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Gas-phase structures of binary cluster ions of 1,4-dioxane and water

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Abstract

1,4-Dioxane–water binary cluster ions are produced by supersonic expansion in gas phase. Ionization using an ArF excimer laser for time-of-flight mass spectroscopy reveals significant magic numbers at $[(C_4H_8O_2)_m(H_2O)_n]H^+$, $(m, n) = (3,1), (4,2), (5,3)$, and $(6,4)$. The structures of the stable binary cluster ions are discussed based on density functional theory.

Keywords: 1,4-Dioxane; Water; Binary cluster ion; Time-of-flight mass spectrometry

1. Introduction

Binary clusters containing water molecules have been studied in various combinations [1,2] to simulate multicomponent solvent systems and clarify the structure of hydrogen-bonded networks of protonated solute ions. Hydrogen-bonded clusters of the type $M_n(H_2O)_nH^+$ have been studied extensively for various molecules M such as $(CH_3)_2O$ [3], CH_3CN [4], NH_3 [5], $C_4H_4N_2$ [6], and ROH [7]. The lowest-energy structures for any hydrogen-bonded cluster ion will be that possessing the greatest number of hydrogen-bonds. Interaction between water and 1,4-dioxane is very interesting because 1,4-dioxane is miscible with water at any composition, despite being a non-polar organic molecule. Binary solutions of 1,4-dioxane–water have been studied over a wide mass range and mixture ratios [8], and the hydrogen-bonded network of water has been found to be predominant at low 1,4-dioxane concentrations. The 1:1 complex of 1,4-dioxane and water has been studied based on the free-jet millimeter-wave absorption spectrum [9], and the structure of 1,4-dioxane–water has been determined.

The aim of the present study is to investigate the structures and hydrogen-bonding nature of 1,4-dioxane–water binary clusters of small mass using an adiabatic expansion method. A 1,4-dioxane molecule contains two oxygen atoms, making it is possible to form two hydrogen bonds with two molecules simultaneously. The structure of the binary cluster ions is expected to be affected by the nature of the hydrogen bonds, and magic numbers resulting from the stability should be observed. However, clear magic numbers for 1,4-dioxane–water cluster ions have not been reported as yet. Magic clusters, appearing as intense peaks in mass spectra, provide clear information on the stability of the structure of clusters. Computational methods also provide detailed chemical information and is useful to support understanding of the experimental observations. Experimental and computational methods are applied in the present study in the examination of hydrogen bonds in 1,4-dioxane–water binary cluster ions.

2. Experimental

Supersonic expansion and time-of-flight (TOF) mass spectroscopy were employed to observe 1,4-dioxane–water binary clusters. Sample vapors (1,4-dioxane and water) were mixed at room temperature with He carrier gas (2 atm). The vapor mixture was then expanded into a vacuum chamber through an electric supersonic valve (General Valve Co.) with He carrier gas, resulting in the formation of neutral clusters by supersonic expansion. The gas-phase cluster sample was introduced into an ionization area through two skimmers in combination with two diffusion pumps. Neutral clusters were then ionized by pulses from a 193-nm ArF excimer laser (EMG201, Lambda Physik). The cluster ions were accelerated in an electric field (1.6 kV), passed through a 45-cm TOF tube, and detected by a micro-channel plate (MCP) in an area evacuated by a turbo molecular

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pump. The signals from the MCP were captured using a digital oscilloscope (9310A, LeCroy). Typically, 500 signals were accumulated for analysis.

Density-functional calculations were performed using the ADF program package [10] with III basis sets; a double-zeta plus a 3D-type polarized function with frozen core. The geometry of the cluster ions was optimized starting from various initial geometries to obtain the most stable structure.

