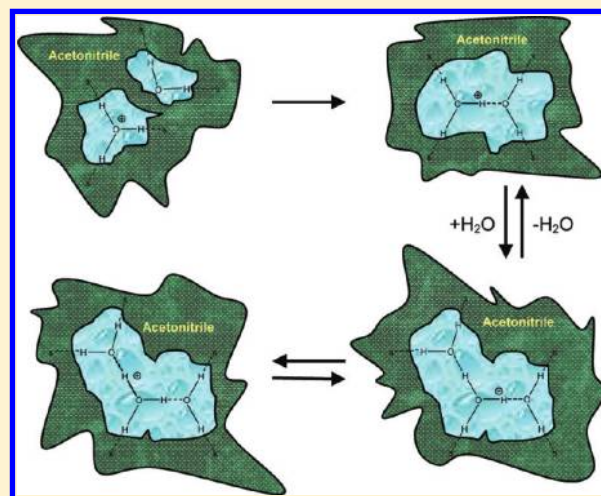


Apparent Stoichiometry of Water in Proton Hydration and Proton Dehydration Reactions in CH₃CN/H₂O Solutions

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ABSTRACT: Gradual solvation of protons by water is observed in liquids by mixing strong mineral acids with various amounts of water in acetonitrile solutions, a process which promotes rapid dissociation of the acids in these solutions. The stoichiometry of the reaction $\text{XH}^+ + n(\text{H}_2\text{O}) = \text{X} + (\text{H}_2\text{O})_n\text{H}^+$ was studied for strong mineral acids (negatively charged X, X = ClO₄, Cl, Br, I, CF₃SO₃) and for strong cationic acids (uncharged X, X = R⁺NH₂, H₂O). We have found by direct quantitative analysis preference of $n = 2$ over $n = 1$ for both groups of proton transfer reactions at relatively low water concentrations in acetonitrile. At high water concentrations, we have found that larger water solvates must also be involved in the solvation of the proton while the spectral features already observed for $n = 2$, $\text{H}^+(\text{H}_2\text{O})_2$, remain almost unchanged at large n values up to at least 10 M of water.



I. INTRODUCTION

Solvation of the proton, H^+ , by water in biological and chemical systems is a fundamental process of well acknowledged importance.^{1–12}

Modern discussions of proton solvation by water in bulk water^{11,13–17} have been greatly influenced by the classic studies of Eigen^{18,19} and Zundel^{20–25} who have each highlighted the importance of a specific proton solvate in water. These have been the protonated water tetramer, the “Eigen” cation, H_9^+O_4 ^{26–30} and the protonated water dimer, the “Zundel” cation, H_5^+O_2 .^{31–79} The protonated water cations have been extensively explored both experimentally and theoretically.^{80–100}

The fluxional nature of the aqueous proton in pure liquid water has posed a fundamental drawback in the quest for elucidating the smallest number of water molecules which may be considered most significant in solvating the proton.^{3,10,34,39}

Pines and Fleming^{101–103} used protonated 1-aminopyrene, a strong cationic photoacid with pK_a^* of about 0.5,^{101–107} and reported in 1991¹⁰¹ that the partial order of the reaction $\text{R}^+\text{NH}_3 + n(\text{H}_2\text{O}) \rightarrow \text{RNH}_2 + (\text{H}_2\text{O})_n\text{H}^+$, where R⁺ is an electronically excited pyrene residue, is higher than 1 in water concentration for small concentrations of water in acetonitrile but did not elaborate on this observation.^{101–103}

In this contribution we have made acetonitrile our solvent of choice in order to investigate the stoichiometry of water in the proton transfer reaction to water and from water to a base while water concentration was kept low enough so to be considered a solute in acetonitrile.

