

On the Search for H_5O_2^+ -centered Water Clusters in the Gas Phase

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In searching for H_5O_2^+ -centered water clusters, we employed vibrational predissociation spectroscopy and *ab initio* calculations. Structures of the clusters were characterized by the free- and hydrogen-bonded-OH stretches of ion cores and solvent molecules. Systematic examination of $\text{H}^+(\text{H}_2\text{O})_{5,7}$ in a supersonic expansion reveals the presence of both cyclic and noncyclic forms of H_5O_2^+ -centered water clusters. The proton transfer intermediate $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_4$ was identified, for the first time, by its characteristic hydrogen-bonded-OH stretches of the ion core at 3178 cm^{-1} . Also discovered at $n = 7$ is the H_5O_2^+ -containing five-membered ring isomer, whose existence is evidenced by the observation of a bonded-OH stretching doublet at 3544 and 3555 cm^{-1} of the solvent molecules. The observations are in accord with *ab initio* calculations which forecast that $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_4$ and $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_5$ are, respectively, the lowest-energy isomers of protonated water hexamers and heptamers.

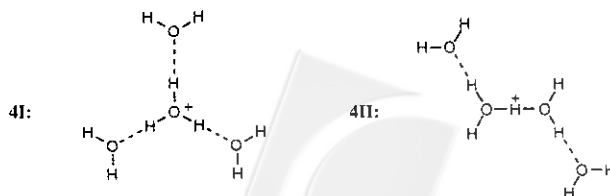
INTRODUCTION

How does an excess proton behave in water clusters? The conventionally used model suggests that the proton is firmly attached to one of the water molecules in the discrete form of H_3O^+ . This model, however, fails to present the quantum nature of H^+ , which can be highly mobile in liquid as well as in clusters.¹ An alternative form for a hydrated proton is H_5O_2^+ ,² where the H^+ is equally shared by two water molecules. This structure has often been overlooked, largely because of the lack of conclusive experimental evidence for its existence in aqueous acids.³ The fundamental question of whether H_5O_2^+ or H_3O^+ is the dominant structure of the hydrated proton remains unanswered.⁴ Recently, increasing computational evidence^{5,6} indicates that the dynamics of proton transfer in liquid water is built upon the existence of such an H_5O_2^+ -centered structure. The proton transfer has been simulated as a consequence of the periodic interconversion between $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_{n-2}$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{n-1}$ driven by thermal and quantum solvent fluctuations.^{1,5,6} Here we summarize the results of a search for this proton transfer intermediate state, and provide both infrared spectroscopic and *ab initio* computational evidence for the existence of H_5O_2^+ -centered water clusters in the gas phase.

The structure of H_5O_2^+ was first predicted by *ab initio* calculations for protonated water clusters by Newton and Ehrenson in the early 1970s.⁷ Since then, H_5O_2^+ -centered water clusters have been associated with the exceptionally large mobility of a proton in liquid water⁷ and in biological systems.⁸ A detailed understanding of the fundamental pro-

ton transfer processes is now being actively pursued using advanced theoretical calculations,⁹ yet no experimental searches have found an H_5O_2^+ -centered structure in an isolated water cluster. Primarily, this is because the H_5O_2^+ cation can only exist in a symmetrical environment. Except for a limited number of isomers, most of the clusters existing in nature are H_3O^+ -centered. The H_3O^+ -centered structures have indeed been considered as the prevailing forms of protonated water clusters [$\text{H}^+(\text{H}_2\text{O})_n$] in the literature.¹⁰

On the search for $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_{n-2}$ using spectroscopic methods, the progress was always hampered by the complex structural isomerism involved in the clusters. The first infrared absorption spectra of protonated water clusters were obtained by Schwarz¹¹ who created the ions by radiolysis of water vapor in a cold static cell. These cluster ions, however, have a size distribution over a certain range, disallowing unambiguous structural identification of isomers. Vibrational predissociation spectra of size-selected $\text{H}^+(\text{H}_2\text{O})_n$, $n = 1 - 9$, were later published by Lee and coworkers using an ion trap tandem mass spectrometer.^{12,13} The spectroscopic study of Yeh et al.¹² confirmed that the predominant form of $\text{H}^+(\text{H}_2\text{O})_4$ contains an H_3O^+ ion core with an open, noncyclic Eigen structure (**4I**) as



