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Investigations on mixed water-clusters: Gas phase titration with cyclopentanone and identification of some isomers by time-of-flight mass spectrometry

Tahzeeb Momin[a], Sunil K. Ghosh[b], Ashok Bhowmick[a,*]

[a] *Technical Physics & Prototype Engineering Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India*
[b] *Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India*

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ABSTRACT

Mixed-clusters of water with cyclopentanone have been investigated using high resolution time-of-flight mass spectrometry. These clusters are synthesized in a gas-aggregation source at comparatively higher temperature. They contain water-cluster at the core and cyclopentanone molecules hydrogen bonded through ketone oxygen with the dangling OH available at the core. Thus these mixed-clusters may also be considered as the products of a titration in gas phase. The growth reaction reveals that all clusters are protonated. From the configuration of dimer and tetramer, it is suggested that the proton resides as an Eigen ion in the core. The protonated mixed-clusters containing six, seven and eight water molecules substantiate the hydronium contained hexa, hepta and octamer water-cluster structures predicted by $[\mathrm{KJ}(\mathrm{H_3O})^+]$ model calculations. For clusters with 9–19 water molecules, the core appears to have configurations that give less than the predicted number of dangling bonds. In large size clusters having more than 20 water molecules, the water-core appears to have open configuration like the melted structures obtained as a result of increase in temperature.

1. Introduction

Water-clusters in gas phase are studied extensively because of its tremendous implications in atmospheric [1–3] and biological [4–7] sciences as well as in the chemistry of aqueous proton [8]. The study has relevance because of its abundance in interstellar [9], polar stratospheric [10–12] (in the context of ozone hole over Antarctica) and noctilucent clouds [13–15], especially the dominance of the protonated form in ion composition of the D-region in ionosphere [16]. It is also significant because of the role in transfer of protons through proteins embedded in membranes [17–19], and migration of proton in liquid water [20–27].

The Bernal–Fowler ice-rule [28] has been applied most extensively since its inception in 1933 to explain the properties of water-clusters. According to this rule, there can be only one covalent and one hydrogen bond along any edge of the structure of a water-cluster. This leads to an availability of certain number of free OH-bonds in any structure that remain non-hydrogen bonded (NHB) or dangling [29]. The number of dangling bonds varies even between isomeric structures of a specific size. The availability of dangling bonds could be utilized to experimentally identify its structural configuration and stability.

A suitable second molecular species may be chosen to saturate the dangling bonds in a water-cluster. Mixed (or binary) hydrogen bonded molecular clusters are thus produced in the process where the proton donor acts as an acid and the acceptor as base [30]. Hence, the reaction might also be looked as 'titration' in gas phase [31–33]. The hydrogen bonded external species thus effectively works as an *in situ* probe to the structure. A count of the total number of second molecular species in any mixed-cluster assists to distinguish between the different calculated structures.

Mixed-clusters with water have been reported with acetone [34–38], ammonia [39], and trimethylamine (TMA) [40], etc. In fact, the report with TMA [40] was the first attempt to substantiate the predicted dodecahedral structure of 20/21 water-cluster by determining the number of dangling bonds. It is therefore interesting to carry out a systematic probe of the structures of other water-clusters through this method by adding suitable molecules to the dangling OH-bonds. The variation in the number of dangling bonds in different isomers of a specific size, as predicted in different calculations, could then be utilized to experimentally identify the particular isomeric form that is most abundant in natural synthesis. Thereby, the mixed-cluster structure may substantiate for a particular water-cluster structure under certain conditions. This is consequently an alternative non-spectroscopic approach to verify an isomeric structure predicted theoretically.

It has been shown from microwave spectroscopy that cyclobutanone forms stable hydrogen bond with water [41] and there is no secondary interaction as seen in formaldehyde–water [42]. We

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[*] Corresponding author.
E-mail address: ashokb@barc.gov.in (A. Bhowmick).

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choose the next member of the family, cyclopentanone to synthesize the mixed-clusters because, (i) cyclobutanone is a strained molecule, (ii) cyclopentanone is approximately 2D[1] in structure, and (iii) it has lower C=O stretching vibration (1740 cm^{-1} approx.) similar to that of acetone [34–38].

In this paper, the first investigation on water–cyclopentanone mixed-clusters is reported where cyclopentanone is the second molecular species. The abundance spectra of mixed-clusters obtained using high resolution time-of-flight mass spectrometry are analyzed to retrieve the number of cyclopentanone molecules bonded per water-cluster and thereby reveal the structural information. The stability of the mixed-clusters over a wide size range has been studied with respect to different predicted structures published in literature.

2. Experimental

The details of the reflectron time-of-flight mass spectrometer have been reported earlier [43–45]. To complete, we include a brief description of the experimental arrangement and the procedure followed. The spectrometer has an effective ionization volume of 2 mm^3 located within the gridless (extraction) ion-optics. This is a four quadrant four electrode system which makes a linear field gradient along the long axis (beam direction) [43]. Three of the electrodes are applied with DC extraction pulse (rise time ~50 ns with load) simultaneously (synchronizing the time) using a microprocessor and a desired ratio of amplitude is applied effecting maximum extraction. Ions are inserted through the short (cross) axis and are pulsed to inject orthogonally into the TOF. Only the positive ions are extracted in the present measurement. Ions are subsequently focused into the gridless reflectron using a five piece lens system and detected in turn using a channelplate based (Chevron) commercial detector (APTOF from Burle Electroptics, USA). The 500 ps resolution P7886 processing card (FastcomTec, Germany) is employed for data acquisition. As reported earlier, the spectrometer has a time-resolution greater than 40,000 with a dynamic-range larger than 2000 and picomole sensitivity [44].

A diagram and some details of the source are also described previously [44]. Briefly, the hybrid ion source is comprised of a tiny cylindrical (0.8 mm ID) volume of 50 μL made out of eight small coaxial copper pieces. This volume ends with a pointed needle having sharp 45° elliptically cut orifice (0.2 mm ID) and is placed very close (within 10 mm) to the TOF optics. The needle is electrically isolated and applied with a positive potential (1.0–1.2 kV). Entire volume (including that of the needle) essentially works as aggregation-reaction zone for gaseous species where the internal pressure is orders of magnitude higher compared to the typical base pressure within the ion-extraction chamber. The internal pressure is sufficiently large to reduce the mean free path to less than the dimension of the orifice (0.2 mm). The effective pumping speed of this volume is 8 μL/s (approx.) imposed by restrictions through successive differential stages in the spectrometer. The pumping condition creates a very long dwell time (in seconds) for particles inside the volume which assists in complete growth reaction between the interacting species. Clusters grown inside become well thermalized suffering through huge number of collisions with the carrier gas atoms during their long dwell and drift through the volume. The long period of dwell time is sufficient for any chemical reaction to complete and produce stable end products. Complete reaction or titration or solvation is therefore ensured. This is the major advantage in this source compared to synthesis in supersonic expansion that in general produces colder clusters. The conditions and time scale of events make our method comparable to a typical reaction in a flow reactor or collision induced diffusion (CID) cell.