The advantages of using acetonitrile/water solutions for studying protonated water solvates in the liquid were first utilized by Kolthoff and Chantoni^{108,109} and are summarized below:

First, acetonitrile is an aprotic nonassociating solvent which mixes in all proportions with water to form highly polar solutions. This enables rich acid–base chemistry in acetonitrile/water solutions.^{110–119}

Second, liquid acetonitrile is a very weak Brønsted base, with basicity much weaker than the Brønsted basicity of H₂O in acetonitrile.^{108,109}

The very weak basicity of CH₃CN ensures that it is not directly protonated to form CH_3CNH^+ in strong-acid solutions in the presence of water even at trace concentrations of water.^{110,120} It follows that in the event of protons introduced into acetonitrile/water mixtures by the dissociation of strong acids, the core solvation of the proton is practically in the form of $(\text{H}_2\text{O})_n\text{H}^+ \cdot \text{acetonitrile}$.^{110,120}

Third, mineral acids such as perchloric acid (HClO₄) and triflic acid (CF₃SO₃H) are strong acids in acetonitrile and practically completely ionize in acetonitrile/water solutions from about 1:1 molar ratio of H₂O:acid.^{111–113}

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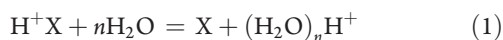
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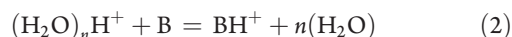
In addition, the acids may be quantitatively titrated in water/acetonitrile solutions by suitable Brønsted bases. With vanishing concentrations of water, the degree of ionization of these acids may be independently measured in acetonitrile by monitoring vibrational markers of the intact acid or its conjugated base. We have also found out that the somewhat less strong halogen acids such as HCl are also ionized in acetonitrile in the presence of a moderate excess of water, i.e., $[\text{H}_2\text{O}]/[\text{HCl}] > 3$.

Fourth, as we demonstrate in this study, the concentration of water in acetonitrile may be quantitatively determined by monitoring the optical density (OD) of the bending ($\text{H}-\text{O}-\text{H}$) vibration of the water monomer at 1635 cm^{-1} up to about a molar fraction of $\chi(\text{H}_2\text{O}) = 0.2$ where water begins to form microphases in acetonitrile.¹²¹ We believe that acetonitrile/water solutions allow the direct observation of a stepwise solvation of the proton by water in liquid solutions. A similar tactic for forming protonated water clusters in the liquid had been used by Stoyanov et al.^{90–96} using nonpolar solvents which do not mix with water and do not support the formation of “free ions” and in alcohols which unlike acetonitrile are protic and strongly mix with water.

In this study we have explored the apparent stoichiometry of the aqueous proton in acetonitrile/water solutions, n , for two types of proton transfer reactions



and



We have measured the OD of the 1635 cm^{-1} bending transition of the water molecule to probe the number of the unprotonated water molecules either introduced into or taken out of the acetonitrile solution for each hydrated/dehydrated proton. The two experiments, (1) and (2), probe two different but related processes in acetonitrile solutions and have complemented each other. As described below, the agreement between the two types of experiments has made it possible to determine the apparent stoichiometry of the hydrated proton in acetonitrile in a wide range of water concentrations.

In addition, we have also carried out kinetic measurements on the proton transfer reaction from photoacids to water in acetonitrile, similar to experiments reported by Pines and Fleming^{101–103} but using a different protonating acid which is commercially available in its anhydrous form.

II. EXPERIMENTAL SECTION

A. Materials. We used 1-APminopyrene (1-AP, Aldrich, 97%) after it was recrystallized from cyclohexane, anhydrous CH_3CN 99.8% (Sigma-Aldrich), 70% perchloric acid 99.999% purified by redistillation (Sigma-Aldrich), trifluoromethanesulfonic acid (“Triflic Acid”) 99% extra pure (Acros), hydrochloric acid 37% in water ACS reagent (Acros), hydrobromic acid 48 wt % in H_2O , $\geq 99.99\%$ (Sigma-Aldrich), and hydroiodic acid 57 wt % in H_2O , distilled, 99.99% (Sigma-Aldrich).

B. Absorption and Emission Spectra Measurements. UV–visible absorption experiments were carried out on double beam JASCO V-570 UV-vis-NIR spectrophotometer, with resolution of 0.5 nm. Experiments were performed with solvent blank subtraction.