The H_5O_2^+ -centered isomer (**4II**) is less strongly bound by ~ 3 kcal/mol and, hence, it was not found in a supersonic expansion.¹² For larger water clusters, Crofton et al.¹³ reported the spectra of $\text{H}^+(\text{H}_2\text{O})_{5-9}$ in 1994 but they failed to come up with a conclusive interpretation for the prevailing structures. Their work was soon followed by Wei and Salahub¹⁴ who performed *ab initio* molecular dynamics simulations and attempted to identify possible isomers by comparing their calculations with the published spectra. However, the stick diagrams calculated for open, noncyclic H_3O^+ -centered isomers¹³ were at considerable variance with the experimentally observed spectra. Whether H_5O_2^+ -centered water clusters can exist as single identities in the gas phase has remained an open question.

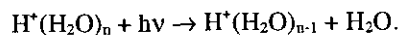
The present investigation successfully identifies $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_{4-6}$ in a supersonic expansion by means of vibrational predissociation spectroscopy and *ab initio* calculations,¹⁵ which characterize the structures of protonated water clusters according to their free- and hydrogen-bonded-OH stretching vibrations. Before this re-investigation of $\text{H}^+(\text{H}_2\text{O})_n$, we have studied three benchmark systems $\text{NH}_4^+(\text{H}_2\text{O})_n$, $\text{H}^+(\text{CH}_3\text{OH})_n$ and $(\text{CH}_3)_2\text{O}\text{-H}^+(\text{H}_2\text{O})_n$ to isolate the problems. New insight on (1) isomeric structures and transitions,^{16,17} (2) intracluster proton transfer mediated by ring opening and closing,¹⁸ and (3) solvation-induced proton migration upon cluster formation¹⁹ was obtained. These studies serve as an important and solid basis for the present structural identification of H_5O_2^+ -centered water clusters. On the premise that the absolute frequencies and relative absorption intensities of OH stretching vibrations are sensitive probes for hydrogen bonding networks^{16,17} and proton locations,^{18,19} careful spectral examination allows us to uncover the $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_{4-6}$ cluster isomers.

METHODOLOGIES

Vibrational predissociation spectroscopy

The experiment was conducted using a vibrational predissociation ion trap spectrometer in combination with a pulsed infrared laser system. Details of the experimental setup have been previously described.¹⁶ Briefly, we generated hydronium ions (H_3O^+) by corona-discharging a flow of H_2O vapor seeded in pure H_2 . Through supersonic expansion, the ions formed clusters with neutral water molecules. The jet-synthesized clusters $[\text{H}^+(\text{H}_2\text{O})_n]$, with a typical internal temperature of 170 K,¹⁵ were first mass-selected and then spectroscopically analyzed by infrared laser inside an octopole ion trap. Upon absorption of resonant laser photons, the size-selected cluster ions dissociated predomi-

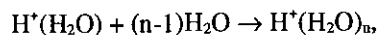
nantly via unimolecular loss of water molecules as



A second mass filter monitored the occurrence of dissociation, from which infrared spectra were obtained by recording the concentration increase of the photofragments.

Ab initio calculations

The calculations were carried out using the commercial Gaussian 94 program package. The effort made it possible to compare the predicted structures, binding energies, harmonic vibrational frequencies and infrared absorption intensities of various structural isomers with measurements. In this work, the *ab initio* calculations were performed based upon density function theory (DFT) using the Becke3LYP functional with the 6-31+G* basis set.¹⁵ This combination of method and basis set has been successfully applied to neutral water²⁰ and hydrated ammonia²¹ clusters before. To ensure correct assessment of the H_5O_2^+ -centered clusters, additional calculations were undertaken for the total interaction energies, according to the clustering of



using the Moller-Plesset second-order perturbation (MP2) method.¹⁵ A single factor (0.973), chosen by referring to the free-OH stretching of two- and three-coordinated H_2O ,²² was employed to scale the frequencies produced by B3LYP/6-31+G*.