The gaseous mixture has been prepared by bubbling the heterogeneous liquid mixture of 2 vol.% high purity water in distilled cyclopentanone (99.9%, Aldrich, USA) with 5.5 grade argon. Thus the approximate molar ratio of water to cyclopentanone is 1:10. The gas-mixture created through simultaneous evaporation is introduced into the aggregation tube to achieve the required pressure within the aggregation volume. The rapid evaporation of the solution from a small (25 ml) sealed container produces slightly colder (container temperature ~277 K) gas-mixture where the latent heat of vaporization mostly comes from the inert carrier gas. The mixture is inserted into the aggregation volume through the control of a precision needle valve. In our pressure limits, the flow at this juncture is effusive.

The experiments have been conducted by standardizing all instrumental parameters to unique values and keeping it unaltered throughout so that the pressure of the gas-mixture becomes the only independent controlling parameter. A set of trial and error leads to perform the final measurements at two different pressure values of the gas-mixture that turned out to be somewhat the beginning and end limits within the source instrumental obligations. The starting end has been decided by the lowest possible pressure limit at 2×10^{-2} mb where the number density is sufficiently low to reduce the collision probability and independent effects from water and cyclopentanone could be expected. Further lowering of pressure takes it beyond the detection limit. The pressure is gradually increased until a sizeable amount of well resolved cluster masses appear at higher mass values. The end-limit measurement is performed at an optimized 1.2 mb pressure in which maximum number of peaks is recorded at higher mass values. This has been the maximum permissible controlled instrumental limit in the source. But the evaporation rate did not augment with any further increase of the buffer gas pressure. The absence of cluster masses at lower pressures suggests of a threshold in the formation process that is decided by a critical number density. The measurements are carried out keeping the pressure and temperature conditions unaltered throughout and repeated with required preconditioning of the setup and sample. The acquisition has been done for a non-interrupted period of 7 h in each case minimizing the statistical error (0.5%).

3. Results and discussion

The mixed-cluster masses are identified following the binary nomenclature (n, m) that has been used for H_2O–TMA [40] and H_2O–NH_4^+ systems [39] where 'n' stands for the number of water molecules and 'm' for cyclopentanone. This has been used as the identity of the peaks shown in Figs. 1–3. The different groups of mixed-clusters as discussed in the following for $6 \leq n \leq 19$ are summarized in Table 1. The conversion of individual masses into the whole number binary format is advantageous in view of the fact that cyclopentanone (84.12 amu) and water (18.01 amu) has a mass ratio of 4.67 (approx.). So the possibility of degeneracy in total mass for singly charged species between, e.g., (n, m) and ($n+x$, $m-y$) would occur most approximately at a repetition of $x = 467$ and $y = 100$ (or vice-versa) which is beyond the domain of concerned mass range being reported here. This is another reason for choosing cyclopentanone to make mixed-clusters. All the detected masses are singly charged. Fig. 1 shows masses up to m/z 200 for both low and high pressure measurements as discussed in previous section. Fig. 2 shows the mixed-cluster masses obtained between m/z 560–800 only in the high pressure measurement. There are no peaks observed in the range m/z 200–560. Fig. 3 displays the peaks recorded in the third set of measurement carried out at iden-

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[1] Less puckered conformations.

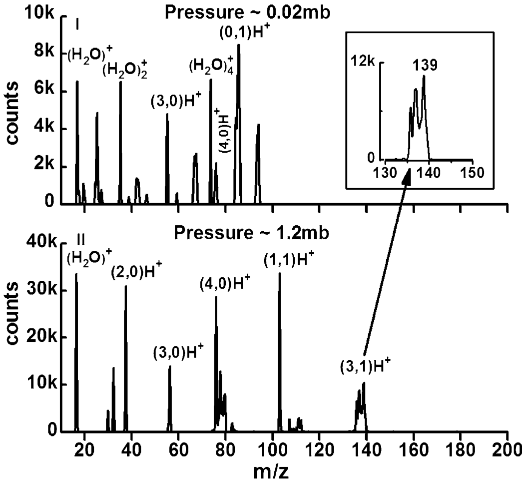

Fig. 1. Masses up to m/z 200 are shown in a comparative scale for two measurements. The masses are identified in binary form with two indices within parenthesis (n, m) where 'n' indicates the number of water molecules and 'm' is the number of cyclopentanone molecules respectively in a mixed-cluster. The mixed-cluster (3, 1)H^+ is shown separately at inset.

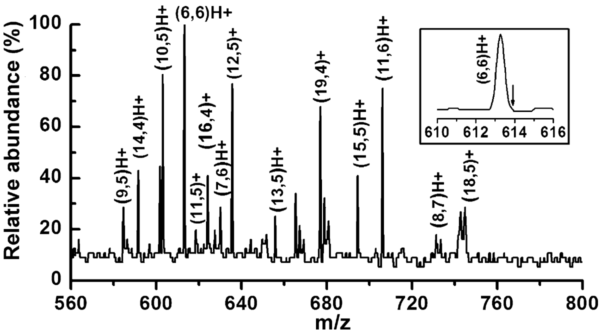

Fig. 2. Mixed-cluster masses in the size range $6 \leq n \leq 19$ are shown with their binary (n, m) identities as in Fig. 1. The size of the mixed-clusters is defined by the number of water molecules 'n' present in each cluster. The (6, 6)H^+ mixed-cluster peak corresponding to water-hexamer is also shown in larger scale at inset.

tical condition as in Fig. 2 but mass tuned to observe in the range beyond m/z 800. There is however no peaks recorded till m/z 2300 and all larger masses are confined in the range m/z 2300–2650. Maximum error in mass measurement throughout the entire range is ±0.3 amu (averaging over all uncertainties along X-axis).[2]

The ionization in our synthesis process is probably initiated by H_2O^+ created through field ionization and/or collision induced ionization. Also, simultaneous scan in a residual gas analyzer[3] held at about 70 mm apart from the TOF optics at mutually 45° upwards within the same chamber detects[4] huge amount of protons that is at least one order of magnitude higher than the normal background level of protons at 10^{-8} mb base pressure. Charge transfer reaction, $H^+ + H_2O \rightarrow H_2O^+ + H$, is hence probable [46]. In general, clusters are produced as neutrals in gas-aggregation process which are then ionized using an additional ionizing source. However, aggregation in an environment containing ions, like in a magnetron based gas-aggregation source [47], clusters are ionized by many charge transfer processes [48]. Clusters in our source are also charged through similar processes.[5] Different ion-molecule reactions [46] finally lead to produce the protonated species. Internal conversion with ionized water of the type, $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$ creates hydronium, leading to the formation of protonated cluster as, $H_3O^+ + (n-1)[H_2O] \rightarrow H^+(H_2O)_n$ in the process [46,49]. Frank-Condon like vertical ionization leading to an excited ion and subsequent return to ground state evaporating the monomer units like, $H_2O^+(H_2O)_n \rightarrow H_3O^+(H_2O)_{n-1-m} + mH_2O + OH$, is another possibility. Sufficiently long dwell time allows all possible internal conversion reactions to complete and finally produce the stable entities. Therefore, all the mixed-clusters detected are protonated in which the proton should reside as an Eigen ion.

