Water Clusters

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Proton Transfer in Ionic Water Clusters**

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Current works in cluster chemistry focus on extrapolating information on bulk properties from gas-phase cluster experiments.[1–3] Concerted proton transfer by the Grotthuss mech-

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anism[4,5] is a key step in aqueous reactions, especially in acid–base chemistry. This process has recently been studied in bulk solution by time-resolved spectroscopy[6] as well as ab initio molecular-dynamics simulations.[7–9] Understanding the conditions for the occurrence of proton transfer in finite clusters is of paramount importance for our qualitative picture of the chemistry of water clusters and their relation to bulk aqueous solution.

It may be expected that protons can wander freely between oxygen atoms in protonated water clusters, as infrared spectroscopic studies[10] of $H(H_2O)_n^+$ indicate the presence of both the Eigen ion (H_3O^+) and the Zundel ion ($H_5O_2^+$) in isomeric clusters with similar energies and sizes. Honma and Armentrout have recently shown that thermally activated proton transfer occurs in the reaction of $H(H_2O)_n^+$ ($n = 1$–4) with D_2O.[11] However, it is not known whether proton transfer occurs in clusters such as $(H_2O)_n^-$ and $O_2(H_2O)_n^-$ that do not contain an excess proton. In solution, proton transfer leads to the formation of H atoms from solvated electrons,[12] and HO_2 radicals from superoxide ions.[13] Recent works by Kuo et al.[14] on neutral $(H_2O)_{20}$ and by Sobolewski and Domcke[15] on $(H_2O)_n^-$ have shown that zwitterionic structures containing an H_3O^+/OH^- ion pair are local minima on the potential-energy surfaces of water clusters. Population of these zwitterionic isomers in an experiment would imply proton transfer. Herein, we present a mass-spectrometric study of the reactions of D_2O with ionic water clusters of the types $H(H_2O)_n^+$, $(H_2O)_n^-$, and $O_2(H_2O)_n^-$, which reveals that only within $H(H_2O)_n^+$ are the isotopically scrambled HDO molecules formed. This result indicates that no autoprotolysis occurs in small clusters of the types $(H_2O)_n^-$ and $O_2(H_2O)_n^-$, and renders the formation of the zwitterionic structures unlikely.

The presence of proton transfer—or lack of it—may be probed chemically by observing isotopic scrambling in mixed $(H_2O)_m(D_2O)_nX$ clusters (X denotes a charge carrier, in our case a proton, an excess electron, or a superoxide ion). In a mass-spectrometric experiment, the loss of HDO from a mixed cluster leads to a characteristic change of the cluster mass and thus serves as direct proof of isotopic scrambling and HDO formation.

We treated $H(H_2O)_n^+$, $(H_2O)_n^-$, and $O_2(H_2O)_n^-$ with gaseous D_2O in the ion trap of a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer, where the cluster temperature is determined by the interplay of radiative heating by room-temperature black-body radiation and evaporative cooling.[16–20] Recently identified chain, net, and cage structures of protonated water clusters[21,22] represent the structural motifs of energetically low-lying isomers. Since the clusters were continuously heated in our experiment to their dissociation limit, their internal energy was sufficient to form a large number of different isomers. The clusters collide with molecules of the reactant gas at a rate of $3\,s^{-1}$, which leaves ample time between collisions for rearrangement of the hydrogen bonds.

A nearly random distribution of clusters with even and odd nominal mass was obtained after the exchange of only a few water molecules within $H(H_2O)_n^+$ (Figure 1a), which provides clear evidence for isotopic scrambling. In the presence of protons, the conversion of D_2O into HDO [Eq. (1)] can proceed as illustrated in Scheme 1.

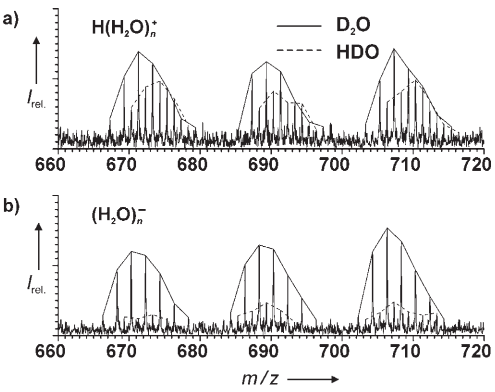
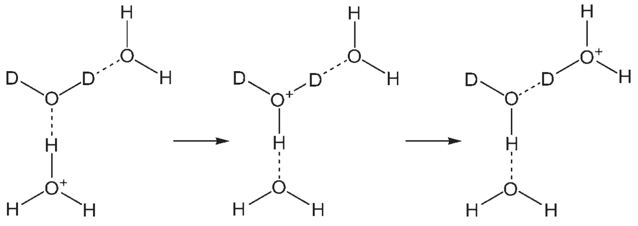