RESULTS AND DISCUSSION

Prior infrared measurements¹² and *ab initio* calculations^{7,14} indicated that a protonated water tetramer preferentially exists in the form $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$, instead of $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_2$. Interestingly, close examination of the calculations reveals that the difference in stability between the H_5O_2^+ -centered and H_3O^+ -centered structures rapidly diminishes as clusters increase in size. Our present calculations found that the $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_{n-2}$ isomers can become more stable than $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{n-1}$ at $n \geq 6$. This surprising feature has, apparently, been previously overlooked.¹⁴ For protonated water hexamers and heptamers, both DFT and MP2 computations accordingly predicted that the $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_{4,5}$ clusters are the lowest-energy isomers (Table 1), and they are more stable than other members (mostly H_3O^+ -centered) of the same solvation group by ~ 1 kcal/mol.¹⁵ In isomers **6II** and **7VI** depicted in Fig. 1, the excess protons are equally shared

Table 1. Comparison of the Calculated Total Interaction Energies (kcal/mol) of H⁺(H₂O)_n Isomers Using Two Different Computational Methods^a

Isomers ^b	ΔE_n	
	B3LYP/6-31+G*	MP2/6-31+G*
6I	-93.9	-88.3
6II	-95.0	-88.8
6III	-93.9	-88.1
6IV	-92.5	-86.5
6V	-93.5	-87.7
7VI	-104.9	-98.2
7VII	-102.1	-95.5
7VIII	-104.0	-97.2
7IX	-103.2	-96.9
7X	-103.7	-97.2

^a ΔE_n , with both basis set superposition errors and zero-point vibrational energies corrected.

^b Structures of the isomers are illustrated in Fig. 5.

by two adjacent water molecules (Nos. 1 and 2), forming an H₅O₂⁺ ion core.

Fig. 2 displays the vibrational predissociation spectra

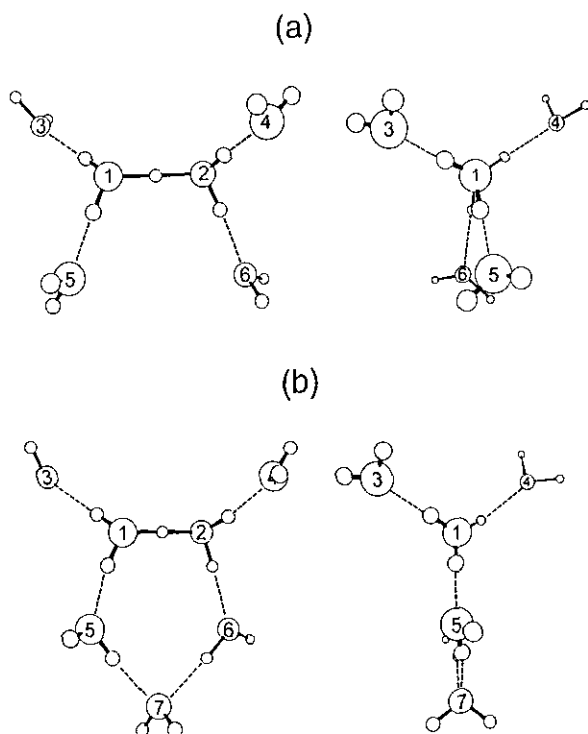


Fig. 1. Front and side views of two H₅O₂⁺-centered water clusters identified by the present experiments: (a) H₅O₂⁺(H₂O)₄ and (b) H₅O₂⁺(H₂O)₅. The H and O atoms are denoted by open and numbered circles, respectively. The associated geometric parameters are listed in Table 2.

of H⁺(H₂O)₅₋₇ obtained using the ion trap tandem mass spectrometer at the cluster temperatures of 170 ± 20 K.¹⁵ As will be elaborated below, noncyclic isomers are mainly responsible for the observed absorption features for clusters with sizes of n ≤ 6. Ring formation occurs at n = 7, evidenced by the emergence of the free-OH stretching absorption of three-coordinated H₂O at 3679 cm⁻¹ and the bonded-OH stretching absorptions of water molecules in a ring at 3500 - 3600 cm⁻¹.^{16,22} The emergence of these spectral features is an important indication of structural transformation from noncyclic to ring-shaped isomers.¹⁵ This transformation closely resembles the structural changeover from cyclic to three-dimensional cage-like structures in neutral benzene-water clusters.²³

