing of a single water molecule to H^+M_m allows more flexibility in the hydrogen-bond network structure construction as well as the proton location.

In the present study, on the basis of the previous analysis of H^+M_m , we explore the proton switch correlated with the morphological development in $H^+M_mW_1$ by density functional theory (DFT) calculations and compared with IR spectroscopic measurements. Energy-optimized structures of $H^+M_mW_1$ ($m = 1-9$) are extensively searched in the systematic manner, and their relative energies and zero point vibrational energy corrections are evaluated. Coexistence of structural isomers is discussed on the basis of the Gibbs free energy evaluation. IR spectral simulations are carried out, and they are compared with the observed spectra.

3.2 Computational methods

Geometries of $H^+(MeOH)_m(H_2O)_n$ were optimized at the B3LYP/6-31+G* level

using the Gaussian 03 program package.⁴⁸ Regarding the use of the B3LYP/6-31+G* level of calculation, this level has been extensively employed in the studies on protonated hydrogen-bonded clusters by Chang and co-workers, and it has successfully reproduced experimental observations.^{2,31,35} For each energy-optimized structure, the frequency calculation was performed to confirm the geometry is an energy minimum, and the zero-point energy (ZPE) correction was estimated by the harmonic approximation ($ZPE \cong \sum_i \hbar \omega_i / 2$). To access the thermal effects, we also calculated the Gibbs free energy at 190 K, which is the estimated temperature of the protonated clusters in the present experimental measurements.

As for the initial input structures for the energy optimization, we employed two methods. For the small-sized clusters of $m \leq 3$, several structures can be formed. These structures can be constructed manually. However, both the complexity in structures and the number of acceptable conformations within a given structure significantly increase with the cluster size. In the construction of a wide variety of input structures for large-sized $H^+M_mW_1$, we rely on previous experience with H^+W_n and H^+M_m .^{31,32} An input structure of an isomer of $H^+M_mW_1$ can be easily obtained by replacing a methanol by a water from H^+M_{m+1} or replacing m water molecules (except for the water sites of which coordination is unreasonable for methanol) by methanol from H^+W_{m+1} .

3.3 Results and discussions

3.3.1 Symbolic hydrogen-bond representations and coordination types of the

building blocks.

In previous study on H^+M_m , a simple symbolic representation for a hydrogen bond is introduced, which is helpful to consider structural development of a hydrogen-bond network.^{30,31} Figure 3.1a shows its definitions. A hydrogen bond is represented by an arrow between proton-donating and -accepting oxygen atoms. Oxygen atoms of methanol molecules are represented by open circles, and all the hydrogen atoms and methyl groups are omitted. The donor–acceptor relation of the hydrogen bond is represented by the direction of the arrow (from a proton donor to a proton acceptor). The oxygen atom of the water molecule is represented by an open diamond. A closed circle or closed diamond represents the oxygen atom in the ion core site. By using these definitions, the possible coordination types of methanol and water are summarized as shown in Figure 3.1b and 3.1c. A methanol molecule can be a proton acceptor (A), proton donor (D), double acceptor (AA), single acceptor single donor (AD), or double acceptor single donor (AAD) site. For water, on top of all the possible coordination types in methanol, double donor (DD), single acceptor double donor (ADD), and double acceptor double donor (AADD) are acceptable coordination types.

Figure 3.1 Definitions of the symbolic representation of hydrogen bonds and

building block patterns of the hydrogen-bond coordination (see text). (a) Definitions of the symbolic representation. The oxygen atom in methanol is represented by an open circle, and the methyl group and hydrogen atoms are omitted in the representation. An arrow indicates a hydrogen bond that binds two oxygen atoms. The direction of the arrow shows the donor–acceptor relation in the hydrogen bond. (b) Possible coordination types for methanol and protonated methanol sites. The oxygen atom of the protonated site is represented by a closed circle. (c) Characteristic coordination types for water and protonated water sites. The oxygen atoms of the water and protonated water sites are represented by open and closed diamonds, respectively.

Exceptional coordination types should be also considered only for the ion cores. For example, D, AD, DD, and ADD are acceptable coordination types for $MeOH_2^+$. However, it has been shown in previous studies on H^+W_n , H^+M_m , and $H^+M_1W_n$ that the coordination of the ion cores shows strong preferences.^{20, 31,32,46} The $MeOH_2^+$ ion core has a strong preference to take up the DD form. This tendency is reasonably understood as follows: the D type means the $MeOH_2^+$ ion core is under coordinated, and it is stable only in very small-sized clusters. On the other hand, AD and ADD are not stable since it requires the positively charged $MeOH_2^+$ ion core to accept a proton from another neutral donor. No stable AD and ADD coordination of $MeOH_2^+$ has been found in $H^+M_1W_n$ and H^+M_m . For the same reason, the H_3O^+ ion core prefers the triple donor (DDD) coordination, and D and DD can be formed only in small-sized clusters before full solvation of the ion core. The AD, ADD, and single acceptor triple donor (ADDD) types have never been found for the H_3O^+ ion core.

3.3.2 Possible morphologies.

It is reasonably anticipated that the structures of the methanol-rich clusters $H^+M_mW_1$ should be similar to those of H^+M_m . The basic morphology development process of H^+M_m was previously demonstrated, and it is briefly summarized in Figure

3.2 with the symbolic representation of the hydrogen-bond network.^{30,31} The simplest morphology is linear structures (L). Starting with the DD configuration of the ion core, AD sites extend the one-dimensional chains, which are terminated by two A sites. When these two terminal A sites are bound to each other, one site becomes an AD site, and the other is transformed to an AA site. Then, the morphology is developed from L to cyclic structures (C). A hydrogen-bond chain can be extended from the AA site (the AA site is then transformed to the AAD site), and such structures are categorized into cyclic structures with a “tail” (Ct). This chain has special importance in structure development because it is terminated with an A site and can be bound to an AD site in the ring moiety (even if there are other side chains in the ring moiety, they are terminated only with D sites and cannot be bound anywhere in the hydrogen-bonded network). When the “tail” in the Ct structures is bound to the ring moiety, the ring is bridged and the morphology is developed to bicyclic structures (bC), which are the terminal of the morphological development in H^+M_m .

Figure 3.2 Schematic representations of the six basic morphologies of

$H^+(MeOH)_m(H_2O)_1$ ($H^+M_mW_1$). The symbolic representation of the hydrogen bond defined in Figure 3.1 is employed, and all the AD sites are neglected in the representations for simplicity. (a) Morphologies only with the $MeOH_2^+$ ion core. (b) Morphologies only with the H_3O^+ ion core. (c) Morphologies having both types of the ion cores.

Addition of a single water molecule into H^+M_m enriches the structure types because of the diversity of the coordination types of water. Not only the L, C, Ct, and bC structures in H^+M_m but also two more new types can be formed in $H^+M_mW_1$. One is tree structures (T), which are favored for the H_3O^+ ion core due to its full solvation. The double (triple) proton-donating ability of the water (protonated water) site enables producing one more side chain ('tail') which is terminated by an A site, in comparison with the cases of H^+M_m . Therefore, two bridges across the ring moiety can finally occur in $H^+M_mW_1$. Then, the cyclic moiety is segmented into three parts in such structures, and we categorize this structural type to tricyclic structures (tC). The inclusion structures proposed by Garvey and co-workers are involved in this category.^{22,23} Existence of a single water molecule also enables several different hydrogen-bond network patterns in the Ct and bC structures.

3.3.3 Stable isomers of $H^+M_mW_1$.

In this study, we systematically searched stable isomer structures of $H^+M_mW_1$ for $m = 1-9$. In Figure 3.3–3.5, we summarize the most stable isomer of each size and morphology.

Because of the strong preference for the full solvation of the ion core moiety, all of the most stable isomers of the L and C structures have the $MeOH_2^+$ ion core while those of the T and tC structures have the H_3O^+ ion core. In the Ct and bC structures,

both ion cores are found in the most stable isomers, depending on the cluster size. In the following, we overview the trends of the most stable isomer structure in each cluster morphology.

Figure 3.3 Most stable structures of morphologies with the methanol ion core, “linear”

(L) and “cyclic” (C) (left and right columns, respectively). The values below the structures are the relative E_0 (the first number), the relative $E_0 + \text{ZPE}$ (the second number), and the relative Gibbs free energy at 190 K (the third number) computed at B3LYP/6-31+G* (in kcal/mol). The zero of these energy scales is set to the energy of the most stable isomer in each size. The positions of the methanol/water ion core are highlighted with the blue circles/green squares, respectively.

Figure 3.4 Energy-optimized stable structures of morphologies with the water ion core, “tree” (T) and “tricyclic” (tC). Two types are presented for tC structures in the figure. (a) With the H_3O^+ ion core in the outskirts (largest) hydrogen-bond ring. ((a)-1) For $m \geq 7$, the structures are constructed by adding methanol molecules (blue one) to the inner segments of $H^+M_6W_1$. Schematic structure representations are used to present clearly. (Different from Figure 3.2, all the molecules are presented including

the AD molecules.) ((a)-2) Constructed by adding methanol molecules to the outskirts of $H^+M_6W_1$. (b) With the H_3O^+ ion core in the center. Note the latter is less stable than the former (see text). The values below the structures are the relative E_0 (the first number), the relative $E_0 + ZPE$ (the second number), and the relative Gibbs free energy at 190 K (the third number) computed at B3LYP/6-31+G* (in kcal/mol).

Figure 3.5 Most stable structures of morphologies with both the methanol and the water ion cores, “cyclic with a tail” (Ct) and “bicyclic” (bC) (left and right columns, respectively). The values below the structures are the relative E_0 (the first number), the

relative $E_0 + \text{ZPE}$ (the second number), and the relative Gibbs free energy at 190 K (the third number) computed at B3LYP/6-31+G* (in kcal/mol).

3.3.3.1 Morphologies with the $MeOH_2^+$ ion core.

Linear Structures (L). Similar to the H^+M_m and H^+W_n clusters, L structures are the simplest and most basic form of $H^+M_mW_l$. The excess proton is found to prefer to reside at the central methanol site of the hydrogen-bond network to stabilize the strong hydrogen bonds around the ion core. In the L structures, the H_3O^+ ion core is not favored because of the lack of full solvation. The water molecule is found to prefer staying at the terminal of the linear structure for all sizes.

Cyclic Structures (C). Cyclic structures are energetically more favorable only in the small sizes up to 6. The excess proton prefers residing on the methanol site due to the similar reason in the L structures. Both the AA site and water molecule favor to be away from the ion core. This trend has also been found in H^+M_m .³¹

3.3.3.2 Morphologies with the H_3O^+ ion core

Tree Structures (T). T structures are characteristic to the H_3O^+ ion core because the DDD coordination (full solvation) of the H_3O^+ ion core is satisfied in these structures. The methanol molecules favor even distribution of the three branch lengths. The T structure with a $MeOH_2^+$ ion core and an AAD methanol branching site is not stable, which is indicated in previous work that there is no T structure in H^+M_m .³¹ The T structures with an AAD water branching site is also not stable, and that with an ADD water branching site are higher in energy. The same trends were seen in $H^+M_lW_n$.⁴⁶

Tricyclic Structures (tC). These particular structures maximize the number of

hydrogen bonds (no free (dangling) OH exists) in clusters with full solvation of the H_3O^+ ion core. Though it is also geometrically possible to construct tC structures with the $MeOH_2^+$ ion core, only the H_3O^+ ion core was found in the stable isomers. Depending on the location of the ion core, there are two types of structures, as schematically shown in Figure 3.2. One has the ion core at the center of the hydrogen-bond network (the “inclusion” structure). In the other type, the ion core locates on the “outskirt” (the largest ring) of the hydrogen-bond network. To explain the magic number behavior of $H^+M_9W_1$, Garvey and co-workers suggested the former type of the tC structure.^{22,23} In the present calculations, the tC structure is found to exist from $m = 6$, because 6 is the minimum number to include another molecule in the hydrogen-bonded ring. Moreover, we found that the latter (“outskirt”) type of tC isomer is more stable than the former (“inclusion”) type in each size, as shown in Figure 3.4. In the 3-D cage structures of H^+W_n , it has been suggested that the excess proton prefers locating on the surface site rather than the interior site.^{20,32,35,37-39} The similar trend was observed for the tC structures.

Although the tC structures are not flat, their network topology is essentially two-dimensional. For $m = 6$, the structure is more symmetric with one methanol in the center and the six other molecules in the outer ring. The big ring is segmented into three 4-membered rings. For larger sizes, the structures can be constructed by adding AD methanols to $H^+M_6W_1$. In Figure 3.4a, two kinds are constructed for the more stable “outskirt” type according to the location of added AD molecules. For (a)-1, AD molecules are added to the inner segments, while for (a)-2, AD molecules are added to

the outer ring. The calculated relative energies show that (a)-1 is more stable with the fact that more molecules are put near the ion core. Our results show that this “outskirt” tC with the 6-membered outer ring is the most stable structure for $m = 6-9$.