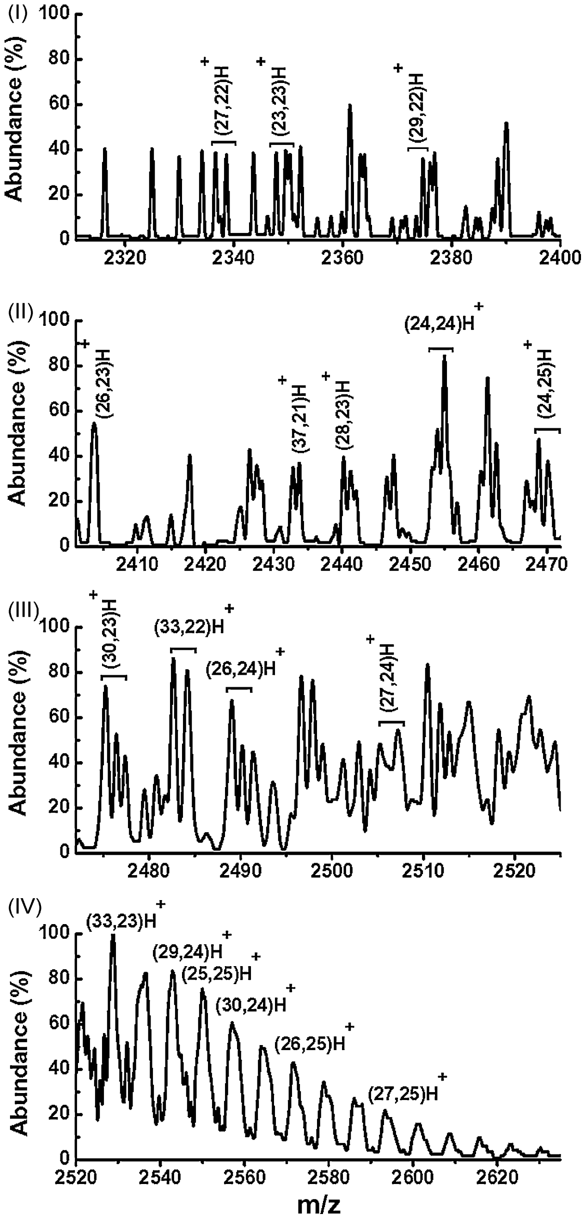

Fig. 3. Mass spectra of large mixed-clusters are shown dividing the mass range into four parts. Only the singly protonated peaks are identified. Each mass is marked with their corresponding isotopic peaks. Intensity ratio of isotopic peaks is highly influenced with contributions from other isotopes and possible fragments from larger masses.

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[2] This includes the very small nonlinearity effect in our ion-optics having extended ionization volume and is taken into consideration in calibration. This effect is practically negligible in lower mass range.

[3] RGA from Pfeiffer Vacuum GmbH, Germany, mass range 100 amu.

[4] Measurement is carried out keeping the RGA filament switched off.

[5] If an water molecule in a cluster is charged, it will undergo the intra-cluster conversion as depicted in Ref. [46].

Table 1
List of mixed-cluster masses shown in Fig. 2.

Mixed-clusters obtained (n, m)	Water (n)	Cyclopentanone (m)	Possible protonated water structure	References
(6, 6) H^+	6	6	[KJ(H_3O)$^+$]	[69]
(7, 6) H^+	7	6	[KJ(H_3O)$^+$]	[69]
(8, 7) H^+	8	7	[KJ(H_3O)$^+$]	[69]
Mixed-clusters obtained (n, m)	Water (n)	Cyclopentanone (m)	Closest neutral structures	References
(9, 5) H^+	9	5	TIP5P, MP2 ab initio	[96,102]
(10, 5) H^+	10	5	Ab initio, TIP5P	[96]
(11, 6) H^+	11	6	TIP5P & MP2 ab initio	[96,103]
(13, 5) H^+	13	5	TIP4P	[96]
(14, 4) H^+	14	4	–	–
(15, 5) H^+	15	5	TIP4P	[96]
(11, 5)$^+$	11	5	TIP4P	[96]
(12, 5)$^+$	12	5	–	–
(16, 4)$^+$	16	4	TIP4P	[96]
(18, 5)$^+$	18	5	TIP4P	[96]
(19, 4)$^+$	19	4	–	–

In order to analyze the results, it is pertinent also to look at the hydrogen bonding of water with the ketone (C=O) group in different molecules. The binding energy between water and acetone is calculated to be between 4.5 (min) and 5.6 (max) kcal mol^{-1} [50]. This is less than the strength of the hydrogen bond between two water molecules (6 kcal mol^{-1}) [51–52]. The protonated water-dimer in which single proton is shared between two water molecules has dissociation energy of more than 5 kcal mol^{-1} [30]. It has been shown that the strength in a hydrogen bond depends sensitively on the inter-atomic distances and angles subtended by respective bonds, e.g., C–O, O$\cdots$H and C$\cdots$H distances and ∠HCO angle [53]. Stronger hydrogen bonds are found to have relatively smaller distances and angle. The O$\cdots$H distance in H$\cdots$O–H between two water molecules is determined to be 1.74 Å from neutron diffraction studies. Neutron diffraction studies on the strength of hydrogen bonds in different amino acid side chains shows that water–water linkage has the smallest values of parameters of the hydrogen bond [53,54]. In water–acetone linkage the length of the hydrogen bond is calculated to be between 1.86 and 2.04 Å [50]. This length is determined to be 1.95 Å in cyclobutanone–water hydrogen bonding [41]. It is expected to be further longer in cyclopentanone–water bonding because cyclopentanone is more lipophilic by the presence of two CH_2. Larger length signifies that the hydrogen bonding between $H_2O\cdots C_5H_8O$ should be much weaker than $H_2O\cdots H_2O$ bonding. This situation is of particular advantage and suggests that, (i) a weaker cyclopentanone–water hydrogen bond will have an inferior tendency to form. That means, H–O$\cdots$H bonding would be more favored over C=O$\cdots$H and, (ii) lower strength of C=O$\cdots$H bond cannot perturb the H–O$\cdots$H bond. It implies that in a mixed-cluster configuration, water–water linkages should make a core structure and weaker ketone–water should be on the periphery. Further, in a three-coordinated DDA situation the ketone oxygen can make only one hydrogen bond unlike water that can make two hydrogen bonds and therefore, from the general coordination characteristics of water-oxygen in water-cluster structures, it should be observed that water–water connections can only construct the core. The bonded cyclopentanone molecules would situate at least 1.95 Å (or more) away from the water-core because of the length of C=O$\cdots$H hydrogen bond. Typical formation energy of 3 kcal/mol (on average) released per keto-water hydrogen bonding is insufficient to break the water–water bonding. Nevertheless, accommodating the larger cyclopentanone molecules might initiate some structural rearrangement.