3. Results and discussion

Neat 1,4-dioxane clusters ions $(C_4H_8O_2)_n$ H^+ ($n = 1$–20) were produced by 1,4-dioxane gas with He carrier gas, and did not produce noticeable magic numbers. The gas mixture of 1,4-dioxane and water produced 1,4-dioxane–water binary clusters, as shown in Fig. 1. The relative intensities of the binary cluster ions varied depending on the ratio of the gas mixture introduced. The spectra obtained in water-rich conditions and 1,4-dioxane-rich conditions are shown in Fig. 1a and b, respectively. Neat water cluster ions were not observed under the present experimental conditions. All cluster ions included 1,4-dioxane molecules, indicating the strong affinity of water cluster ions to 1,4-dioxane molecules. The smallest 1,4-dioxane–water binary cluster ion was $[(C_4H_8O_2)_3(H_2O)_1]H^+$, which was seen in all of the experiments. Magic clusters with strong intensity at a specific mixture ratio, $[(C_4H_8O_2)_m(H_2O)_n]H^+$, $(m, n) = (3,1)$, $(4,2)$, $(5,3)$, and $(6,4)$, were observed very clearly in water-rich conditions. The composition of the cluster ions can be expressed as $(m, n) = (2 + n, n)$ where (1,1) attaches to the (3,1) core. Larger cluster ions were observed for higher 1,4-dioxane concentrations (Fig. 1b). The same magic cluster ions were observed in the mass spectra, along with cluster ions of $m > 8$ having one water molecule, $[(C_4H_8O_2)_m(H_2O)_1]H^+$, as stable cluster ions.

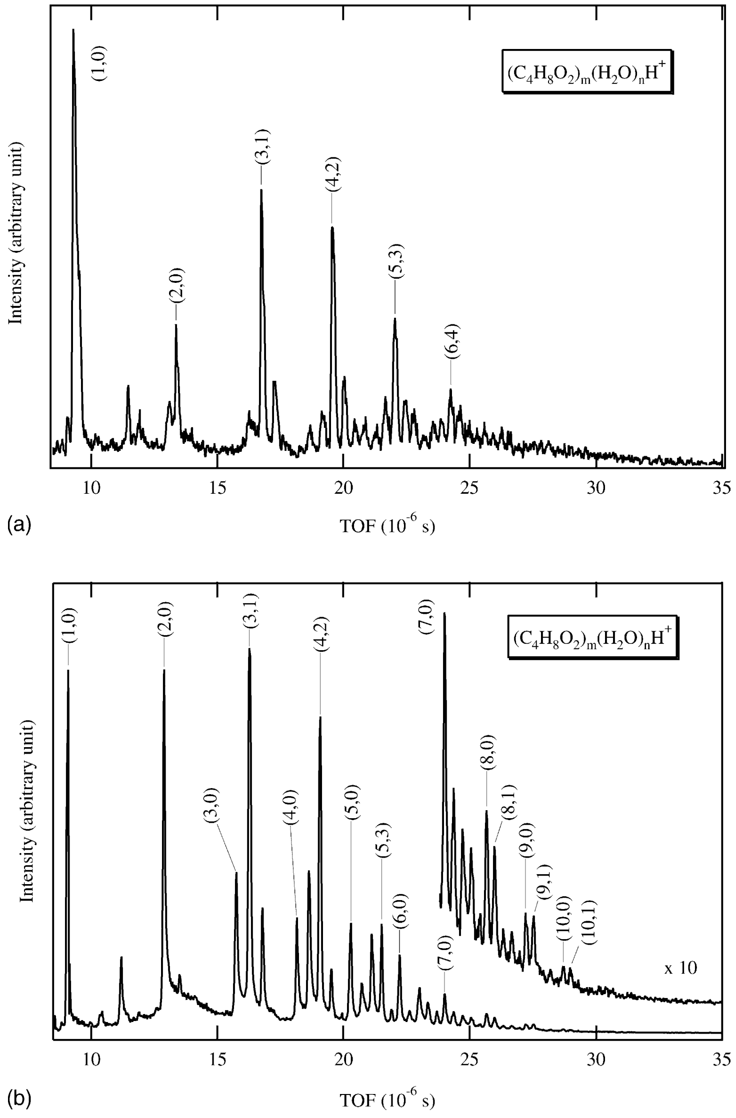

Fig. 1. Time-of-flight mass spectra of $(C_4H_8O_2)_m(H_2O)_nH^+$ clusters. Numbers correspond to $(C_4H_8O_2)_m(H_2O)_nH^+$; (m,n): (a) in water-rich condition and (b) in 1,4-dioxane-rich condition.