The steady-state fluorescence spectra were recorded on a Cary Eclipse Varian spectrofluorometer. Monochromator entrance and exit slit widths were set at 2 nm. Data were collected every 0.5 nm. The excitation wavelength for the 1-AP molecule was chosen from its absorption spectrum near an absorption maximum, 310 nm. The overall concentration of the 1-AP was typically $2 \times 10^{-5}\text{ M}$. Prior to the fluorescence emission measurements 1-AP, a well studied cationic photoacid,^{101–103,107} was protonated on the nitrogen atom in the ground state. Two very strong mineral acids in various concentrations (5×10^{-3} to 0.35 M) HClO_4 and $\text{CF}_3\text{SO}_3\text{H}$ were used for the protonation of 1-AP in the ground state. All solutions were purged for 5 min with Ar before conducting the measurement of the fluorescence emission of protonated 1-AP in order to minimize fluorescence quenching by dissolved oxygen. The fluorescence spectra were collected at suitable pH at which no significant unprotonated 1-AP was present in the ground state. The absorption spectra of the protonated 1-AP molecules remained unchanged during the experiments.

C. Infrared Measurements. Steady-state IR spectra of simple mineral acids in CH_3CN were obtained with CaF_2 plates using several optical path lengths, determined by Teflon spacers, adjusted for the concentration of water. Jasco 6300 FTIR instrument was used with 4 cm^{-1} resolution, with constant N_2 flow to keep low water content in the surrounding atmosphere. Solution preparation was done in Ar atmosphere for the same reason, i.e., to accurately control the water content in the inspected solution.

III. RESULTS AND DISCUSSIONS

A. The Dissociation of Protonated 1-APminopyrene in Acetonitrile–Water Solutions as a Function of Water Concentration. We have repeated the experiment reported by Pines and Fleming^{101–103,107} using triflic acid as the protonating agent of 1-APminopyrene (1-AP) instead of the perchloric acid used originally to protonate the 1-APP molecule. In contrast to the commercial 70% perchloric acid, triflic acid is readily available as a pure anhydrous liquid and the acid is strong enough to completely dissociate in acetonitrile in the presence of about 1:1 molar ratio of water. This allowed much greater experimental flexibility than using commercial 70% HClO_4 which contained about 2.4 water molecules per each acid molecule. Figure 1A shows the steady-state emission spectra of the protonated 1-AP in CH_3CN as a function of the water concentration in the acetonitrile solution. The fluorescence band at 374 nm corresponds to the protonated species, and the band at the 425 nm corresponds to the unprotonated molecule. The emission of the neutral species of 1-AP was increased and the emission from protonated 1-AP was decreased when water was gradually added to solutions of protonated 1-AP with an isoemissive point at 405 nm, indicating an elementary two-state proton transfer reaction initiated by water. In Figure 1B we have compared the Stern–Volmer plot¹²² of this proton transfer reaction when using 99% triflic acid and when using 70% HClO_4 as the protonating agents of 1-AP. We observe a faster initiation of the proton transfer reaction when using 70% HClO_4 due to the water molecules introduced to the acetonitrile solution with the hydrous acid. We offer a simple explanation for this observation: Adding water to anhydrous triflic acid in acetonitrile when the acid is in very large excess over the 1-AP concentration causes the triflic acid to dissociate and protonate the water molecules while also protonating the much smaller concentration of the photoacid. The protonated water molecules