3.3.3.3 Morphologies with the coexistence of the $MeOH_2^+$ and H_3O^+ ion cores.

Cyclic with a Tail (Ct). Two different hydrogen-bond network patterns are found in the stable isomers of this structural category. As shown in Figure 3.2, one has the $MeOH_2^+$ ion core separated far from the 3-coordinated ADD water, which is the branching site to have the “tail”. The other type has the 3-coordinated DDD H_3O^+ ion core with the AA methanol site far from the ion core. The “tail” arises from the ion core. The most stable structures depend on the cluster size as shown in Figure 3.5, and there is no clear trend on the preference of the ion core.

Bicyclic (bC). Unlike the above types of structures, bicyclic structures are complicated and have higher energy, as shown in Figure 3.5. Only two types are presented. Both the water and the methanol ion cores coexist.

3.3.4 Relative Stability

The electronic potential energy (E_0), total energies ($E_0 + \text{ZPE}$), and Gibbs free energy (G) at 190 K are evaluated for all stable structures. The energy evaluation was carried out at the B3LYP/6-31+G* level with the standard harmonic approximation. For E_0 , $E_0 + \text{ZPE}$, and G , those of the minimum energy isomer in each cluster size (m) are set to zero. The relative values among the different structures are shown in Figures 3.3–3.5 and also summarized in Figure 3.6.

Figure 3.6 Relative stabilities (in kcal/mol) of the most stable isomers of each morphology of $H^+M_mW_1$ ($m = 3-9$). The cluster size (m) is indicated by the x axis. (a) Relative potential energies (E_0). (b) Relative energies at the zero vibrational level ($E_0 + ZPE$). (c) Relative Gibbs free energies at 190 K.

The E_0 values in Figure 3.6a are scattered with the increase of the size, and they finally span a range of ~ 17 kcal/mol at $m = 9$. As the cluster size increases, more “compact” structures (bC and tC) tend to gain greater binding energy. This is especially clear for the tC structure, having more than 8 kcal/mol lower energy than

the next stable one at $m = 8$ and 9. This trend is in line with the fact that there are more hydrogen bonds in the compact structures in comparison with the “open” structures (L, T, C, and Ct).

The relative stability of the clusters at 0 K is determined by the competition between ΔE_0 and ΔZPE . The compact structures tend to have larger ΔZPE values because of their higher vibrational frequencies due to the relatively rigid structures, while flexibility of the open structures results in the relatively lower vibrational frequencies. The same trend has been found for H^+W_n , H^+M_m , and water-rich $H^+M_mW_n$ clusters.^{31,32,46} The energy difference at the zero-point level ($\Delta E_0 + \Delta ZPE$) is shown in Figure 3.6b, and its magnitude becomes smaller (~ 12 kcal/mol) than ΔE_0 due to the opposite trends between ΔE_0 and ΔZPE . At 0 K, the energy difference is estimated to be very small in the small-sized clusters ($m \leq 5$), but the large advantage of the tC structure is still seen at $m \geq 7$. For $m = 4$, the C configuration is a five-member ring structure, which is much stable than the four- and six-member ring due to the preference of HB angle. In the cluster with total size less than 4 ($m \leq 3$), the distortion of the hydrogen-bond angle in the ring moieties make them has higher ZPE. Thus the values of ΔE , $\Delta E + ZPE$, and ΔG for $m = 3$ of the C configuration are higher than those for $m = 4$.

To access the thermal effects on the relative stability, the Gibbs free energies at 190 K are also calculated. The temperature of 190 K is the estimated temperature of the protonated clusters in the present experimental measurements. The calculated Gibbs free energy in Figure 3.6c favors the open structures (L, T, C, and Ct) at small

sizes ($m \leq 7$), because of rich low-frequency modes. On the other hand, the tC and T structures have much lower Gibbs free energies than the others at $m \geq 8$. The differences among the Gibbs free energies of the different structures are ~ 8 kcal/mol at 190 K.

As seen from the small Gibbs energy differences, the coexistence of multiple isomers is highly plausible for the small-sized clusters ($m \leq 7$). For $m = 1$ and 2, $H^+M_mW_1$ has only linear structures, and the $MeOH_2^+$ ion core is preferred. For $m = 3-7$, the $MeOH_2^+$ and H_3O^+ ion cores would coexist because of the small energy difference among the multiple isomers. However, the tC and T structures have much lower Gibbs free energy (~ 3 kcal/mol) than the others for $m \geq 8$. Because both of these structures only have the H_3O^+ ion core, the preference of the H_3O^+ ion core for the clusters of $m \geq 8$ is clearly seen. The previous mass spectrometric studies of $H^+M_mW_1$ suggested that the proton switch occurs from the $MeOH_2^+$ ion core to the H_3O^+ ion core at $m \approx 9$.^{14,22} The present theoretical calculations support this suggestion well. The small difference of the critical size of the switching exists between the observation ($m \approx 9$) and theoretical prediction ($m \approx 8$). It would come from the temperature of the observed clusters as well as the precision of the energy evaluation in the DFT level calculations. The tC structures are predicted to be the terminal of the morphological development, which is consistent with previous studies. However, it should be noted that the most stable isomers in large clusters are of the “outskirt” structures and not of the “inclusion” structures assumed in the previous studies.^{22,23} In summary, the present calculations clearly demonstrate the trend of the proton switch in

$H^+M_mW_1$ correlated with morphological development.

3.3.5 DFT Simulations of vibrational spectra and comparison with observed vibrational spectra

Figures 3.7 and 3.8 show the simulated and observed IR spectra of $H^+M_mW_1$ in the 3 μm region. The experiment is carried by Fujii et al.,⁴⁹ and the observed spectra are shown in the rightmost column in each figure. The same observed spectra are reproduced in both Figures 3.7 and 3.8 for convenience of comparison with the simulations. The simulations are on the basis of the most stable isomer of each structure. All calculated harmonic frequencies are scaled by a factor of 0.973, which is determined to reproduce the free OH-stretch band in neat and protonated water clusters.⁵⁰ The stick spectra are converted into the continuous spectra by convolution with a Lorentzian function of 10 cm^{-1} full width at half-maximum.

Figure 3.7 Simulated infrared vibrational spectra on the basis of the most stable optimized structures of L, T, and C morphologies (left) and observed infrared spectra (right, measured by Fujii et al.⁴⁹) of $H^+M_mW_1$. All calculations were carried out at B3LYP/6-31+G* (rescaled by the scaling factor of 0.973). The vibrational bands are color coded with the vibrational modes shown in the schematic representation of the morphologies, and the stripes are made for eye-guiding purposes. In the observed spectra, the water loss channel was monitored for the spectra of $m = 3-8$, while the methanol loss channel was monitored for the spectra of $m = 9$ (see text).

Figure 3.8 Simulated infrared vibrational spectra on the basis of the most stable optimized structures of Ct and tC morphologies (left) and observed infrared spectra (right, measured by Fujii et al.⁴⁹) of $H^+M_mW_1$. All calculations were carried out at B3LYP/6-31+G* (rescaled by the scaling factor of 0.973). The vibrational bands are color coded with the vibrational modes shown in the schematic representation of the morphologies, and the stripes are made for eye-guiding purposes. The observed spectra are reproductions of those in Figure 3.7 for convenience of comparison with the simulations.

First, we overview spectral features in the simulations. In the frequency range of $3000-3600\text{ cm}^{-1}$, strong bands due to hydrogen-bonded OH stretches are expected.

Two different size-dependent trends are seen in these bands. As seen in Figures 3.7

and 3.8, the hydrogen-bonded OH stretch bands in the L, T, C, and Ct structures show a clear tendency to be blue shifted as the cluster size increases. The blue shifts demonstrate the reduction of the hydrogen-bond strength, and their origin is attributed to the increase of the average distance from the ion core and associated charge delocalization.⁴⁶ On the other hand, as shown in Figure 3.8, the slight red shifts with an increase of the size are seen in the tC structure. In such compact structures, the distortion of the hydrogen-bond angle in the ring moieties is reduced with the increase of the size. These red shifts indicate the enhancement of the hydrogen-bond strength with the reduction of the distortion. The similar effects on the hydrogen-bonded OH stretches have been found in the IR spectra of H^+M_m .³¹ Above 3600 cm^{-1} , the free OH stretch bands are expected in all the structures except the tC structure. The absence of the free OH stretch band in the tC structure reflects that all the OH groups are hydrogen bonded in this structure, and this is a unique spectral sign of the tC structure.

In the observed spectra, significant band broadening occurs in the hydrogen-bonded OH stretch region, but some clear band structures are seen. In $m = 3$, the broad absorption observed around 3200 cm^{-1} is attributed to the hydrogen-bonded OH stretch of the L structure. Though the T structure is also expected to be competitive, no hydrogen-bonded OH band is predicted in this region (the hydrogen-bonded OH stretches of the H_3O^+ ion core locate in the much lower frequency region). In $m = 4$ and 5, two broadened bands are observed in the $3200\text{--}3400\text{ cm}^{-1}$ region. Both bands show blue shifts with an increase of the size. As shown in the simulations, such blue shifts are characteristic to the “open” structures.

The lower frequency band (3200–3300 cm^{-1}) is attributed to the hydrogen-bonded OH stretches of the L, T, C, and Ct structures, and the higher frequency band (3300–3400 cm^{-1}) is to the C and Ct structures, which would become competitive in this size region at 190 K (as seen in Figure 3.6c). The dominance of the “open” isomers in the small size range is strongly suggested by the Gibbs energy evaluation, and the observed spectra are consistent with this expectation. The higher frequency band due to the C and Ct structures almost disappears in $m = 6$. This disappearance may be due to the decrease of the relative intensity of this band as seen in the simulations. The hydrogen-bonded OH stretch features seem to converge to a much broadened band centered at $\sim 3400 \text{ cm}^{-1}$ in $m \geq \sim 6$. This is also consistent with the convergence of the blue-shifting hydrogen-bonded OH stretch bands of the “open” isomers into this frequency region. Though the proton switch, i.e., exclusive H_3O^+ ion-core formation, is expected at $m \approx 8$, no drastic change of the spectra is seen in this size region. Isomers of the “compact” structures also show rich band features around the 3400 cm^{-1} region, and it may be the reason for the absence of the clear spectral sign reflecting the proton switch. The broadened band due to the coexistence of the isomers of multiple structures in $m \leq \sim 7$ would smoothly change to that attributed to the rich hydrogen-bonded features of the tC structure in $m \geq \sim 8$.

The dominant contribution of the tC structure in $m \geq \sim 8$ is, however, supported by the size dependence of the free OH stretch band observed at around 3670 cm^{-1} . No free OH group exists in the tC structure, and the disappearance of the free OH band is an indication of the dominant contribution of the tC structure. The free OH band

intensity in the observed spectra decreases with the increase of the cluster size, and it almost disappears at $m = 7-8$. This observation is consistent with the Gibbs energy evaluation and previous mass spectrometric suggestion.^{22,23}

3.4 Conclusions

Extensive DFT calculations of the $H^+M_mW_1$ clusters were carried out. The systematic search of the most stable isomer structure in various morphologies of the clusters clearly demonstrated the correlation between the cluster morphology and the preferential location of the protonated site. The size-dependent development of the hydrogen-bond network of the clusters was examined. The calculation results showed that the L structure and the $CH_3OH_2^+$ ion core is preferred for the small-sized clusters of $m = 1$ and 2. The coexistence of multiple structures and different ion cores ($MeOH_2^+$ and H_3O^+) was suggested for the small-sized clusters of $3 \leq m \leq 7$. Compared with the H^+M_m , adding one water molecule will encourage the formation of two new morphologies, T and tC structures. Both T and tC, which have only the H_3O^+ ion core, were shown to be preferential in $m \geq 8$, consistent with the previous mass spectrometric results. The IR spectra of the clusters were simulated and compared with the observed spectra in the OH stretching vibrational region. The spectral features of the observed spectra were well interpreted by the spectral simulations with the coexistence of the multiple isomers at small sizes. The disappearance of the free OH stretch band shows the dominant contribution of the tC structure (having the H_3O^+ ion core) at $m = 7-8$. All results from our calculation and observed IR spectra suggest

that the proton switch from the $MeOH_2^+$ ion core to the H_3O^+ ion core occurs at $m = 8$ in $H^+M_mW_1$. The small difference of the critical size of the switching between the others' work ($m \approx 9$)^{14,22} and this work ($m \approx 8$) would come from the temperature of the observed clusters as well as the precision of the energy evaluation in the DFT level calculations.

3.5 References

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Chapter 4

Comprehensive analysis on the structure and proton switch in $H^+(CH_3OH)_m(H_2O)_n$ ($m + n = 5$ and 6)

4.1 Introduction

Protonated water and methanol clusters, $H^+(H_2O)_n$ and $H^+(MeOH)_m$, have been studied in detail because of their fundamental importance in understanding the hydrogen bond network structure of protic solvents in chemistry and biochemistry.¹⁻⁹ When methanol mixes with water, the entropy increase is far less than expected for an ideal solution of randomly mixed molecules. This has been attributed to the difference between the preferential hydrogen bond structures of water and methanol molecules.^{10-14,15} Proton location is yet another important issue in $H^+(MeOH)_m(H_2O)_n$ (hereafter abbreviated to $H^+M_mW_n$). The location of an excess proton in two component systems has been discussed in terms of competition between proton affinities of components and preference in hydrogen bond structures. Though the proton affinity (PA) of methanol (180 kcal/mol) is larger than that of water (165 kcal/mol), the difference between the magnitudes is much smaller than the well-studied cases between water and ketones or amines.^{16,17} In $H^+M_mW_n$, therefore, the proton location is expected to be more sensitive to the hydrogen bond network structure.¹⁶⁻²⁴ Further studies on $H^+M_mW_n$ will be helpful to understand the small entropy increase and the proton location in the mixed system.