The largest magic cluster ions in the $(2 + n, n)$ series was (6,4).

The origin of the magic numbers of the cluster ions is attributed to the hydrogen bonds between 1,4-dioxane and water molecules, forming network structures. The proton affinity of water molecules is larger than that of 1,4-dioxane, and the protons may be contained in the cluster ions in the form of the oxonium ion H_3O^+. The smallest 1,4-dioxane–water binary cluster ion (3,1) has three 1,4-dioxane molecules bonded to the hydrogen atoms of the oxonium ion H_3O^+. A similar binary cluster ion structure has been proposed for the water–trimethylamine system [11]. For the (4,2) cluster ions, two kinds of structures are possible: water cluster ion $H_5O_2{}^+$ forming a core ion bonded to four 1,4-dioxane molecules at the hydrogen atoms (Type I, Fig. 2b-I), and 1,4-dioxane molecule in a (3,1) cluster ion bonding to a water molecule that is itself attached to another 1,4-dioxane molecule (Fig. 2b-II). Similarly, the (5,3) cluster ions may have two structures: five 1,4-dioxane molecules bonded to the $H_7O_3{}^+$ ion (Type I, Fig. 2c-I), or two pairs of water and 1,4-dioxane molecules attach to (3,1) cluster ions (Type II, Fig. 2c-II). Both types of structures at the same composition have the same number of hydrogen bonds; the (5,3) cluster ion has 7 hydrogen bonds irrespective of the structure. Therefore, both structures should have similar total stabilization energies. The difference