Fig. 3 presents the spectrum of the protonated water pentamer H⁺(H₂O)₅. The observed free-OH stretching transition at 3709 cm⁻¹ is that of the two-coordinated H₂O, which is distinguished from the symmetric (3647 cm⁻¹) and asymmetric (3736 cm⁻¹) stretches of the peripheral H₂O molecules acting as single proton acceptors. The hydrogen-

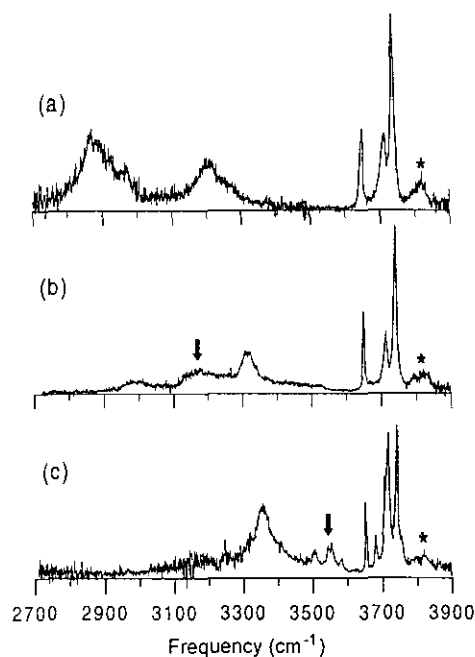


Fig. 2. Vibrational predissociation spectra (a-c) of H⁺(H₂O)₅₋₇ in the OH stretching region. Arrows in (b) and (c) denote, respectively, the spectral signatures of H₅O₂⁺(H₂O)₄ at n = 6 and H₅O₂⁺(H₂O)₅ at n = 7. Compared to that of (a) n = 5 and (b) n = 6, the H⁺(H₂O)₇ spectrum in (c) exhibits new features for free-OH stretches at 3679 cm⁻¹ and bonded-OH stretches at 3500 - 3600 cm⁻¹. Asterisks denote the combination bands of the free-OH stretches of single-acceptor H₂O with intermolecular vibrations (Ref. 12).

bonded-OH stretches are resonant at 2879 and 2967 cm^{-1} for the ion core and at 3208 cm^{-1} for the solvent molecule situated in the first solvation shell (1°). From systematic temperature dependence measurements over the range of 160 - 190 K,¹⁵ it is concluded that predominantly only one type of isomer is present in the supersonic jet. Detailed analysis of the spectrum revealed that all the prominent features in Fig. 3 can be attributed to the H_3O^+ -centered noncyclic isomer **5I**, which is predicted to be lowest in energy of $\text{H}^+(\text{H}_2\text{O})_5$ by the present and prior calculations.²⁴ This isomer has the fifth water molecule situated on the second solvation shell (2°) of H_3O^+ , yielding a two-coordinated H_2O acting both as a single proton acceptor and a single donor (AD) on the first shell. Structural identification of this isomer is confirmed by matching the observed spectral pattern with the theoretical prediction for $\text{H}^+(\text{H}_2\text{O})_5$, as depicted in Fig. 3.¹⁵ None of other low-energy isomers produced a spectrum in reasonable agreement with the measurements.²⁴ The satisfactory agreement between calculations and observations in Fig. 3 leads to the suggestion that a combination of vibrational spectroscopy and *ab initio* calculations can be an effective