Previous structural studies on $H^+M_mW_n$ mixed clusters have mainly focused on the evolution of water clusters doped with one or a few methanol molecules ($m \ll n$) and vice versa ($m \gg n$).^{5,18-22} It has been shown that both the morphology (broad type of isomer structures) and ion core type has clear size-dependence. So far, very little attention is paid in examining intermediate cases that connect the above two extremes. To our knowledge, the most extensive work done to address this issue is that by Wu et al., and they studied the structure and the proton location of $H^+M_mW_n$ for $m + n = 4$ by using a combination of density functional theory (DFT) calculations and infrared (IR) spectroscopy.²³ They manually constructed clusters in structures and used relative energies as a mean to discuss the stabilities. They found the switch from the closed-shell H_3O^+ -centered form to the open-chain $CH_3OH_2^+$ -centered form as the number of the methanol molecules increases. The exponentially increasing number of isomers, however, prohibits from applying such methodology to larger clusters.

In this work, we begin with a systematic method to construct hundreds of competing isomers of $H^+M_mW_n$ (for $m + n = 5$ and 6) based on previous studies on the pure species.^{24,25} For systems containing such a large number of isomers with small energy difference, which is compatible with thermal energy, we abandon the traditional method, that is, comparison of the spectral features of selected isomers with experimental data. In the present work, we engage harmonic superposition approximation (HSA) to calculate averaged properties of these isomers at finite temperature. In particular, we analyze the population of each morphology and ion core type depending on temperature and mixing ratio. With the extensive set of stable isomers and HSA, we offer quantitative and direct comparisons between the experimental and first-principles spectra.

The remainder of this chapter is structured as follows. In section 4.2, we present a detailed description of the methodology. In section 4.3, we briefly summarize the morphology change associated with temperature and water/methanol ratio (mixing ratio). This paper concludes with a discussion of our results.

4.2 Methodology

A set of theoretical methods was integrated to tackle the intrinsic complexity of the mixed cluster. Local minima structures of H^+W_n clusters were collected with basin-hopping method and an empirical model.²⁶ These structures of H^+W_n , refined by DFT methods, were then used to construct initial input structures of $H^+M_mW_n$ by replacing m water (except for the water sites without free OH) by methanol molecules. After archiving a sufficient number of local minima structures, we employed HSA to analyze the canonical average of these clusters based on the energy landscape described by DFT calculations. Experimental IR spectra were also measured by IR dissociation spectroscopy of size-selected clusters. The details of these methods are described as follows.

4.2.1 Initial input structures. The structures of pure protonated water clusters are obtained by using a basin-hopping method with OSS2 potential. OSS2 is a polarizable potential proposed by Ojamae et al.,^{27,28} which is suitable for studying $H^+(H_2O)_n$ systems since it can describe the dissociation of water molecules. Under the basin-hopping algorithm, the original potential energy surface (PES) $[E(\mathbf{R})]$ is first transformed into a new form $\tilde{E}(\mathbf{R}) = \min_{\mathbf{R}}[E(\mathbf{R})]$ by an energy minimization with respect to nuclear coordinates $(\mathbf{R})$.^{29,30} In the transformed PES of $\tilde{E}(\mathbf{R})$, the

barriers between the “basins” have been removed and thus the efficiency of Monte Carlo sampling can be improved. In the present study, three independent runs of 2000 basin-hopping “moves” were performed for H^+W_5 and H^+W_6 . The number of “moves” is large enough to guarantee that the same global minimum is located successfully in all three independent runs. Each “move” consists of a random number of atomic and molecular movements followed by an unconstrained energy optimization. More details on the basin-hopping algorithm and the OSS2 potential can be found in the ref 24.

4.2.2 DFT calculations. DFT calculations are used to refine the structure of H^+W_n obtained from the OSS2 potential, and we found 14 and 43 isomers for H^+W_5 and H^+W_6 , respectively. $H^+M_mW_n$ clusters are constructed from H^+W_n by substitution scheme, and they also go through the same refinements by DFT calculations. Geometries were optimized without any symmetry constraints at the B3LYP level of computations with the 6-31+G* basis set, using the commercial Gaussian 03 program package.³¹ The reliability of this level of calculation for protonated clusters has been well established by previous studies.^{18,22,23,32} For each energy optimized structure, frequency calculations were performed to confirm the geometry is an energy minimum, and to predict the IR spectrum of the individual structure.

4.2.3 Harmonic superposition approximation. For convenience in discussion the structural transformation, isomers of $H^+M_mW_n$ from the DFT results are classified into different groups according to their topology and ion core type. The population or canonical probability is calculated using HAS, which represents an effective approach for acquiring diverse physical properties of a system from the collection of isomers instead of directly exploring the potential energy landscape.

Each local minimum is treated as a harmonic and infinite basin which is characterized only by its vibrational frequencies and relative energy.³³⁻³⁵

The population or the canonical probability of the system in topology A is

calculated as $P_A(T) = \frac{\sum_{a \in A} Z_a(\beta)}{Z(\beta)}$, where the total partition function $Z(\beta)$ of an N -

atom system at temperature T is given by $Z(\beta) = \sum_a n_a Z_a(\beta)$. $Z_a(\beta)$, under

quantum HSA, is given by $Z_a^Q(\beta) = \exp(-\beta E_a) \prod_a \frac{\exp(-\beta \hbar \omega_{af} / 2)}{1 - \exp(-\beta \hbar \omega_{af})}$, where the

contribution of the vibration modes is treated in quantum mechanical footing.³⁴⁻³⁶

Similarly, an averaged physical property $Y_{total}(\omega, T)$ at temperature T is calculated as the weighted sum of $Y_a(\omega)$ with the canonical probability $P_a(T)$ of isomer a

derived from the thermodynamic simulations $Y_{total}(\omega, T) = \sum_a Y_a(\omega) P_a(\omega, T)$, where

is $Y_a(\omega)$ is the individual contribution of isomer a .

4.3 Results and discussion

4.3.1 Structure and relative energy

The full list of pure protonated clusters H^+W_n ($n = 5$ and 6) are obtained from the OSS2 potential. Among these structures, some have very similar geometries except for a small difference in the orientations of the free OH. For such cases, we only chose the lowest energy one as representative. At last, 7 and 18 isomers were chosen as the initial input structure for H^+W_n ($n = 5$ and 6 , respectively), as shown in Figures 4.1 and 4.2. These isomers are sorted by their relative binding energy and we can clearly see that these isomers can be roughly classified into two groups. In group (a), the hydronium ion core is fully solvated, while the solvation of the

ion core is not full in group (b). As is reasonably expected, isomers in group (a) are energetically more favorable than those in group (b). Our list of water clusters not only includes all the stable structures found by other works^{7,37-39} but also includes the water isomers with higher energies, that is, group (b). The latter has not been explored much but is needed here because those corresponding structures have lower energies in $H^+M_mW_n$, as described in the following sections.

Figure 4.1 Structures of H^+W_5 calculated in this work. These isomers are classified into two groups according to the solvation of the hydronium ion core (marked with green squares). Isomers in (a) have the fully solvated (three coordinated) ion core, and isomers in (b) have the partly solvated (two coordinated) ion core with one free OH. The values below the structures are the relative energy (the first number), the relative energy with zero-point correction (the second number), and the relative Gibbs free energy at 190 K (the third number) computed at B3LYP/6-31+G* (in kcal/mol).

Different isomers of $H^+M_mW_n$ can be easily derived from H^+W_{m+n} by replacing m dangling hydrogen atoms by methyl groups. We systematically made all the possible replacements for the selected H^+W_{m+n} , which are described above. It is reasonable to anticipate that the replacement by methyl groups would not change the overall cluster structure. Our DFT optimization confirms this notion and reveals only some small change in bond lengths and angles from the initial

structure. All of the stable minima can be categorized into five morphology groups: linear (L), tree (T), cyclic (C), cyclic with tail (Ct), and bicyclic (bC). The last group is stable only for $m + n = 6$. The numbers of stable isomers in each group are summarized in Table 4.1.

Figure 4.2 Structures of H^+W_6 calculated in this work. These isomers are classified into two groups according to the solvation of the hydronium ion core (marked with green squares). Isomers in (a) have the fully solvated (three or four coordinated) ion core, and isomers in (b) have the partly solvated (two coordinated) ion core with one free OH. The values below the structures are the relative energy (the first number), the relative energy with zero-point correction

(the second number), and the relative Gibbs free energy at 190 K (the third number) computed at B3LYP/6-31+G* (in kcal/mol).

Table 4.1 Number of $H^+M_mW_n$ ($m + n = 5$ and 6) isomers calculated in this work. They are grouped into different morphologies: L, T, C, Ct, and bC structures.

$m + n = 5$						$m + n = 6$					
m	L	T	C	Ct	Total	L	T	C	Ct	bC	Total
0	1	1	2	3	7	1	3	1	7	6	18
1	3	3	8	11	25	6	8	4	30	26	74
2	4	4	10	16	34	5	16	3	41	37	102
3	4	3	12	11	30	10	14	6	51	43	124
4	3	1	8	6	18	15	8	9	38	40	110
5	1	0	2	3	6	6	2	4	16	15	43
6						1	0	1	2	2	6

The relative energies of the most stable isomers in $H^+M_mW_n$ ($m + n = 6$) are given in Figure 4.3. The isomer structure types are categorized with the same indexes as those for H^+W_6 in Figure 4.2. The close resemblance of energetic trends among mixed clusters and H^+W_6 (except for isomers in group (b)) is in line with the expectation that methyl groups only play a secondary role in determining the relative stability. As shown on the right-hand side of Figure 4.3, isomers of H^+W_6 in group (b) have higher relative energy, but the corresponding isomers of $H^+M_mW_n$ become comparable in energy with those isomers in group (a). That is due to the strong preference for the full solvation of the ion core moiety. In other words, when the free hydrogen atom of a H_3O^+ ion core is replaced by a methyl group, the ion core becomes a fully solvated $MeOH_2^+$ and the relative energy of the mixed clusters remarkably decreases. An interesting zigzag behavior of relative energy with respect to the isomer structure types is shown in Figure 4.3. This is due to that, with the stepwise replacement of water by methanol, more “compact” structures are preferred. No. 7, 9, and 11 are all T structures, which are more “open” than No. 6, 8, and 10 (Ct and bC). Therefore, the energy of T structure (NO. 7, 9 and 11) of $H^+M_mW_n$ will be much higher than that of compact structure (NO. 6, 8, and 10).

Figure 4.3 Relative energy of $H^+M_mW_n$ ($m + n = 6$). Indexes in the abscissa are the isomer structure types defined in Figure 4.2. The energy of the most stable isomer in each structure type is shown (see text). The structures are grouped in (a) and (b) according to the categorization in Figure 4.2.

4.3.2 Stabilities of different morphologies

In the work by Wu et al. on the $m + n = 4$ clusters, stabilities of different isomers were compared by checking their relative potential and free energies. In the present work, instead of looking at individual isomers, we engaged the HSA method to show the averaged properties of the five morphologies at different temperatures by taking account of all the calculated isomers. It is clearly demonstrated in Figure 4.4 that the dominant morphology is very sensitive to the temperature and mixing ratio of the two components. L, T, C, and Ct take turns to be the main player while only bC is left out with nearly zero population. This notion is consistent with the previous work on the water-rich and methanol-rich clusters.⁵ In the following, we will discuss how the population of each morphology changes on temperature, mixing ratio and cluster size.

Figure 4.4 Temperature-dependent population of L, T, C, Ct, and bC structures in the $H^+M_mW_n$ ($m + n = 5$ and 6).

Reading the subfigures of Figure 4.4 along the temperature axes, it is clear that most of the species we considered here, except the very water-rich clusters (H^+W_5 ,

$H^+M_1W_4$, and H^+W_6), go through a “phase transition” at ~ 150 K. At low temperature ($T < 150$ K), cyclic species are preferred and C and Ct have very high populations for $m + n = 5$ and 6, respectively. On the other hand, L and T are dominant in the high temperature region ($T > 150$ K), except for H^+M_m , which does not have T structures because of the strong preference for the two-coordination of the ion core. Chang et al. Carried out IR spectroscopy of H^+M_5 , and they showed that the phase transition of the structure from L to C occurs in the range of 200 K.⁴⁰ This is in good agreement with our calculated results.

When we examine the subfigures from top to bottom, we find T structures gradually give ways to L structures as the concentration of methanol increases and eventually T structures disappear in H^+M_m . This change of morphology is associated with switching of the ion-core and we will elaborate in the next section.