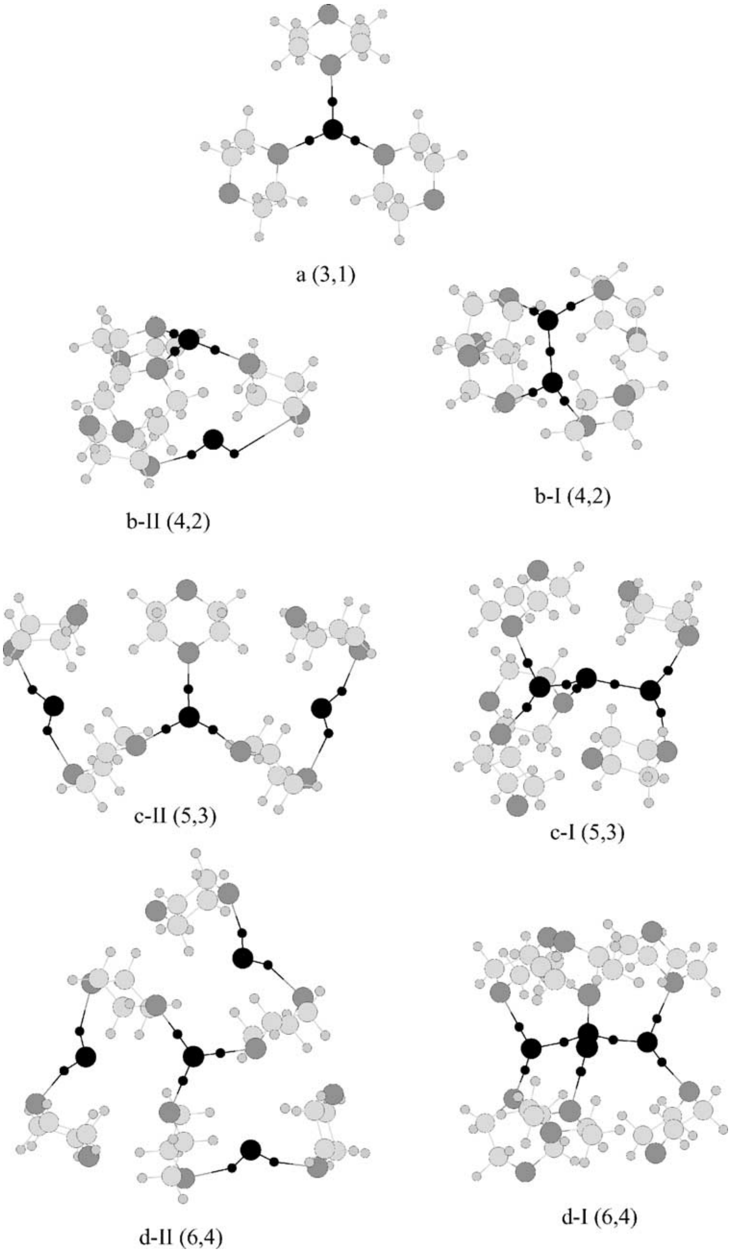

Fig. 2. ADF-optimized structures of 1,4-dioxane–water binary cluster ions. Large balls denote carbon and oxygen, small balls denote hydrogen. Water is rendered in black, and 1,4-dioxane is rendered in light gray and dark gray.

Table 1
Hydrogen-bonding energy of 1,4-dioxane–water binary cluster ions calculated by ADF

Species	Type I (eV)	Type II (eV)	Number of oxygens
(3,1)	−5.5424		7
(4,2)	−7.0106	−6.7147	10
(5,3)	−8.7587	−8.0400	13
(6,4)	−11.0847	−10.0321	16
(7,5)	−12.3380	−11.2277	19
(8,6)	−13.9042	−12.3910	22

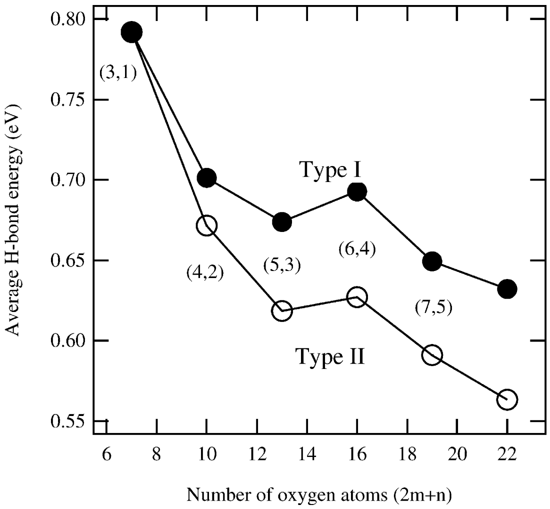

Fig. 3. Average hydrogen-bonding energies per unit oxygen for two types of cluster ions calculated by ADF. Numbers correspond to $(C_4H_8O_2)_m(H_2O)_n{}^+$; (*m*,*n*).

will be in the position of the non-hydrogen-bonded oxygen atoms: Type I structures have a non-hydrogen-bonded oxygen atom in the 1,4-dioxane molecules, whereas the non-hydrogen-bonded oxygen atoms occur in both water molecules and 1,4-dioxane molecules in the Type II structure.

Density functional calculations [10] were performed for the stable (magic number) 1,4-dioxane–water cluster ions (3,1), (4,2), (5,3), (6,4). For the cluster ions (4,2), (5,3), (6,4), calculations were conducted for the two structures for each cluster ion. The optimized structures and hydrogen-bonding energies are summarized in Fig. 2 and Table 1. Hydrogen-bonding energies were calculated by subtracting the energies of constituent molecules in the ground state from the total energies of the cluster ions. The cluster ions of Type I, where 1,4-dioxane molecules surround the core water cluster ions, are more stable than the corresponding clusters of Type II, although Type I structures have greater steric hindrance between 1,4-dioxane molecules. The optimized structures of clusters show that the hydrogen atoms in a 1,4-dioxane molecule also interact with an oxygen atom in the water molecule, which can clearly seen in the Type II structure. This structure has also been reported to be stable for the 1:1 complex between 1,4-dioxane and water [9]. The dependence of the hydrogen-bonding energy on the cluster size is examined for two types of cluster binary ions in Fig. 3, which shows the hydrogen-bonding energy per oxygen atom for (*m*,*n*) cluster ions with $2m + n$ oxygen atoms. The average hydrogen-bonding energies decrease with increasing cluster size, and the difference between the hydrogen-bonding energies of the Types I and II structures become larger. The Type I (6,4) was found to be the most stable of the magic clusters.