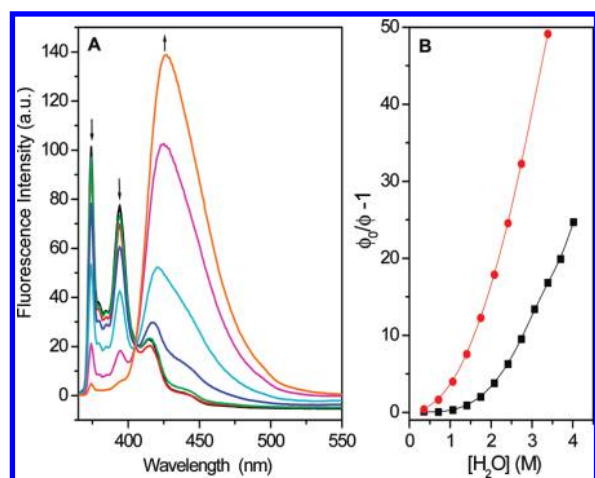


Figure 1. (A) The effect of adding water on the emission of 2.0×10^{-5} M 1-AP protonated in the presence of 0.35 M CF_3SO_3H (triflic acid) in acetonitrile. Arrows indicate increasing water concentration from 0 to 3.703 M. Black line, 0 M; red line, 0.358 M; green line, 0.712 M; blue line, 1.062 M; cyan line, 1.406 M; magenta line, 2.083 M; orange line, 3.703 M of water. (B) Stern–Volmer plots of the rise in the fluorescence intensity of 1-AP as a function of water concentration in acetonitrile measured at 374 nm following the proton transfer reaction of the photoacid: red line, using 0.35 M $HClO_4$ (70%) to initially protonate the photoacid in the ground state; black line, when using 0.35 M (99%) triflic acid. ϕ and ϕ_0 are the fluorescence intensities of 1-AP in presence and in absence of water, respectively.

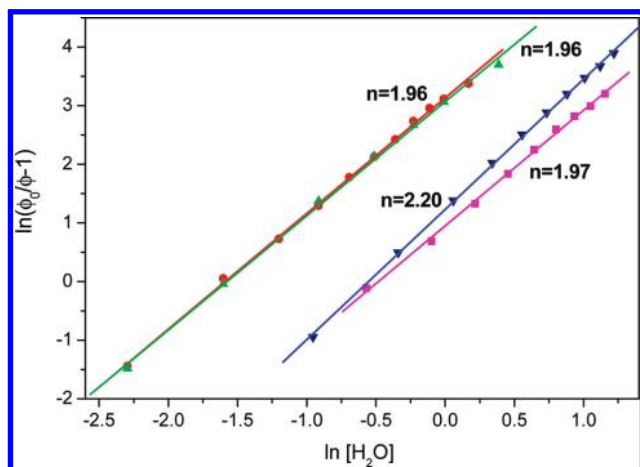


Figure 2. Stern–Volmer plots of $\ln(\phi_0/\phi - 1)$ vs $\ln([H_2O])$ after subtraction of 2.4 water molecules per a mineral acid molecule: red line, 1-AP protonated by 5×10^{-3} M $HClO_4$; green line, using 5×10^{-3} M triflic acid; blue line, 0.35 M $HClO_4$; magenta line, 0.35 M triflic acid as the protonating acids. The absolute proton dissociation rate (but not the slope) was found to depend on the acid concentration, becoming about 3-fold slower at the high concentration (0.35 M) of the acids. The correlation coefficients are $R = 0.999$ for all curves.

which have accepted a proton from triflic acid would not be available to accept an additional proton from the protonated 1-AP photoacid. Only when water concentration in the acetonitrile solution is in excess of the mineral acid concentration, rapid deprotonation of 1-AP may occur.

The dependence of the Stern–Volmer plot on the water concentration when using triflic acid and when using 70% $HClO_4$ becomes almost identical when one assumes that about 2.4 water

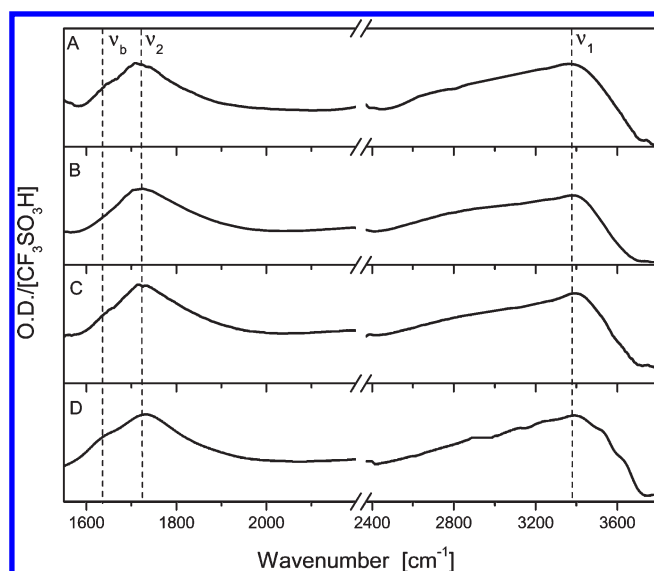
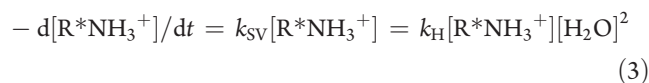