In the low temperature region, the major population of C in $m + n = 5$ is taken over by Ct in $m + n = 6$. This is due to the fact that the five-membered ring is more stable than the four- and six-membered ring. In the high temperature region, T becomes more favorable than L as the cluster size increases from 5 to 6, and the “phase transition” temperatures is also higher in the larger clusters. These size-dependent properties are consistent with our previous work for $H^+M_mW_1$.¹⁸

4.3.3 Population of different ion core

The preference of proton location in $H^+M_mW_n$ has been mainly studied in both extreme ends, $m \ll n$ (water rich clusters) and $m \gg n$ (methanol rich clusters), except the small-sized clusters ($m + n = 4$).^{5,23,32,41-43} It is generally agreed that small-sized clusters prefer the methanol ion core and the proton will switch to the water ion core as the cluster size increases. In this work, we will analyze the interplay of

water and methanol ion cores in response to the change in temperature, mixing ratio of two components, and cluster size.

In Figure 4.5, green dash and pink solid lines represent the population of the methanol and water ion cores, respectively. It is clear that thermal energy plays an important role. At low T (< 150 K), the preference of ion core types is very clear. $H^+M_1W_4$ and $H^+M_1W_5$ prefer the water ion core due to the rich water molecules, and the others prefer methanol ion core. At high T (> 150 K), both kinds of ion core coexist. In particular, we should note that the change of dominating species is not monotonous as the temperature increases. Our guess is that the change in the ion core is driven by the morphology changes. As shown in our previous study, the preferential ion core shows clear correlation with the morphology of mixed cluster. This is because the full solvation of the ion core induces a strong preference of overall hydrogen bond structures of clusters. For example, in $H^+M_5W_1$, the rising of the population of the water ion core at about 150 K coincides with the increase of T structures that favor the water ion core, and as temperature continues to increase, L structures (with the exclusive methanol ion core) kick in, forcing the population of the water ion core to decrease at ~ 300 K.

Regarding the mixing ratio dependence, there is a sudden switch with the addition of the second methanol. Beyond this change, there is only gradual enhancement of the methanol ion core as the concentration of methanol increases. By comparing left ($m + n = 5$) and right ($m + n = 6$) columns, one would notice the preference of the water ion core as the cluster size increases. This notion is consistent with our previous study in methanol-rich mixed clusters that the water ion core is preferred at larger cluster sizes.¹⁸ For example, in $H^+M_5W_1$, the water

ion core still keeps noticeable presence though methanol is the predominant component in the cluster.

Figure 4.5 Temperature-dependent population of $MeOH_2^+$ and H_3O^+ ion cores in $H^+M_mW_n$ ($m + n = 5$ and 6).

4.3.4 IR spectrum in the free OH region

IR spectral simulation of the $H^+M_mW_n$ clusters was performed with the HSA approach, and the calculated spectra are directly compared with experimental

spectra. In this study, we focus on the free OH stretching vibrational region (3600–3800 cm^{-1}). This is because the free OH stretch frequency is a sensitive probe of hydrogen bond coordination numbers of sites of interest, and analyses of the free OH region have been most informative to elucidate hydrogen bond structures of protonated water and methanol clusters.

Figure 4.6 Observed (water-loss channel) and simulated IR spectra of $H^+M_mW_n$ ($m + n = 5$ and 6) at 190 K in the free OH stretch region. The simulated spectra are taken from the average over all isomers by Q-HSA (red dash). The experimental spectra are represented by black solid lines, and the simulated spectra are by red broken line. The Observed IR spectra are taken from ref 44.

To facilitate comparison with experiments, the calculated harmonic frequencies have been scaled by 0.973, which is determined to reproduce the free OH-stretch band in neat and protonated water clusters.¹⁹ From the HSA approach, the statistical weights of the various isomers are estimated using their energies and vibrational frequencies. The stick spectra are converted into the continuous spectra by convolution with a Lorentzian function of 10 cm^{-1} full width at half-maximum. The averaged spectrum over all the isomers is plotted in Figure 4.6.

Figure 4.6 shows the comparison between the experimental and simulated IR spectra of $H^+M_mW_n$ ($m + n = 5$ and 6) in the free OH stretch region. In the experimental spectra (black lines), all the observed bands are reasonably assigned to four different bands. Bands I and IV originate from single acceptor (A) sites of water, which have the symmetric and asymmetric OH stretch modes similar to those of a bare water molecule. The free OH band of A sites of methanol is labeled as band II. In band II, we can see that the observed spectra exist the splitting. This indicates the possibility that band II is not only from free OH of A sites of methanol but the other free OH, like AA water, AA methanol and AAD water. Band III is assigned to the free OH stretch in single acceptor–single donor (AD) sites of water. Bands I–IV are highlighted by red, green, blue, and pink markers, respectively, in the figure. The appearance of these four different bands in the free OH stretch region is well reproduced by the simulation. But a few noticeable discrepancies are still seen on the band positions: (i) The frequency of the symmetric band of the A water site is calculated too low and that of the asymmetric band is too high. This seems to suggest the DFT (B3LYP/6-31+G*) calculation overestimates the coupling between the two free OH oscillators in the

A water site. (ii) The position of band II (the free OH of methanol in the A site) is off by about $7\text{--}8\text{ cm}^{-1}$. A new scaling factor is needed if we want to get better agreement with experiment.

The main features in the observed spectra of $m = 0\text{--}3$ are attributed to the A and AD waters. The A waters locate at terminals of one-dimensional H-bond chains, and they are characteristic to the L and T morphologies. The relative intensities of the A and AD sites clearly demonstrate that such morphologies with the chain terminals are preferred at the experimental “temperature” ($\sim 190\text{ K}$). This is consistent with the calculated relative population that the “open” morphologies become dominant above $\sim 150\text{ K}$, as shown in Figure 4.4. The simulated spectra also clearly reflect this trend, but the intensity of band IV is rather overestimated. With the size change from $m + n = 5$ to 6, the enhancement of the AD water bands is seen in both the observed and simulated spectra. This would arise from the increasing chain length as the cluster size increases.

In $m \geq 4$, the free OH stretch bands of the A and AD water diminish while those of the A methanol become strong. This convergence of the spectral features obviously comes from the increase of the methanol concentration. The appearance of the A site methanol is consistent with the major contribution of L and T at 190 K . It should be, however, noted that free OH does not exist for AD sites of methanol, and the ratio between the A and AD sites of methanol cannot be estimated from the spectra.

The spectral simulation qualitatively reproduces the size and mixing ratio dependence of the observed spectra, and this demonstrates the justification of the HSA approach to interpret observed spectra of clusters at finite temperature. Some additional factors should be considered to improve the agreement between the

experimental and simulated spectra: (i) There is ambiguity in the temperature of the observed clusters, as was described above. (ii) Only the water-loss channel is involved to measure the experimental spectra. For $H^+M_mW_n$ at $m + n = 4$, Wu et al. have shown that the methanol OH band is relatively enhanced by monitoring the methanol-loss channel.²³ In $m + n = 5$ and 6, the yield of the methanol loss is, however, very small (less than $\sim 10\%$). Correction for the contribution of this channel would not be essential for comparison with the present simulation because the HSA approach averages the statistically weighted contribution of all the isomers. (iii) Anharmonicity of the free OH bond is the origin of the band broadening in the observed spectra, and the magnitude of the broadening in each band may change its relative intensity. While thermal population to vibrationally excited levels is involved in the present simulation, the band broadening due to the anharmonicity is not counted.

4.4 Conclusion

An effective theoretical approach was developed to tackle the complexity of $H^+M_mW_n$ ($m + n = 5$ and 6). Basin-hopping method with the OSS2 potential was used to search a diverse set of structural isomers of the H^+W_n clusters, and stable isomers of $H^+M_mW_n$ can be systematically derived by substituting free dangling hydrogen atoms with methyl groups. These structures were reoptimized with DFT methods and vibrational normal modes were calculated for a better description of energy landscape at the first-principles level. The existence of hundreds of energetically competitive local minima complicates the theoretical analysis, and we therefore engaged harmonic superposition approximation to calculate physical properties of the mixed clusters at finite temperature. With the above-mentioned

theoretical scheme, we further analyzed the concentration and temperature dependence of the morphology development and the switch of ion-core between water and methanol. While most of the “predictions” cannot be verified directly with experimental means, we hope our work can simulate further investigations on the mixed cluster and lead to a better understanding for mixed clusters which can have numerous isomers.

4.5 References

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Chapter 5

Blue shifts in the IR spectra induced by mixed solvation in

5.1 Introduction

When a hydrogen bond (HB) forms between two molecules, the redistribution of electrons changes the ability for further HB formation. This electron redistribution thus results in both the cooperativity and the anticooperativity in HB networks. The molecule donating a proton has increased electron density in its lone pair orbitals. This encourages proton acceptance but discourages further donation. On the other hand, the proton-accepting molecule has reduced electron density centered on the proton and remaining lone pair orbitals, which encourages further proton donation but discourages further acceptance.

Although the concept of cooperativity is well established and widely used,^{1,2} the concept of anticooperativity seems to be much less studied. Scheme 5.1 gives descriptions of the anticooperative effect in protonated methanol–water mixed clusters. An arrow indicates the HB direction from the proton donor to the acceptor. The open symbols ($\diamond$ and $\circ$) represent water and methanol molecules, respectively, and the closed symbols ($\blacklozenge$ and $\bullet$) represent the corresponding protonated water and methanol sites, respectively. In the typical anticooperative effect, formation of one more HB reduces the strength of others (Scheme 5.1a). When a HB is newly formed, electron

density is transferred to the proton-donating molecule. This makes the donating molecule a poorer proton donor for subsequent HBs.³⁻⁶ Thus, when a molecule acts as a multiple proton donor, individual HB strength decreases as solvent molecules are successively added. Another kind of anticooperativity can be caused by stepwise substitution in mixed solvation clusters, as shown in Scheme 5.1b. When a solvent molecule is replaced by another molecule with larger proton affinity, the strength of all other HBs decreases. In this work, we study this type of anticooperativity for the first time by successive substitution in the protonated methanol–water clusters. Since the proton affinity of methanol (180 kcal/mol) is higher than that of water (165 kcal/mol),⁷ on replacing water molecules in the mixed clusters by methanol step by step a decrease of the strength of other HBs is expected.

Scheme 5.1 Concept of the anticooperativity^a

Anticooperative effect

^a(a) Successive solvation by a single species. (b) Successive substitution in a two-component system. In both the schemes, the oxygen atoms in water and methanol are represented by an open diamond and an open circle, respectively, and methyl groups and hydrogen atoms are omitted in the representation. The oxygen atoms of the protonated water and methanol sites are represented by a closed diamond and a closed circle, respectively. An arrow indicates the hydrogen bond forming between two species. The direction of the arrow shows the donor–acceptor relation in the hydrogen bond.

Methanol–water mixtures are widely used in studies of chemical and biological processes and have attracted much attention.⁸⁻¹⁵ In view of the preceding description, attention is merited to the properties of protonated mixed clusters, $\text{H}^+(\text{CH}_3\text{OH})_m(\text{H}_2\text{O})_n$ (hereafter abbreviated to $\text{H}^+\text{M}_m\text{W}_n$). The protonation is expected to enhance the magnitude of the charge transfer associated with HB formation and result in more significant anticooperativity. Furthermore, the charge of the excess proton enables us to select the size and component of the clusters with mass spectrometric techniques. For $\text{H}^+\text{M}_m\text{W}_n$, the cluster size effect on the HB network has been well studied by fixing the size of one component while changing the total cluster size.^{9,11,16-19} Less attention has been paid to changing of the mixing ratio. Meot-Ner found the trend of the increasing stability with the methanol concentration in the thermochemical experiment.²⁰ Wu et al. studied the HB structure and proton location for $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 4$) by infrared (IR) spectroscopy combined with quantum chemical calculations, and they found a switch from the closed-shell H_3O^+ -centered form to the CH_3OH_2^+ -centered chain form as the number of the methanol molecules increases.¹⁵ Our previous IR and theoretical study on $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 5$ and 6) also showed that both the preferences for the morphology and the protonated site change gradually depending on the mixing ratio.²¹ The IR spectra in the free OH stretch region were studied in that work, because the free OH frequency is a sensitive probe of the HB coordination number. However, no attention was paid to the hydrogen-bonded (H-bonded) OH stretch region.

In this work, we examine the role of the anticooperativity in the evolution of HB properties in response to the change of the component ratio in the $\text{H}^+\text{M}_m\text{W}_n$ mixed

clusters. We choose total cluster sizes ($m + n$) of 5 and 6 as these sizes refer to the second solvation shell formation, where both the ionic HB and the neutral HB exist. We focus on the HB strength and IR spectra in the hydrogen-bonded OH stretch region, which should be useful in elucidating HB properties in liquid water–methanol mixture.

5.2 Methodology

Local minimum structures of H^+W_n clusters were collected with a multiscale method by combining the basin-hopping method and an empirical model.^{22,23} The initial structures of $\text{H}^+\text{M}_m\text{W}_n$ clusters were obtained from H^+W_{m+n} clusters by replacement of hydrogen atoms of free OH groups with methyl groups.²¹ After archiving a sufficient number of local minimum structures, density functional theory (DFT) calculations were carried out using the Gaussian 03 program package.²⁴ Geometries were optimized without any symmetry constraints at the B3LYP level of computations with the 6-31+G* basis set. For each energy-optimized structure, the frequency calculation was performed. Thermally averaged IR spectra are simulated by using the quantum harmonic superposition approximation theory (Q-HSA) method, in which contributions from all possible structures are summed up according to their statistical weight. These averaged IR spectra can be directly compared with the experimental spectra, which would be also composed of contributions from isomers. The details of these methods have been reported in our recent work.^{21,25}

5.3 Results and discussion

The details of calculated structures and relative stabilities of $\text{H}^+\text{M}_m\text{W}_n$ clusters have already been discussed in our previous work²¹ and will not be present here. The remainder of this section is structured as follows. In section 5.3.1, experimental IR spectra are shown, and in section 5.3.2, their qualitative interpretation in terms of the anticooperativity is proposed and discussed. In sections 5.3.3 and 5.3.4, calculated IR spectra and charge transfer in some selected isomers are analyzed quantitatively to support the interpretation. In section 5.3.5, the averaged IR spectra by the Q-HSA method are compared with the experimental spectra.