The 'mixed-cluster' approach is limited to species in which there are atoms available to make a hydrogen or chemical bond. It is therefore specific in nature. In water, this scope has essentially originated due to the restriction imposed by ice-rule [28]. The dangling OH can only bond with molecular species capable of forming a hydrogen bond that is partially electrostatic and directional [55–56], e.g., cyclobutanone–water hydrogen bond is not along the sp^2 lone pair [41]. This specific chemical situation is different in character than situations for example, in physisorbtion which happens through van der Waals interaction and has long-range existing over all the atoms on surface [57]. Physisorbtion has also been used to probe the structures of some metal clusters [58–60]. It should be pointed out that the physical nature of this interaction makes it highly sensitive to the partial pressure of the adsorbent molecular species and for that matter, also to the exact thermal condition. There is no specific bonding in physisorbtion between a particular adsorbent atom/molecule with a specific constituent atom/molecule in the cluster. Nevertheless, in hydrogen bonded mixed-clusters, an effect due to steric hindrance might occur in case there are too many bonded second molecular species crowding onto one core structure.

At the lowest possible pressure (Fig. 1-I), protonated water-trimer (3, 0)H^+, tetramer (4, 0)H^+ and singly protonated cyclopentanone (0, 1)H^+ are separately detected with high intensities. This reveals that there is no bond formation between water and cyclopentanone at this condition. Moreover, larger bare water-clusters are also not produced at this situation. Interestingly, at the highest attainable pressure (Fig. 1-II), the single cyclopentanone (0, 1)H^+ peak is absent and a new mass appears at m/z 103 that corresponds to a (1, 1)H^+ molecular system. This formation suggests of a bonding between the ketone–oxygen and one hydrogen in water molecule (C=O$\cdots$H) and is the first evidence of hydrogen bonding [61] with the next higher member in cycloalkanone family.[6] The high abundance of this dimer (H_2O–C_5H_8O)H^+ reveals that large number of cyclopentanone molecules is actually converted into this mixed-cluster.

The growth reaction in our synthesis indicates that this protonated dimer should contain a hydronium. However, it is well known that protonated water-dimer is the Zundel ion [62–65]. Therefore, (1, 1)H^+ could possibly be a species resulted by replacing one water molecule by a cyclopentanone giving it a configuration like ($H_2O\cdots H^+\cdots OH_8C_5$). In a recent review [30] the central proton in $H_5O_2{}^+$ has been described to be actually an incipient hydronium with two water molecules and to be considered as a bound species

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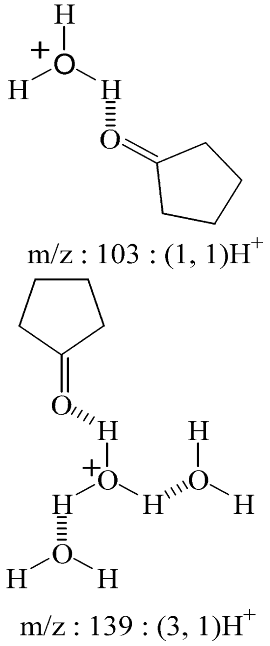
[6] Very recently, IUPAC has defined hydrogen bond as follows: "The hydrogen bond is an attractive interaction between a group X-H and an atom or group of atoms Y in the same or different molecule(s), where there is evidence of bond formation" [61].

rather than hydrogen bonded one. On the other hand, the proton in an Eigen ion has coordinate valence that essentially reorganizes the electron density and the dipole moment of this molecule is different from neutral water. In view of the fact that cyclopentanone has 1.8 times larger dipole moment than water [66], (1, 1)H^+ species is more likely to have $H_3O^+\cdots C_5H_8O$ configuration where the ketone oxygen makes a hydrogen bond with one of the three OH of the Eigen ion. Moreover, it is also to be noted that the strength of water–cyclopentanone hydrogen bond is comparable to that of the Zundel dimer $H_2O\cdots H^+\cdots OH_2$. Therefore, the former might effectively compete with the latter shifting the equilibrium to an Eigen ion based structure.

Interestingly, the above proposition is substantiated by observing the molecular species with *m*/*z* 139 amu that has approximately one-third the intensity of (1, 1)H^+ mass (shown separately in Fig. 1I inset). This species appears as if two additional water molecules are added to the (1, 1)H^+ dimer and thus making a (3, 1)H^+ mixed-cluster. Calculations[7] on protonated trimer, tetramer and pentamer water-clusters show that they contain an Eigen core [67–70]. Therefore, (3, 1)H^+ mixed-cluster could be viewed as one of the following two possibilities; (i) the protonated water-trimer which bonds with a cyclopentanone or (ii) a hydronium centered water-tetramer where one H_2O is replaced with a C_5H_8O. It is to be noted that both protonated water-trimer and tetramer are detected at high pressure measurements (Fig. 1-II) where (4, 0)H^+ is twice more abundant than (3, 0)H^+. Protonated water tetramer is highly symmetric in which single Eigen ion is completely solvated by three water molecules and thus it forms a very stable configuration to be more abundant. On the other hand, protonated trimer is a partially solvated Eigen ion with two water molecules. From infrared measurement Headrick et al. [70] perceived that there is a concentration of excess charge onto the two shared protons in protonated water-trimer. This in turn pulls the two solvating water molecules closer to the Eigen core producing a red shift of the OH stretch bands. It suggests that trimer is asymmetric and the left out dangling OH of the Eigen ion should have more affinity towards bonding. Bonding with a water molecule results into (4, 0)H^+ whereas bonding with a cyclopentanone results into the (3, 1)H^+ mixed-cluster. Besides, because water makes stronger hydrogen bond with water than with cyclopentanone, it is unlikely that a cyclopentanone can replace a water from (4, 0)H^+. Also to be noted that both (3, 0)H^+ and (3, 1)H^+ has comparable intensities (Fig. 1). Therefore, it is perceived that (3, 1)H^+ should essentially form through the bonding of one cyclopentanone onto protonated water-trimer. Eventually, in the final configuration the hydronium appears as the core of this mixed-tetramer that should rather be seen as a tetramolecular complex. However, single Eigen ion solvated by three cyclopentanone molecules and expected at *m*/*z* 271, is not observed in our case. Scheme 1 shows a drawing of (3, 1)H^+ formation.



Scheme 1.

3.1. Small mixed-clusters and different isomeric structures

Mixed-clusters in the range of 6–19 water molecules per clusters are shown in Fig. 2 and arranged in Table 1. Fourteen binary species could be identified in total. These masses are analyzed in the following in context of their calculated structures reported in literature.