The core-type structure of the Type I binary cluster ions is notable. The hydrogen-boding nature of water clusters have been studied extensively, and a hydration model for protons in aqueous solution and ice proposed by Eigen and coworkers [12,13] also describes a core oxonium ion H_3O^+ surrounded by three water molecules in a first solvation shell. The (3,1), (5,3), (6,4) cluster ions have a central oxonium ion H_3O^+, whereas the (4,2) cluster ion has a $H_5O_2{}^+$-centered structure. Calculations were also performed for the (6,4) cluster ions assuming an $H_5O_2{}^+$-centered structure, and it was found that the H_3O^+-centered structure is 0.376 eV more stable than the $H_5O_2{}^+$-centered structure. For the pure water cluster ion $H_9O_4{}^+$, it has been reported that the H_3O^+-centered structure is more stable than the $H_5O_2{}^+$-centered structure [14]. Similarly, the larger cluster ions, such as (7,5) or (8,6), should also have water cluster ions ($H_{11}O_5{}^+$,$H_{13}O_6{}^+$) in the center. For the $H_{11}O_5{}^+$ ion, three water molecules occur in the Eigen-like structure first-shell of H_3O^+ and a fourth water molecule occurs in the second shell. The $H_{11}O_5{}^+$ ion has been studied theoretically, and it has been reported that cyclic four-member-ring structures are also possible [15]. Although the (6,5) cluster ion was expected to form through combination of 1,4-dioxane molecules and a four membered ring-structured $H_{11}O_5{}^+$ ion, no such cluster was observed in this experiment. The (6,4) binary cluster ion is very stable in the series of magic cluster ions because the H_3O^+ ion is hydrogen-bonded to three water molecules in the first solvation shell and all of the hydrogen atoms in outer water molecules are bonded to 1,4-dioxane molecules. Therefore, core water cluster ions smaller than $H_{11}O_5{}^+$ can form stable structures, and thus binary cluster ions having more than five waters ((*m*,*n*); $n > 5$) were not observed under the present experimental conditions. Assuming that the (7,5) cluster ion would have a core $H_{11}O_5{}^+$ ion, additional water molecules have to bond in the second solvation shell of the core H_3O^+ ion. Therefore, (7,5) should be less stabilized by hydrogen bonds than (6,4), and such larger cluster ions were not observed in the experiments. 1,4-Dioxane–water binary cluster ions with more 1,4-dioxane molecules were observed as (*m*,1) cluster ions, having one water molecule that retains the proton in the form of H_3O^+. Water cluster ions larger than $H_9O_4{}^+$ may not be stable in the 1,4-dioxane–water system, and large 1,4-dioxane–water binary clusters with more 1,4-dioxane molecules typically have a H_3O^+ core.

4. Conclusion

1,4-Dioxane–water binary cluster ions in gas phase have significant magic numbers at $[(C_4H_8O_2)_m(H_2O)_n]H^+$, $(m, n) = (3,1), (4,2), (5,3)$, and $(6,4)$. The structures of the stable binary cluster ions were discussed with the aid of density functional theory, and it was demonstrated that the binary cluster ion has a stable structure with a water cluster ion as a core surrounded by 1,4-dioxane molecules. The (6,4) cluster ion is the most stable among the series of magic clusters because of the filled first solvation shell of the $(H_2O)_4H^+$ ion.

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