5.3.1 Observed IR spectra

Figure 5.1 shows the observed IR spectra of $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 5$ and 6) in the H-bonded OH stretch region taken from ref 26. All spectra except H^+M_5 and H^+M_6 were measured by monitoring fragmentation to the $\text{H}^+\text{M}_m\text{W}_{n-1}$ (water-loss) channel. The spectra of H^+M_5 and H^+M_6 were recorded by monitoring the methanol-loss channel. These sizes of the clusters ($m + n = 5$ and 6) are large enough to form the second (or third) solvation shell to the protonated site. The two bands in the higher frequency region (above 3200 cm^{-1}) in the spectra are attributed to H-bonded OH stretches in the outer (second or third) shell, and the broader absorptions below 3200 cm^{-1} are attributed to those of the inner (first^t or second) shell.

For $\text{H}^+\text{M}_m\text{W}_n$, the stepwise replacement of water by methanol is exothermic in every step, as shown in the mass spectrometric measurements by Meot-Ner²⁰ (hereafter stepwise replacement in this paper is defined as that from water to methanol, as default). This means that the total stability of the cluster increases in the change from H^+W_{m+n} to H^+M_{m+n} . In the observed spectra, however, two H-bonded OH stretch

bands above 3200 cm^{-1} show clear blue shifts with increasing mixing ratio of methanol to water. The blue shifts demonstrate that these HBs become weaker in every replacement step, and on the first sight, it seems to be in conflict with the larger stability of the methanol-rich clusters.

Figure 5.1 Observed IR spectra of $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 5$ and 6) taken from ref. 26. These IR spectra show two high-frequency shifting bands with increase of the methanol concentration in the clusters. The color stripes are made guide the eye.

5.3.2 Qualitative interpretation of the observed IR spectra

Proton-accepting abilities of methanol and water molecules. To interpret the spectral behavior described above, we first examine the assignments of the two high-frequency shifting bands. $\text{H}^+\text{M}_m\text{W}_n$ is a mixed cluster in which both the components

can act as a proton donor (D) and a proton acceptor (A) of HBs. In the cluster, therefore, four types of D–A combinations can be considered.

Figure 5.2 gives the binding energies of H-bonded dimers involving water (W) and methanol (M) evaluated by Fileti et al. at various calculation levels.²⁷ Several different methods were used to check the calculation error, and the results are quite consistent. By replotting their data, we can see that the dimers with methanol as the acceptor have higher binding energies (~ 1 kcal/mol) than those with water as the acceptor. In addition, the binding energies are almost irrespective of the choice of the donor, with a small difference of less than 0.1 kcal/mol. The absolute value may have some error of ab initio calculation, but an interesting trend is clearly seen that the energy difference is much larger between dimers with different accepters than those with different donors. Because of the electron transfer from a proton acceptor to a proton donor on the formation of a HB, the methyl group is electron withdrawing in the donor site and electron releasing in the acceptor site, both making a positive contribution to the HB.²⁸ However, the contribution of the methyl group in the acceptor site is more significant than that in the donor site due to the positive inductive effect (electron releasing) of the methyl group, and it affects the property of the binding energies of methanol–water mixed clusters.^{29,30}

The calculations of the neutral dimers by Fileti et al. strongly suggest that the HB strength in the methanol–water mixed system is governed by the choice of the acceptor site. Therefore, two types of H-bonded OH stretch bands are expected for $H^+M_mW_n$: one is for HBs in which methanol is the acceptor, and another is for those where water in the acceptor site. These two types of H-bonded OH bands in the

outermost solvation shell can be assigned to the two bands in the experimental spectra at around $3200\text{--}3300\text{ cm}^{-1}$ and $3300\text{--}3400\text{ cm}^{-1}$, respectively. These assignments are consistent with the observation that the former band is absent in H^+W_6 and becomes stronger on increasing the ratio of methanol, while the latter becomes weaker with replacement of water by methanol and is totally missing in H^+M_6 . Further confirmation of these assignments on the basis of DFT calculations will be given in section 5.3.3.

Figure 5.2 Binding energies (kcal/mol) of heterodimers involving water (W) and methanol (M) calculated by various levels of theory. All calculation data are taken from Ref. 27. The acronym D→A stands for the proton donor and acceptor. It is seen that dimers with methanol as the acceptor have higher binding energies (~ 1 kcal/mol) than those with water as the acceptor regardless of the choice of the donor site.

Blue shifts of the H-bonded OH stretch bands. Both bands above 3200 cm^{-1} show the blue shifts with an increase of the methanol concentration, as shown in Figure 5.1. This means HBs of both the methanol and the water acceptors become weaker with replacement of water to methanol. As discussed above, a HB of the methanol acceptor is stronger than that of the water acceptor. Then, the observed blue

shifts can be explained by the second type of anticooperativity, as described in the Introduction. Enhancement of one HB by replacement sacrifices the strength of all other HBs, resulting in overall high-frequency shifting. Though almost all bands show the blue shifts with replacement, the increase of the total stability is achieved by an increase of the number of stronger HBs with the methanol acceptor. This anticooperative effect is quantitatively examined by simulations of IR spectra and calculations of natural bond orbital (NBO) charge in $H^+M_mW_n$ ($m + n = 5$ and 6), as described in the following sections.

5.3.3 Calculated IR spectra

All local minima of $H^+M_mW_n$ ($m + n = 5$ and 6) can be grouped into five morphological groups, linear (L), tree (T), cyclic (C), cyclic with a tail (Ct), and bicyclic (bC).²¹ Our previous studies have confirmed that H^+M_m does not have T isomers³¹ and bC can exist only for $m + n = 6$.²¹ While there are hundreds of isomers for the clusters for $m + n = 5$ and 6 , in this section, we focus on the most stable isomers of T and L to study the nature of H-bonded OH stretching vibrational modes, since the population predicted by Q-HSA shows that T and L isomers are dominant over other isomers at the experimental temperature (~ 190 K).²¹ We should note that individual isomers cannot quantitatively represent an ensemble average of isomers. Therefore, in part 5.3.5, we will offer quantitative and direct comparisons between the experimental IR spectra and the first-principles spectra by Q-HSA.

Figures 5.3 and 5.4 show the simulated IR spectra of $H^+M_mW_n$ ($m + n = 5$ and 6), respectively, by changing the water–methanol mixing ratio. The stick spectrum is converted into the continuous spectrum by convoluting with the Lorentzian function

of 50 cm^{-1} full width at half-maximum. The schematic representation of each structure is also shown. The vibration modes are color coded according to the solvation shell and the acceptor molecule of HB. For every mode, the high-frequency shift with increasing methanol concentration was found. This trend was also found in the other morphologies, such as C and Ct.

Figure 5.3 Calculated vibrational spectra of the most stable isomers in the T and L morphologies of $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 5$) at the B3LYP/6-31+G* level. The definitions of the symbolic representation of structures can be found in Scheme 5.1. The vibrational bands are color coded according to the solvation shell and the acceptor molecule shown in the schematic representation of the structures. For T, the region below 2800 cm^{-1} is also presented to give a complete picture. In the second solvation shell (above 3200 cm^{-1}), the band coded green and blue are attributed to the stretch of OH donating to the water and methanol molecules, respectively. In the first solvation shell (below 3200 cm^{-1}), the band coded red and pink are attributed to the stretch of OH donating to the water and methanol molecule, respectively.

In Figures 5.3 and 5.4, the bands coded red and pink below 3200 cm^{-1} are attributed to the H-bonded OH stretches in the inner (first or second) solvation shell, which donate their proton to water and methanol, respectively. The H-bonded OH stretch bands in the outer (second or third) solvation shell appear above 3200 cm^{-1} , and the bands coded by green and blue are attributed to OH donating the proton to water and methanol, respectively.

Figure 5.4 Calculated vibrational spectra of the most stable isomers in the T and L morphologies of $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 6$) at the B3LYP/6-31+G* level. The vibrational bands are color coded according to the solvation shell and acceptor molecule shown in the schematic representation of the structures. In the outermost (second or third) solvation shell (above 3200 cm^{-1}), the band coded green and blue are attributed to the

stretch of OH donating to the water and methanol molecules, respectively. In the inner (first or second) solvation shell (below 3200 cm^{-1}), the band coded red and pink are attributed to the stretch of OH donating to the water and methanol molecules, respectively.

Replacement of water by methanol strengthens one of the HBs in which the replaced molecule acts as the acceptor. At the same time, this methanol molecule attracts more positive charge from the protonated site, which will decrease the strength of other HBs. To confirm this notion, we examine the spectra of the T isomers in Figure 5.3, where the region below 2800 cm^{-1} is also presented to give a complete picture. The interactions among the three A molecules are anticooperative, but the interaction of DDD-AD-A is cooperative. The formation of AD-A HB enhanced the DDD-AD interaction, so that the H-Bonded OH of AD has a lower frequency than that of A molecule in the first shell. From H^+W_5 to $\text{H}^+\text{M}_1\text{W}_4$, one water molecule of the first solvation shell is replaced by methanol, then one of the vibration modes jumps from $\sim 3000\text{ cm}^{-1}$ to below 2800 cm^{-1} , as indicated by the arrow. With this jump, all other H-bonded OH modes show blue shifts simultaneously. The similar jump and shifts occur with the substitution from $\text{H}^+\text{M}_1\text{W}_4$ to $\text{H}^+\text{M}_2\text{W}_3$. From $\text{H}^+\text{M}_2\text{W}_3$ to $\text{H}^+\text{M}_3\text{W}_2$, the acceptor–donor (AD) water in the first solvation shell is replaced by methanol, which makes the corresponding mode at $\sim 2500\text{ cm}^{-1}$ jump to a lower frequency (below 2200 cm^{-1} , not shown). Replacement of water by methanol also affects the second solvation shell. In this respect, the figure shows that from $\text{H}^+\text{M}_3\text{W}_2$ to $\text{H}^+\text{M}_4\text{W}_1$ the enhancement of the HB in the second solvation shell weakens the HBs in the first shell.

The same phenomena are also seen in the spectra of the L isomer for $m + n = 5$ and L and T isomers of $m + n = 6$, as depicted in Figures 5.3 and 5.4, respectively. It is

clearly shown that by stepwise replacement one mode with the water acceptor jumps to that with the methanol acceptor, and it simultaneously causes the blue shifts of all other H-bonded OH stretch bands. In Figure 5.4, the band near 3040 cm^{-1} which associated with the second shell methanol is red shifted to $\sim 3000\text{ cm}^{-1}$. This is due to the slightly change of the charge position in the L structure. Proton prefers to stay at the center of the L structure. When the water in the 3rd shell is replaced by methanol, the accept ability increase in this side, so the proton will move to this side. Thus the second shell HB will be stronger due to closer to the ion core.

5.3.4 Charge transfer

Figure 5.5 Total NBO charge transferred from the ion-core (a1 and b1) and charge distribution (a2 and b2) of the most stable T and L isomers in $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 5$), respectively. In a2 and b2, each symbol represents the charge of each site, as shown as an insert in a1 and b1 respectively. The points in lower-left corner shaded by gray color present the charges of water molecules, and those in the white area present the charges of methanol molecules. The arrow connecting the points means the replacement of the solvent species from water to methanol.

Previous studies have shown that the influence of the proton extends up to four molecules either side of the proton. The positive charge of proton will diffuse and delocalize among the whole cluster. The molecule near the proton will get more positive charge and the molecule far away from the proton will get less positive charge. The anticooperative effect can be understood by analyzing the magnitude of the charge transfer with HB formation. A net transfer of charge occurs between the donor and the acceptor molecules upon formation of a HB. In protonated clusters, the positive charge partially transferred from the proton to the solvated molecules through partial donation of negative charges from the proton-accepting sites. Methanol has a high capability to attract positive charges rather than water. Accordingly, when methanol substitutes water, the attraction of positive charges increases, causing a redistribution of charges with a diminution of the positive charges placed in other sites. The magnitude of charge transfer, then, is an indication of enhancement and reduction of HBs. To estimate the anticooperativity in the stepwise replacement, natural bond orbital (NBO) analysis was performed for $H^+M_mW_n$ ($m + n = 5$ and 6) and is summarized in Figures 5.5 and 5.6.