3.1.1. The hexamer

Hexamer appears as protonated (6, 6)H^+ mixed-cluster. This should be viewed as the protonated water hexamer bonded to six cyclopentanone molecules. Clearly, there should have six dangling bonds available in the core (water-cluster) structure to accommodate six cyclopentanone molecules. No other mixed-cluster is observed that contains six water molecules with different numbers of cyclopentanone.[8]

Water-hexamer is important to be the transitory mass between planer and three-dimensional forms [71,72]. Cyclic hexamer is shown as a prominent morphology of liquid water and is a structural motif for ice [73,74]. High abundance in early mass measurements established it as a 'magic' cluster [75,76]. Experiments in liquid helium droplet [77–78] and in para-hydrogen matrix [79] showed that hexamer evolves with a cyclic structure and infrared studies confirmed its cyclic formation on nickel (1 1 1) surface [80]. Recently, signature of a cyclic hexamer is shown within neon matrix [72]. The 'book' isomer has been reported at 40–60 K [81] and the existence of a cage isomer has been reported at 5 K [82]. Computations predicted all different isomers for neutral hexamer in which the minimum energy structure varies on the method used [78,83–96]. These are cyclic (chair), boat, book, prism and cage.

The existing results on protonated water-hexamer show some discrepancies. Early density functional calculations [67,68] report both Eigen and Zundel type open isomeric structures. Putative basin-hopping global minimum using empirical Kozack-Jordon potential [KJ(H_3O^+)] (polarizable model) shows a cage structure containing five neutral water with one hydronium that has six dangling bonds [69]. Ab initio calculations predict many different open and closed isomeric configurations among which the Zundel ion centered non-cyclic structure is suggested to have the lowest energy [97]. Infrared (IR) measurement at 170 K and thermodynamic consideration reveal this open Zundel structure for hexamer [97]. IR measurement along with MP2/aug-cc-pVDZ level theory supports the Zundel motif. Further, the presence of Zundel proton is confirmed by identifying its characteristic IR transition [70]. This non-cyclic structure may be viewed as a completely solvated Zundel dimer with filled first solvation shell. It appears that the solvation shell does not perturb the core dimer. On the other hand, it can also be looked as two neutral trimers joined together with a

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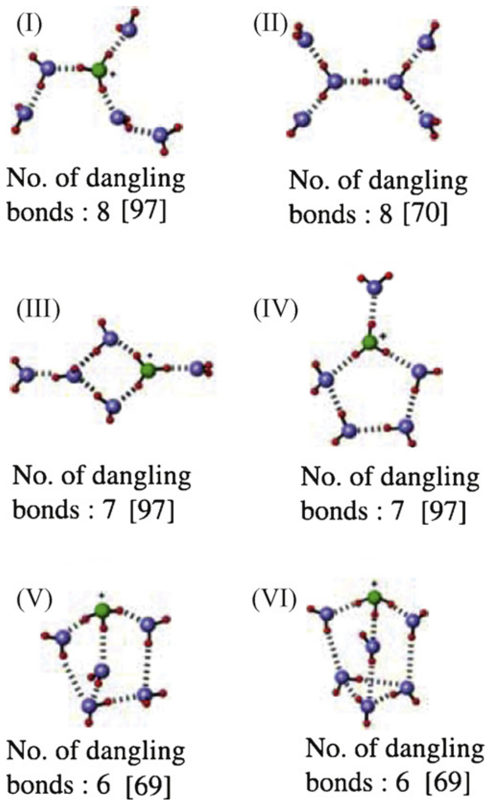
[7] These include, density functional [67,68], basin-hopping algorithm using KJ(H_3O^+) empirical potential [69], ab initio and MP2/aug-cc-pVDZ level [70], etc.

[8] The corresponding ^{13}C peak is indicated at inset of Fig. 2. However, the intensity is lower than 30%.



Scheme 2.

proton. This structure has eight dangling bonds in the second solvation stage. Some of the prominent isomers of protonated hexamer as obtained in different works are redrawn in Scheme 2.[9] Except the global minimum obtained through [KJ(H_3O^+)] empirical potential (Scheme 2-V) [69], none has six dangling bonds.

The formation of (6, 6)H^+ mixed-cluster in our case suggests six cyclopentanone bonded to the protonated water-hexamer. In case each dangling bond in the core water structure are bonded, then this formation supports the [KJ(H_3O^+)] structure. The hydronium contained formation is probable also in view of the growth motif in our synthesis procedure where both (1, 1)H^+ and (3, 1)H^+ smaller formations are revealed to be with hydronium. Hence, the formation of (6, 6)H^+ is an evidence of hydronium contained protonated water-hexamer. Perhaps, the Zundel-hexamer [70] is not stable as mixed-cluster in our synthesis because of (i) the comparatively higher temperature and (ii) possible reorganization in accommodating the larger cyclopentanone molecules.

3.1.2. *The heptamer*

The protonated heptamer appears as (7, 6)H^+ mixed-cluster that has six bonded cyclopentanone molecules. Clearly, in hydronium motif, this result once again substantiates the global minimum obtained in [KJ(H_3O)$^+$] structure [69]. However, the same contradiction with the observation of Zundel signature in IR data [70] also prevails here. Several ab initio optimized structures are considered for protonated heptamer in Ref. [97] that includes completely noncyclic to ring network configurations. The net-type structure with the Zundel cation is calculated to have the minimum energy. All of (I–XII) could in general be looked, as if an initiation of a 2D network. Hydronium contained structures XIII and XIV are compact 3D ones and both has six dangling bonds. The MP2/aug-cc-pVDZ calculated Zundel heptamer structure in support to IR data contains eight dangling bonds like in Zundel-hexamer [70]. The formation of (7, 6)H^+ once again reveals that in our mixed-clusters the excess proton resides as hydronium.

3.1.3. *The octamer*

Octamer is found as (8, 7)H^+ mixed-cluster which clearly shows a bonding with seven C_5H_8O molecules. Once again, this formation can be explained with [KJ(H_3O)$^+$] global minimum structure where proton is in the form of H_3O^+ [69]. The contradiction with the IR measurement [70] that shows Zundel signature remains in this case as well like in hexamer and heptamer. The ab initio optimized structures also show the Zundel ion (8II in Ref. [97]) contained structure as the minimum energy one. But, three-dimensional '8V' isomer with hydronium has seven dangling bonds. The (8, 7)H^+ mixed-cluster formation in our case once again sustains the hydronium motif of the excess proton in mixed-clusters.

The variation of our result from the IR [70,97] and ab initio [97] minimized structures that has the excess proton as Zundel ion should be understood from the difference in actual condition of cluster formation. The temperature in our case is much higher compared to their [70,97] synthesis procedures. The water-clusters in their experiments are sufficiently cold [70] or estimated to be 170 K [97]. In fact, Jiang et al. [97] suggested the formation of a five member ring having proton as a Zundel ion, as the result of a delicate balance between entropy and enthalpy effects. Recent understanding of the proton transfer intermediate $H_5O_2{}^+$ as embryonic H_3O^+ [30] suggest that formation containing Zundel ion should be conditional. Intra-cluster conversion in a stressed chemical environment at elevated temperature leading to fragmentation and evaporation like, $H_5O_2{}^+ \rightarrow H_3O^+ + H_2O$ might ensue in structural reorganization. In addition, as explained in the case of (1, 1)H^+ dimer, the competitive strength of hydrogen bonds between water–cyclopentanone and a Zundel configuration is likely to shift the equilibrium towards Eigen ion base structures. Besides, all Zundel structures have open configurations unlike the 3D closed cages shown in some ab initio structures [97] or in [KJ(H_3O)$^+$] structure [69] that the mixed-clusters corroborates with. The mixed-clusters in our case are species stable at sufficiently high temperature in a comparative scale and should therefore be considered as entropy minimized structures. Therefore, within the incongruity among IR measurement, ab initio, empirical and other model calculations in six, seven and eight molecule protonated water-clusters, our data could suggest that hydronium contained hexa, hepta and octamer are also probable to form as stable entities depending on the situation and course of growth.