Figure 1. Sections of the mass spectra of the products of the reaction of $H(H_2O)_n^+$ (a) and $(H_2O)_n^-$ (b) with D_2O after 1.4 s (which corresponds to about four collisions with the reactant gas). a) Rapid rearrangement of hydrogen and deuterium in the protonated water cluster leads to formation of HDO, which can be lost by evaporative cooling or exchanged in a collision, thus changing the cluster mass from odd to even. After four D_2O molecules have been exchanged, clusters with odd (solid line) and even (dashed line) nominal mass are already randomly distributed. b) Solvated electrons undergo sequential exchange of H_2O with D_2O without formation of HDO (solid line). The minor amounts of species with odd nominal mass (dashed line) result from the HDO content of the D_2O reactant in the vacuum chamber and the natural deuterium content of the water clusters. The mass window shown covers $n = 37$–39.

$$H_3O^+ + D_2O \rightarrow H_2O + HD_2O^+ \rightarrow H_2DO^+ + HDO \qquad (1)$$



Scheme 1.

Proton transfer by the Grotthuss mechanism will quickly randomize H and D atoms within the cluster, thus forming a significant fraction of HDO molecules. Consequently, HDO species can also be lost by evaporative cooling, which changes the cluster mass from odd to even, or vice versa.

For comparison, we repeated the experiment with water cluster anions ($(H_2O)_n^-$; Figure 1b) as well as with hydrated superoxide ions ($O_2(H_2O)_n^-$). The efficient exchange of D_2O for H_2O and gradual deuteration of the clusters were also observed in this case. Such exchanges [Eq. (2)] result in increases of the cluster mass in increments of two mass units.

$$(H_2O)_{n-m}(D_2O)_m^- + D_2O \rightarrow (H_2O)_{n-m-1}(D_2O)_{m+1}^- + H_2O \qquad (2)$$

Clusters with even mass were present almost exclusively after the same reaction time as that in Figure 1a, which indicates that isotopic scrambling and proton transfer processes do not occur in water-cluster anions or hydrated superoxide ions in their electronic ground state. The minor contribution of odd-mass clusters in Figure 1 b is attributed to HDO, which was present as a contamination in the reaction gas.

To verify that HDO impurities were indeed responsible for the odd-mass clusters, we treated $(H_2O)_n^-$, $O_2(H_2O)_n^-$, and $H(H_2O)_n^+$ with D_2O for 3.6 s and removed the HDO-containing clusters from the ICR cell by resonant excitation. This selection worked well for $(H_2O)_n^-$ and $O_2(H_2O)_n^-$, whereas for $H(H_2O)_n^+$, the HDO-containing peaks reappeared even during mass selection (Figure 2 a,c,e). After an additional 1.6 s, the $(H_2O)_n^-$ and $O_2(H_2O)_n^-$ mass spectra consist exclusively of even-mass species (Figure 2 b,d), whereas the mass spectrum of the $H(H_2O)_n^+$ reaction products shows an almost statistical distribution of clusters with odd and even mass (Figure 2 f). This mass-selection experiment allows unambiguous discrimination between clusters in which proton transfer occurs and those in which it does not, thus removing the uncertainty introduced by the HDO content of the reaction gas.