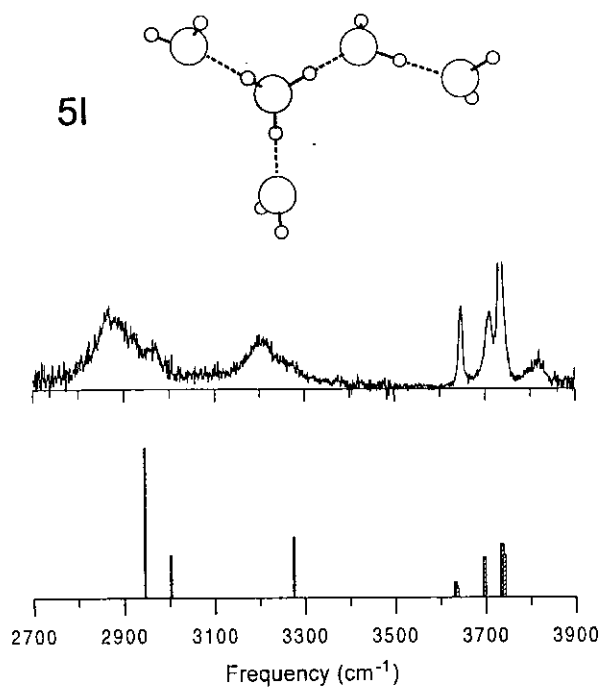


Fig. 3. Vibrational predissociation spectrum of $\text{H}^+(\text{H}_2\text{O})_5$ and its comparison with the *ab initio*-calculated stick diagram of isomer **5I** whose structure is illustrated at the top. Note that the intensities of free-OH stretches (\square) have been amplified by a factor of 5 for clearer comparison with that of bonded-OH stretches (\blacksquare). The O and H atoms are denoted by O and o, respectively, and the ion core units are gray-shaded for clarity.

approach for the identification of H_3O_2^+ -centered water clusters in the gas phase.

The transitions observed in Fig. 4 for $\text{H}^+(\text{H}_2\text{O})_6$ are the free-OH stretches at 3651, 3713 and 3741 cm^{-1} , and the bonded-OH stretches at 2988, 3178 and 3320 cm^{-1} . In interpreting the observed spectrum, it is necessary to assume the presence of an H_3O_2^+ -centered isomer in the detection region. This assumption is justified by the DFT and MP2 computations (Table 1), which agree on the prediction that structure **6II** is lowest in total interaction energy of $\text{H}^+(\text{H}_2\text{O})_6$ isomers presently considered. In addition to **6II**, a second noncyclic structure **6I** is also predicted to be stable, and they both (**6I** and **6II**) are significantly lower in Gibbs free energy than the ring-shaped isomers (**6III** - **6V**) by 1-3 kcal/mol at the given cluster temperature of 170 K (Fig. 5). The formation of either four- or five-membered rings is energetically unfavorable owing to entropy effects. Such computational findings correspond well to the observed emptiness in the fingerprint region of the ring isomers in the spectrum (Fig. 4), namely at 3500 - 3600 cm^{-1} for bonded-OH

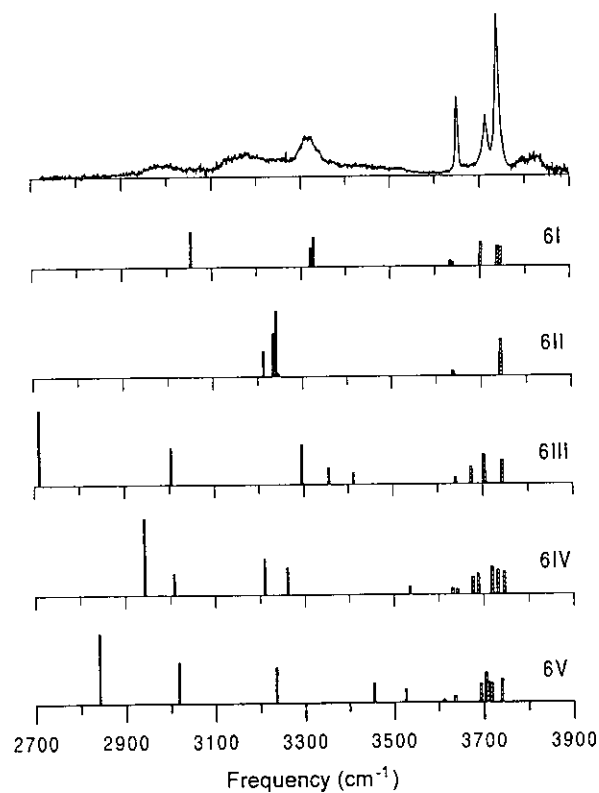


Fig. 4. Vibrational predissociation spectrum of $\text{H}^+(\text{H}_2\text{O})_6$ and its comparison with the *ab initio*-calculated stick diagrams of isomers **6I** - **6V**. Note that the intensities of free-OH stretches (\square) have been amplified by a factor of 5 for clearer comparison with that of bonded-OH stretches (\blacksquare).