3.1.4. *The nonamer*

Protonated nonamer appears as (9, 5)H^+ mixed-cluster, i.e., with five cyclopentanone molecules. The basin-hopping [KJ(H_3O)$^+$] global minimum [69] differs here which predicts a cage structure containing six dangling bonds. All structures obtained by QSS2 force field calculations over the [KJ(H_3O)$^+$] structure show more than six dangling bonds [98]. It is noteworthy that herein, IR measurement [70] shows a reemergence of Eigen signature suggesting that protonated nonamer is a hydronium contained formation even at cold temperature. This supports the growth motif in our synthesis. Interestingly, the neutral global minimum structures have been predicted to contain five dangling bonds in several calculations [71,96,99]. However, it is now well understood through many studies on protonated clusters that incorporation of proton cause restructuring and protonated clusters are a class by themselves. Neither the proton remains superficial onto a structure nor can reside hanging within. The variation in (9, 5)H^+ with the [KJ(H_3O)$^+$] global minimum structure might have several reasons

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[9] Large blue spheres represent oxygen, small red spheres for hydrogen and the hydronium oxygen is in green.

like, structural reorganization or an unsaturation due to steric hinderance where one of the dangling bonds remains non-bonded. However, these two situations are practically opposite to each other. In the first, it is inherently assumed that each available dangling OH should make hydrogen bond with one cyclopentanone. In the later, the [KJ(H_3O)$^+$] minimal structure [69] is considered to be the absolute.[10]

Even though the formation of this mixed-cluster proposes an isomeric form of the water-core having five dangling bonds as per the first scenario, this definitely cannot be the same isomer as predicted for the neutrals. Because, conversion of a water molecule into hydronium increases one OH that can remain bonded or dangling. That means with hydronium, either the edge or dangling bond increases by one. In order that the structure can have five dangling bonds, there should be 13 edges including the hydronium. To our knowledge, there is no ab initio or other sophisticated calculations for protonated nonamer. Any 2D network as proposed by Miyazaki et al. [100] would certainly have many more dangling bonds.

It is mentioned earlier that in cyclobutanone–water the H···O═C angle is found to be 100°. This means that 1.95 Å long hydrogen bond is not along sp^2 lone pair of the keto-oxygen [41]. Moreover, there is no secondary interaction between water-oxygen and any C_α atom of cyclobutanone which is located 3.01 Å away, well beyond the critical limit (2.5–2.7 Å) for this kind of interaction. Cyclopentanone being the next higher member in the cycloalkanone family, this nature should essentially remain the same. Therefore, the possibility of perturbation due to steric hinderance while making only five external hydrogen bonds is practically negligible. In other words, it is pertinent to consider that preferential bonding or unsaturation due to crowding does not happen in a structure containing only a few number of cyclopentanone molecules. Besides, also to mention that the mixed-clusters in our case are grown allowing a very long dwell time that certifies a complete reaction of any kind and there is no possibility of any transient situation like what might occur in the case of adiabatic expansion. Nevertheless, protonated mixed-nonamer manifests an interesting situation to initiate a theoretical challenge in view of Timothy Zwier's general comment on this class of clusters [101].

3.1.5. The 10-, 11-, 13-, 14- and 15-mer clusters

As sizes grow larger, the mixed-clusters do not corroborate anymore with the [KJ(H_3O)$^+$] scenario [69] in terms of total number of dangling bonds in each structure. The clusters detected are (10, 5)H^+, (11, 6)H^+, (13, 5)H^+, (14, 4)H^+ and (15, 5)H^+ showing the maximum number of bonded cyclopentanone molecules to be six. These clusters, except 14-mer, surprisingly agree in terms of number of dangling bonds with some calculated neutral global minimum structures [96,102,103]. In view of the previous discussion for nonamer, it should be suggested that these protonated mixed-clusters also have a reorganized water-core. However, it would be relevant to reiterate the note of caution sounded by Lin et al. [98] on the direct comparison of calculated results with experimental observations because in our case also the clusters are stable entities at a finite high temperature and thermal effects might populate the structures other than the true ground states. The QSS2 force field variation on the basin-hopping [KJ(H_3O)$^+$] structures for decamer and 11-mer [98] shows more dangling bonds than in their parent structures. Hodges and Wales [69] suggested the initiation of cage configuration beginning with decamer (i.e., $n = 9$ in their paper) where the hydronium connects two pentagonal rings. One isomer of 11-mer with QSS2 force field shows a hydronium connecting three pentagonal rings. Lin et al. [98] observed that cage-like structures are less stable than the structures with multiple rings under QSS2 model. Here, the structures assume more opened configuration, i.e., more like a 2D network and obviously the total number of dangling bonds increases as is also suggested by Miyazaki et al. [100]. The reduction in number of dangling bonds in the mixed-clusters thereby signifies an opposite tendency in which perhaps the water-core becomes more compact as a result of accommodating large cyclopentanone molecules or the large cyclopentanone molecules compress the water-core initiating a reorganization to assume a more compact 3D configuration. Hodges and Wales [69] calculated the relative stabilities up to a size of $n = 21$, for each pair of cluster with n and $(n - 1)$ water molecules to be (approximately) between 10 and 15 kcal/mol. Until a certain limit, these fairly stable structures should be able to cope up the chemical stress due to the external hydrogen bonds with cyclopentanones incorporating some modifications in the respective structures. A change in the angle of hydrogen bonds is more likely and thereby an increase in number of three-coordinated oxygen atoms within the water-core. A detailed calculation of modifications in small protonated clusters under stress could be useful to resolve this kind of issues important in view of the fact that water-clusters in upper atmosphere are more likely to be found as bonded to various organic wastes.