Figure 5.5a1 and 5.5b1 shows the magnitude of the total charge transfer from the protonated site to solvent molecules in the T and L isomers for $m + n = 5$, respectively. It is clearly seen that the charge transfer to the solvent molecules increases with increasing methanol concentration. Because of the coordination nature of the protonated site, all T isomers have the water ion core while all the L isomers have the methanol ion core. From Figure 5.5a1 and 5.5b1, it is also seen that the total charge

transferred from the ion core is higher in T than in L, which suggests that H_3O^+ is a better proton donor than CH_3OH_2^+ . This behavior can be explained because the methyl group attracts a part of the positive charge in protonated methanol and makes it release less charge to the solvent molecules.

Figure 5.5a2 and 5.5b2 shows the charge distribution in the T and L isomers for $m + n = 5$. Each symbol represents the charge of each site of the clusters as shown on the top of the figures. The points in the gray area show the charges of the water sites, and those in the white area are of the methanol sites. When a water molecule is replaced by methanol, the amount of charge transferred to that site is remarkably increased (indicated by an arrow) and, simultaneously, the charge transferred to all other molecules decreases (shown by dashed lines). This decrease of the charge transfer in the other molecules is reflected in the blue shifts of the H-bonded OH stretch bands as shown in Figure 5.3. All outermost molecules in the HB network (second solvation shell) receive much less charge (0.040–0.055) than the molecules in the first solvation shell, and the magnitude of the charge transfer in the second shell is very similar between T and L in spite of the difference of the morphology. This indicates that the partial positive charge on the outermost molecule is almost independent of the morphology of the HB network.³² On the other hand, the charges on the inner solvation shell are quite different for T and L.

In Figure 5.6, similar results are found for $m + n = 6$. In Figure 5.6b1, the sudden increase of the magnitude of the total charge transferred from the ion core at $m = 2$ is due to the existence of the Zundel cations where the proton is shared between the two methanol molecules in the center of the linear chain.³² When we compare Figures

5.5(a1-b1) and 5.6(a1-b1), we find the total charge transferred is ~ 0.1 higher when $m + n = 6$ than that when $m + n = 5$, which is due that there are five solvent molecules when $m + n = 6$ but only four when $m + n = 5$. It is also seen that the charge transferred to the outermost solvation shell is less when $m + n = 6$ than that when $m + n = 5$ (Figures 5.5(a2-b2) and 5.6(a2-b2)), which is consistent with the observed IR spectra shown in Figure 5.1. The H-bonded OH stretch frequencies of the outermost shell ($3200\text{--}3400\text{ cm}^{-1}$) are higher when $m + n = 6$ in comparison with those when $m + n = 5$.

Figure 5.6 Total NBO charge transferred from the ion-core (a1 and b1) and charge distribution (a2 and b2) of the most stable T and L isomers in $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 6$), respectively. In a2 and b2, each symbol represents the charge of each site, as shown as an insert in a1 and b1 respectively. The points in lower-left corner shaded by gray color present the charges of water molecules, and those in the white area present the

charges of methanol molecules. The arrow connecting the points means the replacement of the solvent species from water to methanol.

5.3.5 Simulated spectra from Q-HSA and comparison with the observed IR spectra

As shown in part 5.3.3, the IR spectra of selected structures show high-frequency shifting bands due to successive substitution of the water sites by methanol. However, for systems containing a large number of possible isomers with small energetic differences which are compatible with thermal energy, a statistical procedure has to be incorporated to yield a quantitative picture. Therefore, in this part, we engage the harmonic superposition approximation (HSA) to simulate “averaged” IR spectra, which can be compared with the experimental spectra directly.

From the results of DFT calculations, the IR absorption intensity $I_a(\omega)$ of each isomer a is obtained. Then, the averaged intensity of the whole system $I_{\text{total}}(\omega, T)$ at temperature T is calculated as the weighted sum of $I_a(\omega)$ with the canonical probability $P_a(T)$ of isomer a derived from the thermodynamic simulations

$$I_{\text{total}}(\omega, T) = \sum_a I_a(\omega) P_a(\omega, T),$$

where

$$P_a(T) = \frac{\sum_{a \in A} Z_a(\beta)}{Z(\beta)}.$$

The total partition function $Z(\beta)$ of an N -atom system at temperature T is given by $Z(\beta) = \sum_a n_a Z_a(\beta) \cdot Z_a(\beta)$, under quantum HSA, is given by

$$Z_a^Q(\beta) = \exp(-\beta E_a) \prod_a \frac{\exp(-\beta \hbar \omega_{af} / 2)}{1 - \exp(-\beta \hbar \omega_{af})},$$

where the “inverse temperature” is given by $\beta \equiv \frac{1}{k_B T}$, with k_B denoting the Boltzmann’s constant.

The present study is focused on the H-bonded OH stretching vibrational region (3000–3600 cm^{-1}) because the free OH stretch region has been reported in our previous work.²¹ From the HSA approach, the statistical weights of the various isomers are evaluated using their energies and vibrational frequencies. In the calculations, the temperature of the clusters is set to be 190 K, which was discussed in our previous paper.²¹ The stick spectra are converted into the continuous spectra by convolution with a Lorentzian function of 50 cm^{-1} full width at half-maximum.

The averaged spectra over all isomers and the experimental spectra of $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 5$ and 6) are plotted in Figure 5.7. Also, in the averaged spectra, two high-frequency shifting bands are found, and it clearly demonstrates the anticooperativity of the mixed clusters. The appearance of the high-frequency shifting bands agrees well with the computational prediction based on the selected T and L isomers. Though the T and L morphologies are estimated to be dominant in the ensemble, we should note that the anticooperativity is not limited to some selected structures but a common property for all isomers of $\text{H}^+\text{M}_m\text{W}_n$. The peak positions of the simulated and experimental spectra achieve good agreement. All observed bands are reasonably assigned to the bands according to the solvation shell and the acceptor. Above 3200 cm^{-1} are the OH vibrations of the outermost solvation shell. The bands labeled by the green line are due to the HBs with water acceptors, while the bands labeled by the blue line are due to the HBs with methanol acceptors. Below 3200 cm^{-1} are the OH stretch vibrations of the inner solvation shell. The bands labeled by the dark red line

are due to the HBs with water acceptors, while the bands by the pink line are due to the HBs with methanol acceptors.

The blue shift trend of the bands of the outermost HBs can be clearly seen. However, below 3200 cm^{-1} , the other two bands mixed together. These bands cannot be distinguished clearly in the experimental spectra, and much broadened absorption is seen in this region. Evaluation of the charge transfer allows to explain this band behavior. As shown in part 5.3.4, the magnitude of the charge transfer to the outermost molecule is small and the amount of transferred charge is almost irrespective of cluster structures. For the inner solvation shell, however, the isomer dependence of the HB strength is more remarkable and the H-bonded OH frequency shows larger differences among isomers. Overlap of the contribution of many isomers makes the bands due to the inner shell broadened.

Figure 5.7 Observed and simulated IR spectra of $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 5$ and 6) at 190 K in the hydrogen-bonded OH stretch region. The simulated spectra are taken from the average over all isomers by Q-HSA (red dashed line). The bands labeled by the green line are due to the HBs with water acceptors in the outermost solvation shell, while the bands labeled by the blue dashed line are due to the HBs with methanol acceptors. The bands labeled by the dark red color line are due to the HBs with water acceptors in the second outermost solvation, while the bands by the pink dashed line are due to the HBs with methanol-acceptors.

The H-bonded OH stretch band series attributed to the outermost solvation shell with water acceptors exists in all mixing ratios except for H^+M_m , which indicates that water molecules prefer the terminal site. Fujii et al. measured the relative fragment channel ratio, as shown in Table 5.1.²⁶ In the vibrational excitation at 3200 cm^{-1} , the dominant fragmentation channel is the loss of water. For both the $m + n = 5$ and 6 systems, the methanol-loss channel is almost negligible except the cases of neat protonated methanol. The similar preference of the water-loss channel has been reported for collision-induced dissociation measurements of the mixed clusters.^{10,33} If we assume that molecules in the terminal of the H-bonded chain are easier to evaporate with vibrational excitation, this observation supports the computational finding that water prefers the terminal site while methanol tends to be closer to the protonated site. The dominance of water loss even in $\text{H}^+\text{M}_4\text{W}_1$ and $\text{H}^+\text{M}_5\text{W}_1$, where at least one methanol molecule should be in the terminal position, also suggests a HB accepted by water is weaker than that by methanol, consistent with the HB energy evaluation.

Table 5.1 Relative fragment channel ratio in $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 5$ and 6) on the vibrational excitation at 3200 cm^{-1} measured by Fujii et al.²⁶ The ratio is shown in percent.

$\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 5$)

m	H ₂ O loss channel	MeOH loss channel
0	100	—
1	> 95	< 5
2	97	3
3	98	2
4	87	13
5	—	100

$\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 6$)

m	H ₂ O loss channel	MeOH loss channel
0	100	—
1	> 98	< 2
2	98	2
3	> 96	< 4
4	98	2
5	88	12
6	—	100

5.4 Summary

This study focused on the anticooperative effect in protonated methanol–water clusters by changing the mixing ratio of the two components. While the total hydrogen-bond energy increases with successive substitution from water to methanol, the observed vibrational frequencies of the hydrogen-bonded OH stretches show clear blue shifts. To interpret the physical meaning of these shifts, we examined the IR spectral behavior of the T and L isomers of $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 5$ and 6). Substitution of water by methanol reinforces one of the hydrogen bonds in which this methanol acts as the acceptor; thus, the total hydrogen-bond strength is enhanced. However, enhancement of one hydrogen bond simultaneously sacrifices all other hydrogen bonds because the methanol molecule attracts more charge from others. As a result, the individual hydrogen-bond strength shows a gentle decrease by successive substitutions. This is a new type of anticooperativity of hydrogen bonds in two-component systems. The magnitude of charge transfer from the protonated site to solvent molecules has also been examined to confirm the physical meaning of the anticooperative effect. The IR spectra averaged over the possible isomers have been

simulated by the quantum harmonic superposition approximation approach. The simulated spectra reproduce well the high-frequency shift trend of the hydrogen-bonded OH stretch bands, indicating that anticooperativity is a common property for all isomers of $H^+M_mW_n$. Actually, there exist many different interactions in the clusters, and both cooperative and anticooperative effects co-exist in the cluster. The optimized structure and the measured spectra illustrated the net effects not only due to anticooperative effects to explain the phenomena in the bonded stretching region.

5.5 References

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Chapter 6

Proton Location in $X-H^+-(CH_3OH)_m$ ($X = (CH_3)_3N$ and $(CH_3)_2SO$)

6.1 Introduction

Proton transfer in hydrogen-bond systems is an important reaction in many chemical and biological systems.¹⁻⁴ For multicomponents systems, the preference of protonated site has been the subject of extensive studies.⁵⁻¹⁰ Though the proton affinity in the gas phase is a useful index to infer the preference protonated site, recent gas-phase cluster studies have shown that proton migration can occur from the larger PA site to the smaller PA site with the development of stepwise solvation.^{7,8,11} For example, the proton affinity of H_2O and $(CH_3)_2O$ is 165 and 189 kcal/mol, respectively. The position of excess proton in protonated dimethyl ether–water clusters $H^+[(CH_3)_2O](H_2O)_n$ is a sensitive function of cluster size. One would expect that the proton to be taken by $(H_2O)_2$ since the PA (193.2 kcal/mol) of the water dimer is higher than that of $(CH_3)_2O$ by 4 kcal/mol. However, the proton is transferred to the water polymers at $n \geq 3$.⁶ To determine the proton switch point in multicomponent systems is an interesting question to address and deserves further examination.

The problem of developing an accurate molecular description of proton transfer in $X-H^+-(H_2O)_n$ lies in the difficulty of constructing so many isomers. In this work, this difficulty can be addressed by using methanol clusters. Methanol has the same

hydrogen-bonding capability as water, but with only one OH group, propagates intermolecular contacts in a simple linear rather than a more complex 3 D fashion. This simplification allows complete calculation of all possible structures.

Trimethylamine (TMA) and Dimethylsulfoxide (DMSO) are similar to $(CH_3)_2O$ which have no “acidic” hydrogen for extending the hydrogen-bonding network. They can only act as a proton acceptor but with much higher proton affinity of 227 and 215 kcal/mol, respectively. In this work, we systematically studied the $X-H^+-(MeOH)_m$ (hereafter abbreviated to $X-H^+-M_m$) ($X=(CH_3)_3N$ and $(CH_3)_2SO$) system to check the proton location as increasing cluster size. TMA and DMSO were chosen because of the differing proton affinities and can only as proton acceptor but not donor. We study the excess proton location in $X-H^+-M_m$ using a combination of experimental and theoretical methods. Significant features of IR spectra are found to tell the excess proton location.

6.2 Computational Methods

Geometries of $X-H^+-M_m$ were optimized at the B3LYP/6-31+G* level using the Gaussian 03 program package.¹² For each energy-optimized structure, the harmonic frequency calculation, calculations of zero-point energy, and calculations of the Gibbs free energy at 190 K were performed. All calculated harmonic frequencies are scaled by a factor 0.973, which is determined to reproduce the free OH-stretch band in neat and protonated clusters.¹³ The stick spectra are converted into the continuous spectra by convolution with a Lorentzian function of 10 cm^{-1} full width at half-maximum.