Table 2. Calculated Geometric Parameters of H₅O₂⁺(H₂O)₄ and H₅O₂⁺(H₂O)₅ by B3LYP/6-31+G*^a

Isomers	Parameters
6II	d(O ₁ H ⁺) = 1.205, d(O ₂ H ⁺) = 1.210, ∠O ₁ H ⁺ O ₂ = 176.7; ∠H ₃ O ₁ H ⁺ = 113.7, ∠H ₅ O ₁ H ⁺ = 114.4, ∠H ₃ O ₁ H ₅ = 109.3; ∠H ₄ O ₂ H ⁺ = 113.9, ∠H ₆ O ₂ H ⁺ = 114.4, ∠H ₄ O ₂ H ₆ = 109.3; d(O ₁ O ₃) = 2.696, d(O ₁ O ₅) = 2.696, d(O ₂ O ₄) = 2.698, d(O ₂ O ₆) = 2.698; ∠O ₁ HO ₃ = 175.5, ∠O ₁ HO ₅ = 176.8, ∠O ₂ HO ₄ = 175.3, ∠O ₂ HO ₆ = 176.7
7VI	d(O ₁ H ⁺) = 1.209, d(O ₂ H ⁺) = 1.209, ∠O ₁ H ⁺ O ₂ = 179.4; ∠H ₃ O ₁ H ⁺ = 113.0, ∠H ₅ O ₁ H ⁺ = 111.5, ∠H ₃ O ₁ H ₅ = 109.1; ∠H ₄ O ₂ H ⁺ = 113.0, ∠H ₆ O ₂ H ⁺ = 111.5, ∠H ₄ O ₂ H ₆ = 109.1; d(O ₁ O ₃) = 2.704, d(O ₁ O ₅) = 2.679, d(O ₂ O ₄) = 2.704, d(O ₂ O ₆) = 2.679; ∠O ₁ HO ₃ = 176.7, ∠O ₁ HO ₅ = 175.7, ∠O ₂ HO ₄ = 176.7, ∠O ₂ HO ₆ = 175.7; d(O ₅ O ₇) = 2.876, d(O ₆ O ₇) = 2.876, ∠O ₅ HO ₇ = 168.7, ∠O ₆ HO ₇ = 168.8

^a The bond lengths are in unit of Å and angles in degrees. The numbering of the four outer H atoms on H₅O₂⁺ follows that of H₂O hydrogen-bonded to them (Fig. 1).

stretches and at ~3680 cm⁻¹ for free-OH stretches. Note that in this spectrum, the 3713 cm⁻¹ band can only derive from isomer **6I**, since **6II** contains no two-coordinated H₂O (Fig. 4). The observation that this band is relatively weaker than that of H⁺(H₂O)₅ provides the first spectroscopic evidence for the existence of H₅O₂⁺(H₂O)₄ in the supersonic expansion. The second evidence for the H₅O₂⁺(H₂O)₄ formation lies in the new absorption at 3178 cm⁻¹, which is situated in the middle of the 2988 and 3320 cm⁻¹ bands. Since the spectrum of the noncyclic isomer **6I** can only display two distinct types of bonded-OH stretches in the frequency range of

2700 - 3600 cm⁻¹, similar to that of H⁺(H₂O)₅ [Fig. 3(a)], observing this new band suggests the presence of a second isomer, namely **6II**. According to Fig. 4, the calculated spectra of **6I** and **6II** sufficiently agree with the measurements to confirm the proposed structures of these two isomers.

The H₅O₂⁺(H₂O)₄ cluster (**6II**), previously identified in some crystals of inorganic hydrates,²⁵ is discovered here as an isolated entity in the gas phase. Table 2 lists the salient structural features of this cluster. It consists of a filled first solvation shell with four solvent water molecules, each linked linearly to the central ion by a single hydrogen bond.