3.1.6. The 11-, 12-, 16-, 18- and 19-mer clusters

Five masses are detected apparently with no proton. These are identified as mixed-clusters (11, 5)$^+$, (12, 5)$^+$, (16, 4)$^+$, (18, 5)$^+$ and (19, 4)$^+$. It is worth mentioning here that at low pressure condition, the excited water-dimer [$(H_2O)_2$]$^+$ and tetramer [$(H_2O)_4$]$^+$ species are also detected. The apparent anomaly of no explicit proton in these mixed-clusters, may be understood from the ion-molecule reaction, $H_2O^+ + H_2O \rightarrow [(H_2O)_2]^+ \rightarrow H_3O^+ + OH$, causing a protonated formation. It suggests that the radical OH is not free but hydrogen bonded to H_3O^+ creating rather a whole unit ($H_3O^+ \cdots OH$). A mixed-cluster containing such a unit should not show an additional mass of proton. That means, for example, (10, 5)$^+$ contains eight neutral water molecules, one hydronium with OH besides five cyclopentanones whereas, (10, 5)H^+ has nine neutral water molecules and one hydronium besides five cyclopentanone molecules. Therefore, these mixed-clusters are also hydronium contained formations like the others except having one water molecule less than what the first number in the parenthesis quotes. The oxygen of OH can be either as AD (1d or one donor) or AAD (2a or two acceptors) but not ADD (2d or two donors) and it can add one dangling bond as an AAD only. However, a protonated cluster containing an OH should be energetically different compared to that having all water molecules. Hence, ideally, a comparison with even the [KJ(H_3O)$^+$] structures [69] are untenable.

3.2. Large mixed-clusters and polyhedral configuration

In a third set of measurement under identical experimental conditions (i.e., at 1.2 mb pressure), larger protonated mixed-clusters are mass tuned and detected. Size 20 onwards large water-clusters are suggested in literature to have a polyhedral cage (or clathrate) configuration. In fact, neutral cages are proposed even for size as small as $n = 12$ [104]. However, experimental studies on large protonated water-clusters are limited.

From the rules of polyhedral cage [29] it follows that in any closed polyhedral a maximum of ½ n oxygen atoms only can assume three-coordination and the other half oxygen atoms remain two-coordinated. A polyhedral however, may be complete in which all the edges has one covalent and one hydrogen bond (as per ice-rule) or incomplete, where certain edges are opened because of specific constraints. The number of dangling bonds increases at least by one when the polyhedral becomes open through any

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[10] In their paper Hodges and Wales [69] identified the clusters in terms of total number of neutral water molecules excluding the hydronium. In -mer terminology, it is the $(n - 1)$ entity in their description.

edge due to the rupture of a hydrogen bond, i.e., the number of two-coordinated oxygen atoms in the structure augments by one. To enumerate a general description depicting such a scenario, we define a quantity '*r*', as the 'relative-coordination', by the number of (AD-ADD/AAD) or (1d-2d) or the difference between the number of two-coordinated and three-coordinated oxygen atoms in a polyhedral. In the enclosed scenario, '$r = 0$' signifying a complete structure. When '$r = n$', all oxygen atoms are AD or two-coordinated. For all other intermediate values, there are higher numbers of AD (or 1d) oxygen atoms than in a closed polyhedral. Any value of '*r*' other than zero means an opened polyhedral and '*r*' changes in pair, i.e., 2, 4, 6, etc. Therefore, a situation in which $r = n$, means that the hydrogen bonds of one-third of the edges are broken. Hence, the value of '*r*' can be used as the identity of a polyhedral in order to reveal whether it is closed or to what extent opened.[11]

It is well known that for water-clusters the clathrate model has been proposed much before any abundance measurement was reported [105]. Clathrate structure originally proposed by Pauling [106] was based on the experimental evidences in crystalline hydrates as determined by Powell [107,108]. The extension of the clathrate model onto gas phase water-clusters was justified from the standpoint of energetic that it leads to more symmetry than an ice-like lattice [109,110]. Until now, the experimental evidence of polyhedral cage in gas phase water-clusters is rather limited. The XPS and XAS studies [111] only showed that there is no internal structure in large water-clusters as a whole. In the TMA–water mixed-cluster study [40], the 20/21 water-clusters have been investigated which is actually the most widely studied system so far [32,100]. However, reports on larger structures, for example tetrakaidecahedra ($5^{12}6^2$) onwards are very sparse. Their [40] results show a comparative higher abundance of (21, 10) whereas (20, 10) is indeed poorly formed. More interesting is the formation of (20, 11), (20, 12) and (21, 11) with additional TMA molecules accommodated in the cage. Infrared measurement observed that for sizes ≥21, the 2D net-type configurations are converted to 3D cage structures [100]. However, the theoretical prediction of Eigen moiety could not be established from infrared studies [32]. Recent temperature dependence investigations on $n = 21$ and 28 suggested that with the rise in temperature a partial melting takes place and some of the 2d oxygen atoms are converted into 1d ones [112]. Notably, under thermal perturbation the additional energy is utilized in breaking some of the hydrogen bonds and the system tends to achieve a lower symmetry by attaining lower coordination. The reduced stability in such conditions is reflected in its abundance. A conversion from $3 \rightarrow 2$ coordination yields one additional dangling bond. Clearly, melting of hydrogen bond makes the respective covalent OH dangling.

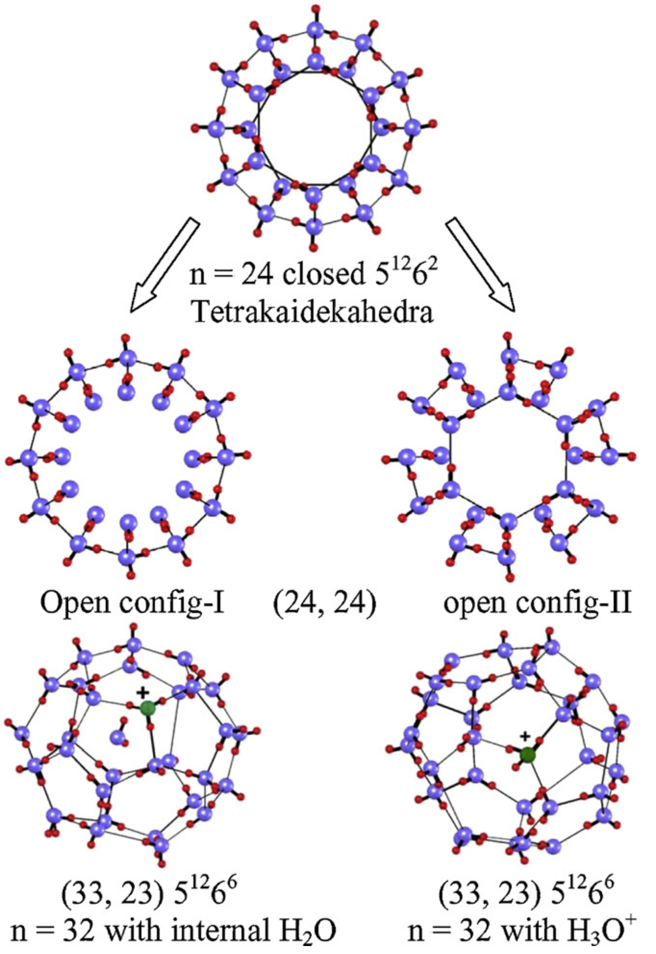

Fig. 4. Two possibilities of open structure configuration based on $5^{12}6^2$ cage are depicted to represent the observed (24, 24)H^+ mixed-cluster. In 'Open config-I' the bonds forming the top and down hexagons are absent and in 'Open config-II', one polar hexagon along with six equatorial ones are not there. The (33, 23)H^+ structure based on $5^{12}6^6$ cage has 23 dangling bonds and is open through nine edges. The surface hydronium is shown in two configurations. The neutral water is inside the cage in one picture whereas it has a provision to be bonded externally with the hydronium in the other.