6.3 $[(CH_3)_3N]-H^+-M_m$

6.3.1 Possible morphologies

The basic morphology development process of H^+M_m was previously demonstrated, only five basic types (L, linear, C, cyclic, Ct, cyclic with a tail, bC1, first type of bicyclic, and bC2, second type of bicyclic) of morphologies can be constructed.¹⁴ TMA- H^+-M_m clusters are constructed by adding the TMA molecule to the free OH of H^+M_m clusters. Therefore, only structures with free OH (L, C, and Ct) can be used to construct new structures, which simplify the calculation.

Figure 6.1 shows the schematic representations of the basic morphologies of H^+M_m and TMA- H^+-M_m . The oxygen atom in methanol is represented by an open circle, and the methyl group and hydrogen atoms are omitted in the representation. The oxygen atom of the protonated site is represented by a closed circle. An arrow indicates a hydrogen bond that binds two oxygen atoms, and the direction of the arrow shows the donor-acceptor relation in the hydrogen bond. Figure 1a gives the schematic representation of L, C, and Ct morphologies of H^+M_m used to construct TMA- H^+-M_m . By adding TMA to the free OH of H^+M_m , two different types of structures can be obtained. The first type with not significant structural change by adding one TMA, and the proton will still stay on methanol site, as shown in Figure 1b. In the first type, the hydrogen bonding direction is same as that in H^+M_m , from the ion core to two direction first, and then (for C and Ct: run together to AAD and) to TMA at the end. Another type is with the proton staying on TMA site, as shown in Figure 1c. The hydrogen bonding direction change significantly, in C and Ct, starting from TMA to the

AAD, then go around the cyclic and finally go back to AAD again. Such difference of the structures with different ion core will be reflected in the IR spectra.

Figure 6.1 Schematic representations of the basic morphologies of H^+M_m and $\text{TMA-H}^+\text{-M}_m$. Definitions of the symbolic representation of hydrogen bonds and building block patterns of the hydrogen bond coordination (see text). The oxygen atom in methanol is represented by an open circle, and the methyl group and hydrogen atoms are omitted in the representation. The oxygen atom of the protonated site is represented by a closed circle. An arrow indicates a hydrogen bond that binds two oxygen atoms. The direction of the arrow shows the donor-acceptor relation in the hydrogen bond. (a) Morphologies of H^+M_m used to construct $\text{TMA-H}^+\text{-M}_m$. (b) Morphologies with the MeOH_2^+ ion core. (c) Morphologies only with the $\text{H}^+(\text{TMA})$ ion cores.

6.3.2 Relatively stabilities

L structures. Linear is the simplest and most basic form. For $n \leq 3$, L is the only possible structure. We first put the proton in the middle of the methanol chain, but the proton will transfer to TMA site during the optimization for $n \leq 5$. For $n \geq 6$, both the TMA ion core and methanol ion core can be found, but the energy of isomers with

TMA ion core is much lower with the energy difference larger than 6 kcal/mol. For L structure with proton on TMA site, these initial geometries were found to undergo reorganization during optimization, with formation of weak HB between methyl group of TMA and oxygen.

Cyclic Structures (C). For $n \geq 4$, we can add the TMA to the AA site of cyclic protonated methanol structures. Thus, the AA methanol molecule becomes AAD, and the proton will still stay on the methanol site. This indicated that adding TMA to cyclic $H^+(MeOH)_m$ will not change the overall morphology except for a small difference in the orientations of the free OH in the calculation. Then, we manually move the proton near to the TMA site by a slight movement of six protons and a rearrangement of covalent and hydrogen bonds, and perform optimization. We get another isomer, which is even more stable than the first type.

Cyclic with a tail (Ct). For $n \geq 4$, TMA molecule can be added to the tail A methanol molecule, which will become AD molecule then. Similar to the other morphologies, two different structures can be got, one with proton on methanol site, another with proton on TMA site.

The electronic potential energy (E_0), total energies (E_0+ZPE) and Gibbs free energy (G) at 190 K are evaluated for all stable structures. The energy evaluation was carried out at the BLYP/6-31+G* level with the standard harmonic approximation. For E_0 , E_0+ZPE and G , those of the minimum energy isomer in each cluster size (m) are set to zero. The relative values are shown in Table 6.1. The structures are separated into two groups, one with TMA ion core (left column), and another with methanol ion core. All the E_0 , E_0+ZPE , and G clearly show that the isomers with

TMA ion core are much more stable than those with methanol ion core. For example, the G has big energy difference 3-12 kcal/mol compared between the same morphology. The energy difference decreases as m increasing, which is because the increasing clusters PA. The energy difference among different morphologies is very small, which indicates that the coexistence of multiple morphologies is highly plausible.

Table 6.1 Calculated relative potential energies (E_0), relative energies at the zero vibrational level (E_0+ZPE), and relative Gibbs free energies (G_0) at 190 K for TMA- H^+-M_m at B3LYP/6-31+G*. (kcal/mol)

	Proton on TMA site			Proton on methanol site		
	E_0	E_0+ZPE	G_0	E_0	E_0+ZPE	G_0
2L	0.00	0.00	0.00	-	-	-
3L	0.00	0.00	0.00	-	-	-
4L	1.42	0.33	0.00	-	-	-
4C	0.00	0.00	1.66	13.91	11.29	12.86
5L	2.33	1.05	0.00	-	-	-
5C	0.00	0.00	1.26	11.43	7.93	8.64
5Ct	4.13	3.45	2.92	14.28	11.40	11.63
6L	4.46	3.31	1.33	17.12	12.25	8.71
6C	6.92	6.57	5.62	12.93	9.39	8.23
6Ct	0.00	0.00	0.00	13.34	9.79	8.44
7L	2.81	1.49	0.00	15.25	10.44	7.81
7C	0.00	0.00	1.46	10.59	6.63	6.45
7Ct	2.10	1.84	1.88	10.45	6.74	5.93
8L	1.53	1.04	0.54	13.86	9.64	7.11
8C	2.09	2.65	4.27	9.13	6.52	7.63
8Ct	0.00	0.00	0.00	8.87	5.88	5.66
9L	6.97	4.85	0.00	18.92	13.19	6.65
9C	0.00	0.00	0.40	14.49	9.98	7.69
9Ct	5.58	4.66	2.58	13.46	9.37	7.03

6.3.3 Vibrational spectra

Since the relative energies show that all the isomers with methanol ion core have higher energies, the spectra of them are not present in this paper and put in the supporting information. Figures 6.2, 6.3 and 6.4 show the simulated IR spectra in the range of 2000–3800 cm^{-1} for L, C, and Ct with proton on TMA site.

Figure 6.2 Simulated IR spectra of L TMA- H^+ - M_m ($m = 2-9$) with proton on TMA site.

Above 3600 cm^{-1} , the free OH stretch bands are expected only in L structures, and this is a unique spectral sign of the L structure. The absence of the free OH stretch band in C and Ct structure reflects that all the OH groups are hydrogen bonded in these structures.

Figure 6.3 Simulated IR spectra of C TMA- $\text{H}^+\text{-M}_m$ ($m = 4-9$) with proton on TMA site.

In the frequency range of $3000\text{--}3600\text{ cm}^{-1}$, strong bands due to hydrogen-bonded OH stretches are expected. In Figure 6.2, 6.3, and 6.4, we can see that all the OH

vibrations are located intensively in the range of $3100\sim3500\text{ cm}^{-1}$. This is because the proton is near to TMA site, and all the other HBs of methanol are far away from the proton. The positive charge has small influence on methanol hydrogen bonding strength, thus vibrational frequencies of all the hydrogen bonded OH have a small range.

Figure 6.4 Simulated IR spectra of Ct TMA- H^+-M_m ($m = 5-9$) with proton on TMA site.

The frequency in the range of $2000\sim3000\text{ cm}^{-1}$ belongs to the vibration stretches of ion hydrogen bonded NH^+ . Only one single vibrational mode is seen in this whole range, which is a significant sign of the proton on TMA site. If the proton is on

methanol site, two vibration modes will be found, which are due to the symmetric and asymmetric vibration.

Figure 6.5 Simulated infrared vibrational spectra of Ct structures for H^+M_5 , $TMA-H^+-M_5$ with proton on methanol and TMA site, and M_5 . Attachment of TMA to H^+-M_5 has small influence on the overall structural. The free OH of the tail molecule in H^+M_5 becomes hydrogen bonded, and makes the neighboring HB strengthened due to cooperativity. However, for the isomers with proton on TMA site, the hydrogen bonding direction changed, which makes the spectra totally different, but more similar to M_5 . The first solvation shell OH stretches below 2600 cm^{-1} disappear and all the OH vibrational stretch are above 3000 cm^{-1} . The most significant feature is the vibration of the 5th and 6th solvation shell above 3400 cm^{-1} , which can be used to check the excess proton location in the experimental spectra.

To further understand how the attachment of TMA molecule can change the vibrational frequencies, we compared the spectra of H^+M_m , $TMA-H^+-M_m$ and M_m . Figure 6.5 represents the simulated infrared vibrational spectra of Ct structures for H^+M_5 , $TMA-H^+-M_5$ with proton on methanol and TMA site, and M_5 . Attachment of

TMA to H^+-M_5 has small influence on the overall structure. The free OH of the tail molecule in H^+M_5 becomes hydrogen bonded, and makes the neighboring HB strengthened due to cooperativity. However, for the isomers with proton on TMA site, the hydrogen bonding direction changed, which makes the spectra totally different and more similar to M_5 that all the H-bonded OH vibrational frequencies located intensively in the range of 3100~3500 cm^{-1} . The solvation shell is counted from the position of the excess proton, and along the hydrogen bonding direction. The first solvation shell OH stretches below 2600 cm^{-1} disappear and all the OH vibrational stretch are intensively above 3000 cm^{-1} . The most significant feature is the vibration of the 5th and 6th solvation shell above 3400 cm^{-1} , which can be used to check the excess proton location in the experimental spectra.

The measured IR spectra of $m = 3-6$ in the range of 2400–3800 cm^{-1} are shown in Figure 6.6, taken from ref. 15. The simulated spectra are also presented, taken from the most stable structure in each size according to Gibbs free energy in Table 1. In the spectra, the relative sharp feature at ~3670 cm^{-1} is assigned to the free OH stretching vibration, which indicates the existence of L structure. The broadened bands in the 3200–3400 cm^{-1} are assigned to the H-bonded OH stretch of the methanol moiety. The band at 3000 is attributed to the CH stretches of methyl group, and the CH bands show no remarkable changes with the cluster size. As seen in the spectra, a band due to the NH^+ vibration mode at around 2850 cm^{-1} is seen in the observed spectra, which agree with the calculated results.

The spectra are quite different to those of H^+M_m . In the observed spectra of H^+M_m , the peak position of the broad hydrogen-bonded OH stretch band shows gradual blue

shifts with the increase of the cluster size.^{14,16} Looking at TMA- $\text{H}^+\text{-M}_3$, TMA- $\text{H}^+\text{-M}_4$ and TMA- $\text{H}^+\text{-M}_5$, there is a significant difference around 3400 cm^{-1} (which are not present in H^+M_4 and H^+M_5 - there is no H^+M_3 in our previous paper). The peak at 3400 cm^{-1} is a good sign that proton stays on TMA side (the OH stretch on MeOH that is adjacent to ion core is very much red-shifted). Since only when the HB is far away from the ion core, the HB strength can be so weak. This band remains intense at TMA- $\text{H}^+\text{-M}_6$ implies that proton does not migrate to MeOH site (if so the OH will be red-shifted).

Figure 6.6 Observed (at 190 K) and simulated IR spectra of TMA- $\text{H}^+\text{-M}_m$ ($m = 3\text{--}6$) in the bonded-OH stretch region. The simulated spectra are taken from the most stable structure in each size according to Gibbs free energy in Table 1.

6.4 $[(CH_3)_2SO]-H^+-M_m$

DMSO has attracts much attention due to its excellent solubility to both inorganic and organic compounds and wide applications in various fields.^{17,18} Recently, Li and co-workers investigated the interactions between DMSO- d_6 and [bmim][BF₄], and observed a blue shift in the C–D stretching vibrations of DMSO- d_6 . They attributed this to the indirect influence of the H-bond formed by the nearby functional group S=O with C2-H of the cation.¹⁹ However, most of the studies are on neutral DMSO-water systems,²⁰ our study on protonated DMSO-methanol system will get more information on the HB nature.

6.4.1 Coordination types of $OS(CH_3)_2$ and $H^+OS(CH_3)_2$ sites

Figure 6.7 Coordination types of the DMSO and H^+DMSO sites. DMSO can act as single acceptor (A) or double acceptor (AA), thus can form two coordinate structures. Protonated DMSO, due to the attachment of the proton, the oxygen atom becomes less negative and is forbidden to accept another hydrogen atom, so can only act as single donor (D).

Prior to detailed descriptions on the energy-optimized isomer structures of DMSO- H^+-M_m , we shall briefly summarize the possible coordination types of $OS(CH_3)_2$ and $H^+OS(CH_3)_2$ sites and morphology types of DMSO- H^+-M_m . As shown in Figure 6.7,

DMSO can act as single acceptor (A) or double acceptor (AA), thus can form two coordinate structures. On first sight, the coordination type for a H^+DMSO seems comparable to that of a DMSO molecule, but it is not true. Protonated DMSO, due to the attachment of the proton, the oxygen atom becomes less negative and is forbidden to accept another hydrogen atom, so can only act as single donor (D). Though it is geometrically acceptable for a H^+DMSO to be a AD site, it is easy to understand such coordination types are energetically not favorable.