Figure 3. IR absorption spectra of CF_3SO_3H in CH_3CN measured in 50 μm cells in presence of water. The concentration of water was chosen so that the molar ratio $[H_2O]/[CF_3SO_3H]$ was kept about 2.5. From (A) to (D), the acid concentrations were 2.20, 0.56, 0.11, and 5×10^{-3} M. The absorption of pure acetonitrile was subtracted from the total absorption of the solution. The three broken lines mark the position of the 3 main absorption bands: ν_b , absorption band corresponding to the free water bending band (1635 cm^{-1}), ν_2 absorption band (1725 cm^{-1}) associated with the hydrated proton complex and ν_1 (3370 cm^{-1}) associated with the OH stretching vibration.

molecules (similar to the H_2O /acid molar ratio in 70% $HClO_4$ solutions) are needed to solvate the proton and the triflate anion in acetonitrile. These water molecules are not kinetically available as proton acceptors and were subtracted from the total concentration of water present in the acetonitrile solution.

It was tentatively suggested that a proton transfers in acetonitrile to water rapidly enough so to be observed within the excited-state lifetime of 1-AP only above a certain molecular size of water solvate.^{101–103,107} In order to determine the number of water molecules required for efficient proton solvation in acetonitrile, the emission spectra of protonated 1-AP in acetonitrile with various concentration of water was kinetically analyzed by the Stern–Volmer plots assuming water is the quencher of the fluorescence of protonated 1-AP. The Stern–Volmer analysis has clearly indicated (Figure 1B) that in the case of 0.35 M of 99% triflic acid the $\phi_0/\phi - 1$ plot remains almost unchanged up to about 0.7 M of water. Above 1 M of water there was a rapid increase in the $\phi_0/\phi - 1$ value. In the case of 70% $HClO_4$ the $\phi_0/\phi - 1$ value increases immediately upon further addition of water to the acetonitrile solution. The $\ln(\phi_0/\phi - 1)$ vs $\ln([H_2O])$ plots were taken for both acids at various concentrations. Linear dependence was obtained with slopes values around 2 (Figure 2). The results in Figure 2 reveal second-order dependence in the water concentration as if two water molecules are kinetically involved in the proton transfer reaction from the excited protonated 1-AP molecule, eq 3



Where k_{SV} is the Stern–Volmer rate constant of quenching the fluorescence of the photoacid by proton transfer and k_H is the

proton dissociation rate of the photoacid in acetonitrile/water solutions

$$k_{SV} = k_H[H_2O]^2$$

As shown in Figure 2, the slope of the Stern–Volmer plots was about 2 for both the triflic and perchloric acids after subtracting from the total water concentration 2.4 water molecules per each mineral acid molecule. These were the water molecules needed to solvate the protons that were introduced to the acetonitrile/water solutions by the self-dissociation of the mineral acids. We rationalize the need for reducing the concentration of water in the context of the Stern–Volmer plots by assuming that water molecules which have already solvated a proton become kinetically unavailable for accepting an additional proton from the $R^*NH_3^+$ photoacid and so are practically unable to participate in the nanosecond fast proton transfer reaction from the photoacid.