Isomers	6I	6II	6III	6IV	6V
Structures					
ΔH _n ²⁹⁸	-96.9	-97.6	-97.4	-96.1	-97.2
ΔG _n ²⁹⁸	-56.2	-57.6	-54.6	-53.0	-53.4
ΔG _n ¹⁷⁰	-73.7	-74.8	-73.0	-71.5	-72.2
Isomers	7VI	7VII	7VIII	7IX	7X
Structures					
ΔH _n ²⁹⁸	-108.4	-106.1	-108.2	-107.2	-107.7
ΔG _n ²⁹⁸	-58.7	-54.5	-56.3	-55.7	-57.0
ΔG _n ¹⁷⁰	-80.0	-76.7	-78.6	-77.8	-78.8

Fig. 5. Calculated enthalpies and Gibbs free energies (kcal/mol) of H⁺(H₂O) + (n-1)H₂O → H⁺(H₂O)_n using the Becke3LYP functional with the 6-31+G* basis set. The experimentally measured values (in unit of kcal/mol) of (ΔH_n²⁹⁸, ΔG_n²⁹⁸) are (-97, -56) for H⁺(H₂O)₆ and (-109, -62) for H⁺(H₂O)₇ (Ref. 30). The O and H atoms are denoted by O and o, respectively, and the ion core units are gray-shaded for clarity.

The two O-H⁺ bonds sharing the excess proton are essentially identical, with lengths of $r_{\text{OH}^+} = 1.205$ and 1.210 Å and an angle of $\angle\text{O-H}^+\text{-O} = 176.7^\circ$.¹⁵ Furthermore, the two molecules in direct contact with the proton are aligned in two intersecting planes (Fig. 1), yielding a C₂ symmetry, similar to that of the isolated protonated water dimer H₃O₂⁺.¹² Owing to this symmetry, the species has a simplified OH-stretching spectrum for both the ion core and the solvent molecules. No absorptions arise from the free-OH stretching of two-coordinated H₂O at ~ 3710 cm⁻¹ and the four vibrationally coupled bonded-OH stretches of the ion core are all resonant at the frequency region of ~ 3200 cm⁻¹ (see the calculated spectrum of **6II** in Fig. 4).

The search for H₃O₂⁺(H₂O)₅ found isomer **7VI**. At $n = 7$, three isomers (**7VI**, **7VIII**, and **7X**) were identified and they all belong to a five-fold ring family (Fig. 5). The structural identification is based upon the distinct vibrational features at 3500 - 3600 cm⁻¹ (Fig. 4), along with the energetics calculations given in Fig. 5.¹⁵ Fig. 6 displays the enlarged portion of the spectrum containing absorption bands of the characteristic free-OH stretch of three-coordinated H₂O at 3679 cm⁻¹ and the bonded-OH stretches of outer-shell water molecules at 3502, 3544, 3555 and 3581 cm⁻¹. The observation of these bands manifests the ring formation, which is favored by Gibbs free energy at $n = 7$ as a result of delicate balancing between enthalpy and entropy effects at 170 K. Fig. 6 compares the observed spectrum with the stick diagrams of **7VI** - **7X** provided by B3LYP/6-31+G*. In this comparison, we deliberately rule out the presence of **7VII** and **7IX** in the detection region, according to the predictions that they are significantly higher in energy than other five-membered ring isomers by >1 kcal/mol. The comparison clearly favors identification of isomers **7VI**, **7VIII** and **7X**, although a systematic deviation of ~ 40 cm⁻¹ between observations and calculations was observed for these four absorption bands. We have previously found a similar underestimation in the study of NH₄⁺(H₂O)₄₋₆,¹⁶ where the B3LYP/6-31+G* calculations underestimated the stretching frequencies of the bonded-OH groups involved in a ring by ~ 35 cm⁻¹. This underestimation originates, in part, from the omission of vibrational anharmonicities in the computations and, conceivably, also from the choice of a single factor (0.973) to scale the DFT-calculated frequencies. Taking this ~ 35 cm⁻¹ shift into account, the predicted frequencies agree simultaneously with that observed for these five bonded-OH stretches to within 10 cm⁻¹ (Fig. 6). The conformity, unlikely to be fortuitous, supports the assignment of these spectral features to the three ring-shaped low-energy isomers.