6.4.2 Morphological development of $DMSO-H^+-M_m$

For 1 coordinated DMSO, we can add it to the free H of the protonated methanol molecule just like in $TMA-H^+-(MeOH)_m$. Based on these structures, we can move the proton from methanol site to DMSO site to construct another kind of structures, which involves the 1 coordinated H^+DMSO .

For 2 coordinated DMSO, the only possible morphology is C, where the two terminate A of the $L H^+M_m$ was connected by DMSO. This is a new morphology that $TMA-H^+-M_m$ does not have.

Figures 6.8 and 6.9 depict the optimized geometries of low-energy of $DMSO-H^+-M_m$. The electronic potential energy (E_0), total energies (E_0+ZPE) and Gibbs free energy (G) at 190 K are evaluated for all stable structures. For E_0 , E_0+ZPE and G , those of the minimum energy isomer in each cluster size (m) are set to zero.

Figure 6.8 depicts the optimized geometries of L and C morphologies:

Linear structures (L) are the simplest and most basic form. For $m \leq 2$, L is the only possible structure. We first put the proton in the middle of the methanol chain, but the proton will transfer to DMSO site during the optimization for $m \leq 2$. For $m \geq 3$,

proton will stay on methanol site after optimization, though we put the proton in the center methanol site in the input structure. This is consistent with the fact that the proton affinity of M_3 exceeded that of DMSO.

Figure 6.8 Energy-optimized stable structures for “linear” (L) and “cyclic” (C). The values below the structures are the relative E_0 (the first number), the relative $E_0 + ZPE$ (the second number), and the relative Gibbs free energy at 190 K (the third number) computed at B3LYP/6-31+G* (in kcal/mol). We can see that proton switch from DMSO site to methanol site at $m = 3$. The positions of the methanol and DMSO ion cores are highlighted with the blue circles and pink triangles.

Cyclic Structures (C). The minimum size for cyclic is $m = 3$. The two terminate A of the $L H^+(MeOH)_m$ was connected by DMSO. All the C structures have methanol ion core. They are the most stable structure by comparing the relative energy. If we try to move the proton near to DMSO, the C structure will be optimized to L structure. It

is easy to understand that C are more stable than L, since all the OH in C are H-Bonded.

Figure 6.9 depicts the optimized geometries of Ct morphologies:

Cyclic with a tail (Ct). We can add the DMSO to the AA site of cyclic or A site of Ct protonated methanol structures. Thus, the AA/A methanol molecule become AAD/AD, and the proton will still stay on the methanol site. This indicated that adding DMSO to $C H^+M_m$ will not change the overall structure in the calculation. Then, we manually move the proton near to the DMSO site, and perform optimization. We get another isomer, which is even more stable than the first type. Ct structures with proton on DMSO site have much higher relative energy and we can conclude that proton prefer to stay on methanol site.

Figure 6.9 Energy-optimized stable structures for “cyclic with a tail” (Ct). The values below the structures are the relative E_0 (the first number), the relative $E_0 + \text{ZPE}$ (the second number), and the relative Gibbs free energy at 190 K (the third number) computed at B3LYP/6-31+G* (in kcal/mol). All the structures with DMSO ion core have much higher energies. The positions of the methanol and DMSO ion cores are highlighted with the blue circles and pink triangles.

From the relative energies of the three morphologies L, C, and Ct, we can get the fact that proton switch from DMSO site to methanol site at $m = 3$. For $m \leq 2$, L with

DMSO ion core is the only possible structure. For $m \geq 3$, three morphologies coexist and all are with methanol ion core. C is the most stable morphology.

6.4.3 DFT Simulations of Vibrational Spectra

Figure 6.10 IR spectra of the most stable structures. Blue shift is found similar to the H^+M_m system, which is an important signal that proton stay on methanol site.

Figure 6.10 represents the IR spectra of the most stable structures in each size. In the frequency range of $3000\text{--}3600\text{ cm}^{-1}$, the hydrogen-bonded OH stretch bands in L and C structures show a clear tendency to be blue shifted as the cluster size increase. Above 3600 cm^{-1} , the free OH stretch bands are expected only in L structures, and this is a unique spectral sign of the L structure. The absence of the free OH stretch band in

C and Ct structure reflects that all the OH groups are hydrogen bonded in these structures.

Figure 6.11 and Figure 6.12 represent IR spectra of all the isomers of $m = 4$ and 5, respectively. There is a significant difference between the isomers with different ion core. We can see that the vibrational frequency at $\sim 3500\text{ cm}^{-1}$ for the isomers with proton on DMSO site. For the isomers with methanol ion core, the hydrogen-bonded OH stretches are all below 3400 cm^{-1} . If we measure the experimental IR spectra for $X = \text{DMSO}$, the spectra will be found different from $X = \text{TMA}$. It is a good method to tell proton transfer for $X-H^+M_m$ systems.

Figure 6.11 IR spectra of the H^+M_4 . When proton is on DMSO site, there is a vibration mode above 3500 cm^{-1} .

Figure 6.12 IR spectra of the H^+M_5 . When proton is on DMSO site, there is a vibration mode above 3500 cm^{-1} .

6.5 Conclusions

For $\text{TMA-H}^+\text{-M}_m$, all the calculated E_0 , $E_0+\text{ZPE}$ and G clearly show that the isomers with TMA ion core are much more stable than those with methanol ion core. The NH^+ vibration mode at 2800 cm^{-1} is one significant sign of proton on TMA site.

Another one is that the spectra with the broad band peak at 3400 cm^{-1} independent of cluster size. For $DMSO-H^+-M_m$, the relative energies shown that the excess proton will stay on the DMSO site for $m = 1$ and 2, and switch to methanol site at $m = 3$. In the IR spectra of the most stable structures, blue shift is found which is an important signal that proton stay on methanol site. From these two systems, we can get the conclusion that IR spectra of hydrogen bonded OH region is significant sign to tell the location of the excess proton in $X-H^+-M_m$. If the proton is on X site, the IR spectra will be similar those of M_m , with the broad band peak at 3400 cm^{-1} independent of cluster size. If the proton is on methanol site, the IR spectra will be similar those of H^+M_m with a high-frequency shift from 3200 cm^{-1} to 3300 cm^{-1} . This work provides a useful method to check proton location in IR spectra for experiment.

6.6 References

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Chapter 7

Conclusions and future work

This thesis studied the hydrogen bonding structure and proton switch in protonated multiple component clusters. It contains two parts. In the first part, protonated methanol-water clusters are studied by increasing the cluster size and changing the mixing ratio. In the second part, proton location in $X-H^+M_m$ systems ($X = \text{TMA}$ and DMSO) are studied and a method to tell the location of the excess proton by using IR spectra is proposed.

7.1 Protonated methanol–water cluster

(1) The systematic search of the most stable isomer structure in various morphologies of the $H^+M_mW_1$ clusters clearly demonstrated the correlation between the cluster morphology and the preferential location of the protonated site. The size-dependent development of the hydrogen-bond network of the clusters was examined. The calculation results showed that the L structure and the CH_3OH_2^+ ion core is preferred for the small-sized clusters of $m = 1$ and 2. The coexistence of multiple structures and different ion cores (MeOH_2^+ and H_3O^+) was suggested for the small-sized clusters of $3 \leq m \leq 7$. Compared with the H^+M_m , adding one water molecule will encourage the formation of two new morphologies, T and tC structures. Both T and tC, which have only the H_3O^+ ion core, were shown to be preferential in $m \geq 8$, consistent

with the previous mass spectrometric results. The IR spectra of the clusters were simulated and compared with the observed spectra in the OH stretching vibrational region. The spectral features of the observed spectra were well interpreted by the spectral simulations with the coexistence of the multiple isomers at small sizes. The disappearance of the free OH stretch band shows the dominant contribution of the tC structure (having the H_3O^+ ion core) at $m = 7-8$. All the results from our calculation and observed IR spectra suggest that the proton switch from the MeOH_2^+ ion core to the H_3O^+ ion core occurs at $m = 8$ in $\text{H}^+\text{M}_m\text{W}_1$.

(2) An effective theoretical approach was developed to tackle the complexity of $\text{H}^+\text{M}_m\text{W}_n$ ($m + n = 5$ and 6). Basin-hopping method with the OSS2 potential was used to search a diverse set of structural isomers of the H^+W_n clusters, and stable isomers of $\text{H}^+\text{M}_m\text{W}_n$ can be systematically derived by substituting free dangling hydrogen atoms with methyl groups. These structures were reoptimized with DFT methods and vibrational normal modes were calculated for a better description of energy landscape at the first-principles level. The existence of hundreds of energetically competitive local minima complicates the theoretical analysis, and we therefore engaged harmonic superposition approximation to calculate physical properties of the mixed clusters at finite temperature. With the above-mentioned theoretical scheme, we further analyzed the concentration and temperature dependence of the morphology development and the switch of ion-core between water and methanol.

(3) We also studied the anticooperative effect in protonated methanol–water clusters by changing the mixing ratio of the two components. While the total hydrogen-bond energy increases with successive substitution from water to methanol,

the observed vibrational frequencies of the hydrogen-bonded OH stretches show clear high-frequency shifts. To interpret the physical meaning of these shifts, we examined the IR spectral behavior of the T and L isomers of $H^+M_mW_n$ ($m + n = 5$ and 6). Substitution of water by methanol reinforces one of the hydrogen bonds in which this methanol acts as the acceptor; thus, the total hydrogen-bond strength is enhanced. However, enhancement of one hydrogen bond simultaneously sacrifices all other hydrogen bonds because the methanol molecule attracts more charge from others. As a result, the individual hydrogen-bond strength shows a gentle decrease by successive substitutions. This is a new type of anticooperativity of hydrogen bonds in two-component systems. The magnitude of charge transfer from the protonated site to solvent molecules has also been examined to confirm the physical meaning of the anticooperative effect. The IR spectra averaged over the possible isomers have been simulated by the quantum harmonic superposition approximation approach. The simulated spectra reproduce well the high-frequency shift trend of the hydrogen-bonded OH stretch bands, indicating that anticooperativity is a common property for all isomers of $H^+M_mW_n$.

7.2 $X-H^+-M_m$ systems ($X = \text{TMA}$ and DMSO)

For $\text{TMA}-H^+-M_m$, all the calculated E_0 , $E_0+\text{ZPE}$ and G clearly show that the isomers with TMA ion core are much more stable than those with methanol ion core. The NH^+ vibration mode at 2800 cm^{-1} is one significant sign of proton on TMA site. Another one is that the spectra with the broad band peak at 3400 cm^{-1} independent of cluster size. For $\text{DMSO}-H^+-M_m$, the relative energies shown that the excess proton

will stay on the DMSO site for $m = 1$ and 2, and switch to methanol site at $m = 3$. In the IR spectra of the most stable structures, blue shift is found which is an important signal that proton stay on methanol site. From these two systems, we can get the conclusion that IR spectra of hydrogen bonded OH region is significant sign to tell the location of the excess proton in $X-H^+-M_m$. If the proton is on X site, the IR spectra will be similar those of M_m , with the broad band peak at 3400 cm^{-1} independent of cluster size. If the proton is on methanol site, the IR spectra will be similar those of H^+M_m with a high-frequency shift from 3200 cm^{-1} to 3300 cm^{-1} . This work provides a useful method to check proton location in IR spectra for experiment.

7.3 Future work

Interesting results are found in $X-H^+-M_m$ systems in Chapter 6. Proton affinity of 1 MeOH is 182 kcal/mol, and reaches a threshold value at $m = 4$, as shown in Figure 7.1. Therefore, the excess proton is expected to transfer from X to MeOH site as the cluster size increasing. However, we carried out the calculation to the size of 9 for $X = \text{TMA}$, proton transfer does not occur up to the bulk limit. Therefore, although the solvent cluster PA is important, it is not the only variable controlling proton transfer. A simple thermodynamic analysis suggests that two factors are decisive in controlling this reaction: the gas-phase proton affinity of the solvent cluster, and the electrostatic stabilization energy of the microsolvated ion pair. The PAs increase with increasing cluster size, but opposing this trend is the decrease in stabilization energy as the clusters grow larger, due to increased anion-solvated proton distance and greater dielectric screening. Therefore, although the PA of methanol clusters increases

substantially beyond the threshold PA for proton transfer observed for the TMA system, no proton transfer occurs up to the bulk limit.

Figure 7.1 Gas-phase proton affinities methanol clusters versus cluster size from ref. [1].

Although many efforts have been made on the study of proton switch, very little work has been carried out on the influence of cluster proton affinity. Dielectric screening is the origin of the contradiction between proton affinity's prediction and actual stabilization energy. Only a few molecules near the proton make contribution to the total proton affinity even in larger cluster size. So in $X-H^+M_m$ systems, the proton affinity of M_m accounted should be much lower. As one of our final aims, we will use methanol cluster as a probe, and choose X molecule with different proton affinities, to

give a complete description on the relation between cluster proton affinity and proton switch. We hope our work can simulate further investigations on the mixed cluster and lead to a better understanding for mixed clusters which have numerous isomers.

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