B. Quantitative Analysis of the Number of Water Molecules Strongly Interacting with the Proton in Acetonitrile/Water Solutions Using IR Absorption Spectroscopy. Acetonitrile as a pure solvent of high dielectric constant ($\epsilon = 37$) supports the partial dissociation into ions of many salts and of several strong mineral acids.^{101–103,107} However, ion pairing is much more important in acetonitrile than in water. In order to assess the importance of contact ion pairing in acetonitrile/water solutions, we have measured the IR spectra of triflic acid in acetonitrile in the presence of about 2.5 molecules of water per an acid molecule, which is in a small stoichiometric excess over an all $(H_2O)_2H^+$ composition. We have found only small changes in the IR absorption spectrum in the spectral range between 1500 and 3800 cm^{-1} when the concentration of triflic acid was diluted by almost 3 orders of magnitude from 2.20 M down to 5×10^{-3} M (Figure 3) where at the lowest concentration contact ion pairing of the form $(H_2O)_2H^+ \cdots O_3SCF_3$ ^{21,22,92} is expected to be much smaller than at the highest concentration of 2.2 M.

Two very broad absorption bands were observed corresponding to OH stretching vibrations at 3370 cm^{-1} , ν_1 , and to a transition associated directly with the hydrated proton at 1725 cm^{-1} , ν_2 . In addition, the normal bending vibration of water in acetonitrile at 1635 cm^{-1} , ν_b , is observed as only a much narrower small shoulder on the 1725 cm^{-1} band. The ν_b transition of free (i.e., not directly solvating H^+) water is most apparent at the lowest concentration we were able to measure, i.e., 5×10^{-3} M, which hints that at high dilutions of the protonated water solvates a small amount of water does not participate in directly solvating the proton and exists in acetonitrile as $(H_2O)_s$ while the protonated water solvates are mainly in the form of $(H_2O)_2H^+$.

We assign the proton and the 1725 cm^{-1} (ν_2) band to either the bending vibration of water molecules directly interacting with the proton or to a highly red-shifted stretching vibration of such a water molecule.⁸⁷ The ν_1 and ν_2 bands are superimposed on a very broad structureless absorption band spanning almost the full spectral range and clearly extending to below 1600 cm^{-1} . We also assign this spectral feature to the absorption of protonated water in acetonitrile akin to the Zundel continuum observed in the solutions of strong acids in pure water.^{20–25} In addition, the absorption of the bending transition at 1635 cm^{-1} (ν_b) of free water molecules that are not in close proximity to a proton becomes gradually apparent with the dilution of the acid in acetonitrile. These observations points to a rather robust core hydration of the proton in acetonitrile/water solutions which is made of an average of less than 2.4 water molecules per a proton.

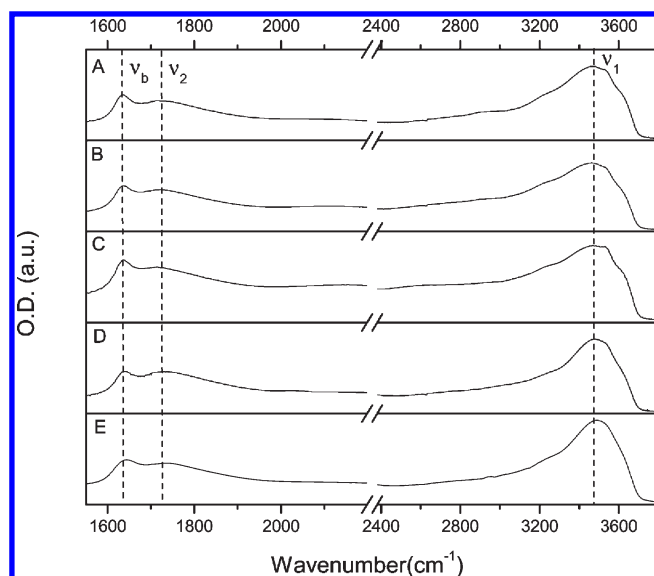


Figure 4. IR spectra, taken with a $50\text{ }\mu\text{m}$ cell, of several mineral acids in acetonitrile in the presence of water having similar water to acid ratios, $[H_2O]/[HA] = 5.3\text{--}6.0$: (A) hydriodic acid (5.3), (B) hydrobromic acid (5.5), (C) hydrochloric acid (5.4), (D) perchloric acid (5.9) and (E) triflic acid (6.0). The acid concentration was kept constant at 0.6 M, and the number in brackets is the water/acid ratio for a particular experiment. The absorption of pure acetonitrile was subtracted from all spectra.