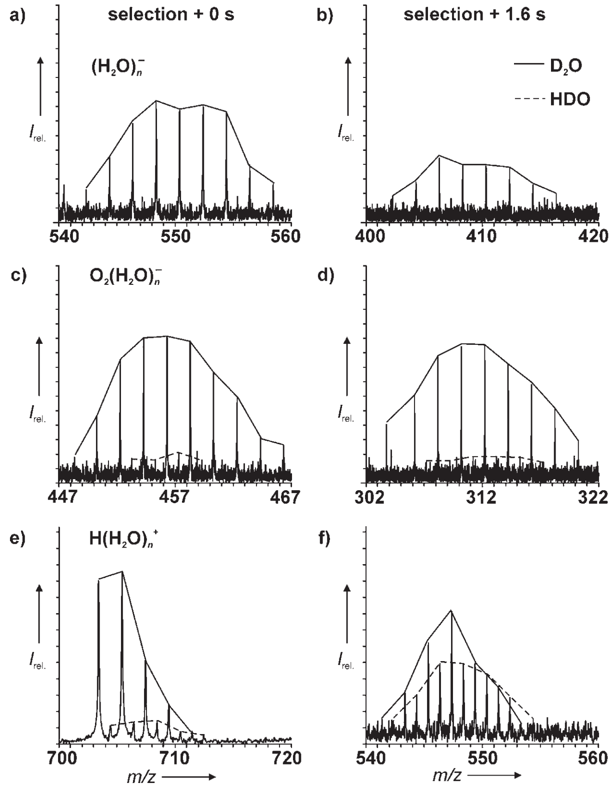


Figure 2. a), c), e) Sections of the mass spectra of the products of the reaction of $(H_2O)_n^-$, $O_2(H_2O)_n^-$, and $H(H_2O)_n^+$ with D_2O at a pressure of 2.5×10^{-9} mbar after 3.6 s; HDO-containing reaction products were removed by resonant excitation. For $(H_2O)_n^-$ (a) and $O_2(H_2O)_n^-$ (c), the selection is almost complete, whereas for $H(H_2O)_n^+$ (e), HDO formation is so efficient that even-numbered mass peaks (dashed line) reappear even during the removal. b), d), f) After an additional reaction delay of 1.6 s, there is still no sign of HDO formation for $(H_2O)_n^-$ (b) and $O_2(H_2O)_n^-$ (d), whereas for $H(H_2O)_n^+$ (f), a statistical distribution of odd- and even-mass species is reached. The intensity loss of $(H_2O)_n^-$ in (b) is due to electron detachment. Cluster sizes shown are a) $n=30$, b) $n=22$, c) $n=23$, d) $n=15$, e) $n=39$, and f) $n=30$.

This absence of proton transfer is in line with the stability of the solvated electron in $(H_2O)_n^-$ on a time scale of many seconds;[23] in contrast, its lifetime in bulk aqueous solution is less than 100 µs.[24] The elimination of atomic hydrogen as a consequence of the recombination of the electron with a proton is not observed in gas-phase water-cluster anions.

Evidently there are significant differences in the long-term dynamics of the two types of clusters in the size range studied: $(H_2O)_n^-$ and $O_2(H_2O)_n^-$ ions are correctly described as a network of hydrogen-bonded water molecules with an excess electron or superoxide ion, in which zwitterionic structures are not formed even transiently. Protonated $H(H_2O)_n^+$ water clusters are acidic nanodroplets in which the O−H bonds are constantly rearranging by the Grotthuss mechanism.

Experimental Section

The experiments were performed on a modified Bruker/Spectrospin CMS47X mass spectrometer equipped with an Apex III data station and an external laser-vaporization source.[25–27] Hydrated electrons ($(H_2O)_n^-$), protonated water clusters ($H(H_2O)_n^+$), and hydrated superoxide ions ($O_2(H_2O)_n^-$) were produced by laser vaporization[28,29] of a solid zinc target with the 5-ns pulse of a frequency-doubled Nd:YAG laser (Continuum Surelite II, 10 Hz, pulse energy 5 mJ), followed by supersonic expansion of the hot plasma entrained in a 50-µs helium pulse which was seeded with traces of water, and, in the case of $O_2(H_2O)_n^-$, O_2. The cluster ions formed were transferred by a series of electrostatic lenses through four stages of differential pumping, decelerated, and stored in the ICR cell. Starting distributions of water clusters typically contained 40 to 60 water molecules. The reactant D_2O (Aldrich, 99.9 % deuterium content) was degassed by three freeze–pump–thaw cycles and was admitted into the ultrahigh-vacuum region of the ICR cell through a leak valve, thus raising the base pressure from 2×10^{-10} to 9.6×10^{-9} mbar. The reaction was monitored by taking mass spectra after varying delays. Because the filling of the cell takes up to 2 s, the reaction had already proceeded to some extent at a nominal time of 0 s.

Although D_2O with a deuterium content of 99.9 % was used, the reaction products as well as an electron-impact spectrum of the reaction gas indicated that 5–10 % HDO was present in the ultrahigh-vacuum region. This HDO is formed by H/D exchange between the D_2O molecules and hydrogen atoms present on the stainless steel, copper, gold, glass, and polymer surfaces of the apparatus. To minimize this effect, the apparatus was conditioned by keeping D_2O present for several days, with repeated heating and cooling cycles. This HDO content is responsible for the peaks with odd nominal mass shown in Figure 1 b. Both spectra shown in Figure 1 were measured within one hour, during which time the D_2O pressure was kept constant, and the HDO content did not change.

Owing to black-body radiation[16–20] and collision-induced dissociation, the clusters lose water molecules one after the other. For clusters with $n \leq 30$,[23] electron detachment competes with water loss for the $(H_2O)_n^-$ species, and their intensity is lost in this size range. Selection of individual cluster sizes is thus not possible because of the gradual shrinking of the clusters. Although there is no evidence for cluster-size effects in the studied mass range, subtle size effects cannot be ruled out.

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