The spectrum for the larger (>20) mixed-clusters in our case (Fig. 3) appears very complicated. This is because of isotopic effect, the presence of fragments from more larger masses and possibility of charge multiplicity. However, at least for singly charged (one proton) case, the mass range is still lower than any possible (*n*, *m*) degeneracy as discussed earlier. Extreme caution is followed in order to identify the singly protonated species. At least two peaks corresponding to the isotopes of carbon are identified for each singly protonated mass.[12] Seventeen different such mixed-clusters are marked in the range $20 < n < 40$. Some of them even occur with multiple numbers of cyclopentanone molecules. The formations corresponding to clusters containing 23–33 water molecules show 23–25 bonded cyclopentanone molecules per cluster. Among these, three masses occur with equal number of water and cyclopentanone (i.e., $m = n$). As pointed out before, for $m = n$ masses, all the water-oxygen atoms has to be two-coordinated (1d) because of hydrogen bonding to one carbonyl (C=O) in cyclopentanone. Under this circumstance, the structures have open configuration. These dilute structures are similar to that observed as a result of increase in temperature [112]. In analogy, it is perceived that some of the hydrogen bonds between water-oxygen atoms are absent in these mixed-cluster structures. In Fig. 4, two representative cases are illustrated (in drawing) for masses (24, 24)H^+ and (33, 23)H^+ as a guide to visualize the scenario. There are in fact many different possibilities that an open structure might be visualized depending on the absence of specific hydrogen bonds from a closed polyhedral. For ($n = m = 24$) tetrakaidecahedra, we depict two possibilities. In 'open config-I' the bonds forming the top and down (polar) hexagons are absent and in 'open config-II', one polar hexagon along with six equatorial ones are absent ($r = 24$). For (33, 23)H^+ mixed-cluster, based on $5^{12}6^6$ polyhedral, there are nine three-coordinated (2d) remaining, i.e., $r = 7$. It is to be noted that in mixed-cluster structures, each water-oxygen atom is ultimately three-coordinated (2d) because of external hydrogen bonding with ketone–oxygen (O=C). For example, in both (24, 24) and (33, 23), all the water-oxygen

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[11] It may be argued that when open, it is not a polyhedral anymore. However, we introduce this to portray the picture onto the same canvas. The value of '*r*' might be figured out just by knowing the composition of any mixed-clusters.

[12] However, the isotopic intensity distribution is overlapped by other contributions and does not show the theoretical expectations.

atoms are 2d; because of bonding with 24 cyclopentanone in (24, 24) and 23 cyclopentanone along with 9 intrinsic ones in the latter. In fact, similar occurrences are also seen in the results of water–TMA mixed-clusters to a minor extent in terms of (20, 12) formation[13] [40].

As Zwier pointed out, in protonated water-clusters, the position of the H_3O^+ ion, interior to the cage or taking up a surface site, is still not well resolved [101]. For size 18 water-cluster, Hodges and Wales [69] calculated the minimum structure containing a central hydronium whereas the rest of the cages are with one neutral water molecule inside. The formation of $n = 21$, both as neutral and protonated, has been explained by a model where a free water molecule is taken inside and the excess proton resides on surface [113]. This was finally confirmed by detailed ab initio studies recently [114,115]. The hydronium on surface has one excess dangling bond. The formation of (21, 11) water–TMA mixed-cluster can therefore be understood in terms of a hydronium on surface. Extending the same argument into our results in the size range of $22 < n < 38$, it is followed that if $(23, 23)H^+$ has an open $5^{12}6^1$ cage with one unbounded water molecule hydrogen bonded inside, the bonding with 23 cyclopentanone molecules suggests one H_3O^+ on surface bonded to an extra cyclopentanone molecule. Similar is the explanation for $(25, 25)H^+$ mixed-cluster viewing it as an open $5^{12}6^2$ polyhedral. Fig. 4 also depicts two alternatives for $(33, 23)H^+$ mixed-cluster visualizing it as an open $5^{12}6^6$ polyhedral ($r = 7$). In both the cases the excess proton locates on the surface. In one picture, the additional water molecule is unbounded inside the cage. Alternatively, it can also be outside the cage and bonded to the H_3O^+.

Looking at the entire size range of mixed-clusters it is seen that smaller ($9 < n < 19$) sizes mostly appear with less than the expected number of cyclopentanone molecules as per $[KJ(H_3O)^+]$ scenario whereas larger sizes show an excess of bonded cyclopentanones than expected under closed polyhedral configurations. The trend of formation for both small and large sizes should be consistent in a single process of growth. Bonding with maximum number of cyclopentanone as the sizes become larger suggests that at least the possibility of a non-bonded dangling bond due to steric hinderance is negligible even in smaller sizes. The open structures are likely because of accommodating large number of cyclopentanone molecules that also involves balancing through the dipole moments of the individual units. The core water structures sustain the chemical stress due to externally bonded molecules until a certain limit by assuming a more rigid configuration. However, the structures melt beyond that limit as sizes grow larger. The rapture gives more dangling OH and the opportunity for bonding with more cyclopentanone molecules. In reality, the complexity of the scenario in such large mixed-clusters can be sensed from the theoretical studies [29] reported for different isomeric configurations in polyhedral structures depending only on the orientation of the dipole moment of water molecules. Therefore, the actual structures of mixed-clusters are bound to have distortions due to many complexities that may be a theoretical challenge. Nevertheless, the new results in this study of a wide range of protonated mixed-clusters contribute in developing the understanding of water-clusters under stressed environment. Since gas-aggregation technique can replicate the conditions in upper atmosphere in laboratory scale, this study has implications in atmospheric applications.

4. Conclusion

Hydrogen bonded protonated mixed-clusters of water with cyclopentanone have been studied using high resolution time-of-flight mass spectrometry. From the analysis of their mass abundance we find,

1. The water-clusters are capped with cyclopentanone molecules which are bonded through the ketone oxygen with the dangling OH available in the water-core.
2. All mixed-cluster contains a hydronium.
3. The dimer forms as $(1, 1)H^+$ and tetramer as $(3, 1)H^+$ mixed-clusters. Hexamer, heptamer and octamer substantiate the predicted hydronium contained water-cluster structures given in $[KJ(H_3O)^+]$ model calculations.
4. Sizes containing $9 \leq n \leq 19$ water molecules appear to have a compact core configuration with lesser number of dangling bonds than suggested in $[KJ(H_3O)^+]$ calculations.
5. Water-core structures in larger ($n > 20$) mixed-clusters are perceived to have open configuration like the melted structures seen as an effect of higher temperature.

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