We have conducted a second set of experiments where both the acids and the H_2O /acid ratio were varied as compared to the triflic acid experiment in order to further check the apparent small effect of the anion on the observed IR spectra of small water solvates hydrating the proton in acetonitrile (Figure 4). In this second set of experiments the IR spectra of several strong mineral acids were measured in the presence of a higher excess of water than the one used in the triflic acid experiment, H_2O /acid ratio of 5.3–6 compared to the 2.5 water/acid ratio used in the triflic acid experiment. The higher concentration of water was needed to induce full dissociation of the less-strong haloacids. At this higher H_2O /HA range a distribution of protonated water solvates is expected to be formed ranging between $n = 1$ and $n = 6$ depending on the concentration of the acid. All acids were measured at a concentration of 0.6 M in acetonitrile. All acid solutions have exhibited similar absorption bands to the one observed in triflic acid solutions in addition to enlarged absorption bands associated with the larger excess in water molecules (Figure 4). The hydrated proton absorption at about 1725 cm^{-1} (ν_2) was almost unaffected by the chemical identity of the anion. In addition, a very broad absorption band which is unevenly structured between 2800 and 3750 cm^{-1} dominates the spectra. This absorption band consists of red-edge OH stretching vibrations of water molecules directly interacting with the proton and of dominating (blue-edge) OH stretching vibration of water molecules further away from the proton which are in excess over the red-edge oscillators and peaking at about 3470 cm^{-1} (ν_1). In accordance with our spectral assignment, the bending transition of the excess water molecules not directly solvating the proton (free water molecules) has become clearly apparent and appears in Figure 3 as a clearly defined and relatively narrow absorption band at about 1635 cm^{-1} ν_b . We have observed this water band only when the ratio $[H_2O]/[HA]$ was higher than 2–2.4,

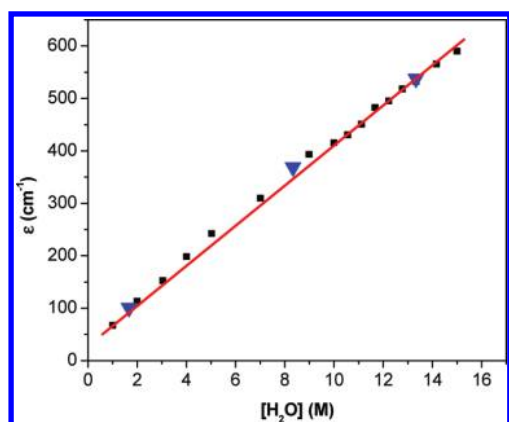


Figure 5. Calibration of the optical density of the H₂O bending mode (1635 cm⁻¹) with the concentration of water in acetonitrile: black squares, using 15 μm optical path length; blue triangles, using 10 μm optical path length.

depending on the acid and on the acid concentration. A closer examination of the OH stretching vibration band does show small changes as a function of the exact [H₂O]/[HA] ratio and to a lesser extent on the type of the anion. The small anion effect was found to be similar in magnitude to the anion effect on the OH stretching vibration observed for the corresponding salts of the acids in acetonitrile, LiClO₄, KClO₄, and KCF₃SO₃, in the presence of similar H₂O/salt ratios. We could not compare our haloacid measurements with the effect of their corresponding halide salts on the H₂O spectra because they did not dissolve well enough in the acetonitrile/water solutions that were under our examination. The effect of cations other than the proton on the IR spectra of water dissolved in acetonitrile was also checked at similar experimental conditions by comparing LiClO₄ with KClO₄ solutions. The halide salts were examined at much higher water contents to ensure ionization of the salts. Using an ATR absorption setup we were able to compare the effect of Li⁺, Na⁺, and K⁺ using KCl, NaCl, and LiCl solutions in acetonitrile. We have observed small changes in the spectrum only at the OH stretching vibration region (not shown).