Of the five pentagonal structures depicted in Fig. 5, only isomer **7VI** contains an H₃O₂⁺ ion core. Two of the four $\angle\text{H-O-H}^+$ angles involved in this isomer are reduced by $\sim 3^\circ$ (Fig. 1), with respect to the corresponding angles in isomer **6II**, owing to the strain accompanied with the ring formation.¹⁵ Also in this cluster, a water molecule acting as a double proton acceptor (AA) is situated on the second solvation shell. The situation produces a distinct absorption doublet, ascribed to the symmetric and asymmetric stretches of the two vibrationally coupled, bonded-OH oscillators of the 1°H₂O(AD) molecules perturbed by the 2°H₂O(AA). This characteristic doublet is distinguished from other lower-frequency bonded-OH stretches, and it can be readily found at 3544 and 3555 cm⁻¹ in the spectrum (Figs. 2c and 6). Notably, these stretches are analogous in frequency, but complementary in the oscillator's structure, to that of the bonded-OH stretches of double-donor H₂O in neutral water clusters.^{23,26}

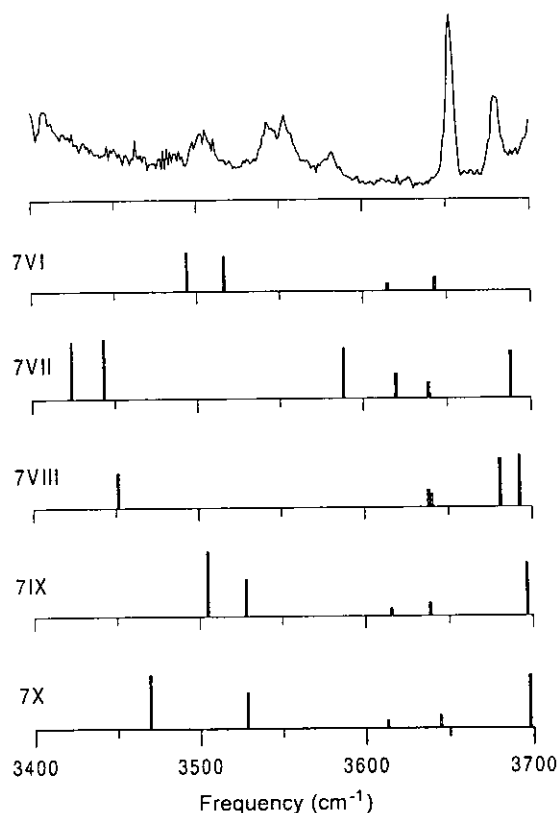


Fig. 6. Enlarged view of the OH stretching spectrum of H⁺(H₂O)₇ and its comparison with the *ab initio*-calculated stick diagrams for isomers **7VI** - **7X**. Note that the intensities of free-OH stretches (○) have been amplified by a factor of 5 for clearer comparison with that of bonded-OH stretches (■).

The H₅O₂⁺-centered five-membered ring (7VI) is structurally different than its neutral counterpart in (H₂O)₅.²⁷ It consists of a symmetrical, but not equilateral, planar pentagon with a contracted interoxygen separation of 2.418 Å for the side containing the excess proton (Fig. 1). Moreover, the cluster contains a 2°H₂O(AA) and two 1°H₂O(AD) molecules, whereas all the water molecules in the cyclic neutral pentamer are in the form of H₂O(AD), producing a chiral, slightly puckered ring. The unique flipping tunneling motions^{27,28} observed in (H₂O)_{2,6} are completely absent in this protonated water cluster.

CONCLUSION

This work provides compelling evidence for the existence of H₅O₂⁺-centered water clusters in the gas phase. The achievement is made possible by performing *ab initio* calculations and vibrational spectroscopic measurements on size-selected water clusters. Starting with protonated water dimers,¹² we have systematically investigated the spectra of H⁺(H₂O)_n as a function of cluster sizes and concluded that the H₅O₂⁺ cation can indeed survive in a symmetrical solvation matrix. This series of investigations is expected to help resolve the controversies concerning the dominance of H₅O₂⁺ or H₃O⁺ in aqueous acids.³⁴ The present investigations demonstrate that an excess proton in protonated water clusters can be either localized on one molecule or delocalized between two water units, depending sensitively on the solvation structures of this hydrogen-bonding matrix.

A natural extension of this experiment is to investigate protonated water clusters containing biologically related species.²⁹ How the interconversion between H₅O₂⁺ and H₃O⁺ cations plays a role in the proton transfer processes in biological macromolecules will be a focus of our future work.

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Key Words

Vibrational predissociation spectroscopy; *ab ini-*

tio calculations; H₃O⁺-centered water clusters; H₅O₂⁺-centered water clusters.

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