In contrast, the 1635 cm⁻¹ water band remained insensitive to the chemical identity of the anion or the cation. We have concluded that the spectral features appearing in the IR absorption spectra between 1600 and 1800 cm⁻¹ of strong mineral acids are relatively robust and could be assigned to the hydrated proton (1725 cm⁻¹) and to free water molecules not solvating the proton (1635 cm⁻¹). Furthermore, the spectral features in this range have been found to be almost unaffected either by additional cations or by the presence of anions. This observation has given rise to performing full quantitative analysis of the number of strongly interacting water molecules with the proton in acetonitrile. The analysis was carried out using the 1635 cm⁻¹ absorption band of water in acetonitrile to determine the concentration of the free water molecules which do not interact strongly with the proton; see below.

C. Quantitative Spectral Analysis of the Average Number of Water Molecules Strongly Interacting with the Proton in Acetonitrile/Water Solutions by Acid–Base Titrations. Figure 5 shows the calibration curve of the optical density of the water absorption band at 1635 cm⁻¹ with the concentration of water in water/acetonitrile solutions. In these experiments no acid was present in the solution. When acids were added or

titrated in acetonitrile/water solutions at constant water concentrations, we have observed a change in the optical density of the 1635 cm⁻¹ absorption band of water. We have attributed this OD change to changes in the concentration of free water molecules solvated in acetonitrile, changes brought about by acid–base titrations. We have found out that the OD of the 1635 cm⁻¹ absorption has scaled linearly with water concentration up to about 16 M of water in acetonitrile with practically a concentration independent extinction coefficient of 37 M⁻¹ cm⁻¹ (Figure 5). Using this extinction coefficient and by measuring the optical density of the 1635 cm⁻¹ absorption, we were able to directly calculate the concentration of the water molecules which did not interact directly with the proton in acetonitrile solutions. In addition, we have observed that the optical density of the IR continuum has scaled linearly with the concentration of the protons which were solvated by water. Adding an acid to the acetonitrile/water solutions resulted in the reduction of the 1635 cm⁻¹ absorption and in a concomitant increase in the absorption of the IR continuum between 1000 and 3000 cm⁻¹. Titration of the acid by a base resulted in the opposite effects, an increase in the 1635 cm⁻¹ absorption of the free water and a decrease in the absorption of the IR continuum. The quantitative analysis of the free water concentration was done after subtraction of both the continuum absorption and the hydrated proton spectrum.

We have been able to carry out a quantitative analysis of the water molecules not solvating directly the proton because of the low sensitivity of the water bending mode to its solvent surrounding, a property of the water bending vibration which was observed before.^{114,123} The total area and the width at half-maximum of the bending transition have also shown linear dependence on water concentration up to at least 16 M of water in acetonitrile. The spectral position of the band was found to very slightly change from 1634 cm⁻¹ at traces concentrations of water to about 1640 cm⁻¹ in 16 M solutions of water in acetonitrile. Typically, the change in the free water concentration induced by the titration was only 0.6 M of water and the absolute concentration of water in the titration experiments did not exceed several molars.

We have also verified that triethylamine and protonated triethylamine do not affect the absorption band of water at 1635 cm⁻¹. In particular, we have protonated triethylamine in anhydrous acetonitrile by adding anhydrous triflic acid. We then added water to the acetonitrile solution, and the concentration of the free water molecules was determined by measuring the optical density of the 1635 cm⁻¹ absorption band. Water concentrations were calculated by Beer's law using the extinction coefficient of the 1635 cm⁻¹ band, (Figure 5). In all cases that were examined the calculated concentration of the free water molecules was practically identical to the concentration of the water added to the acetonitrile solution clearly indicating that the protonated base molecules did not affect the 1635 cm⁻¹ bending transition of water.

We have also measured the degree of dissociation (ionization) of triflic acid in acetonitrile when the water/acid molar ratio was less than 2. This was done by measuring the absorbance of the ν_{as}(SO₂) band at 1406 cm⁻¹ of the undissociated triflic acid.⁹² This band vanishes when the acid dissociates in the presence of water. We have found out that the acid is fully dissociated in the presence of at least 1.1 water molecules per an acid molecule. Zundel and Leuchs^{22,23} examined the degree of dissociation of anhydrous triflic acid in pure aqueous solutions and found that

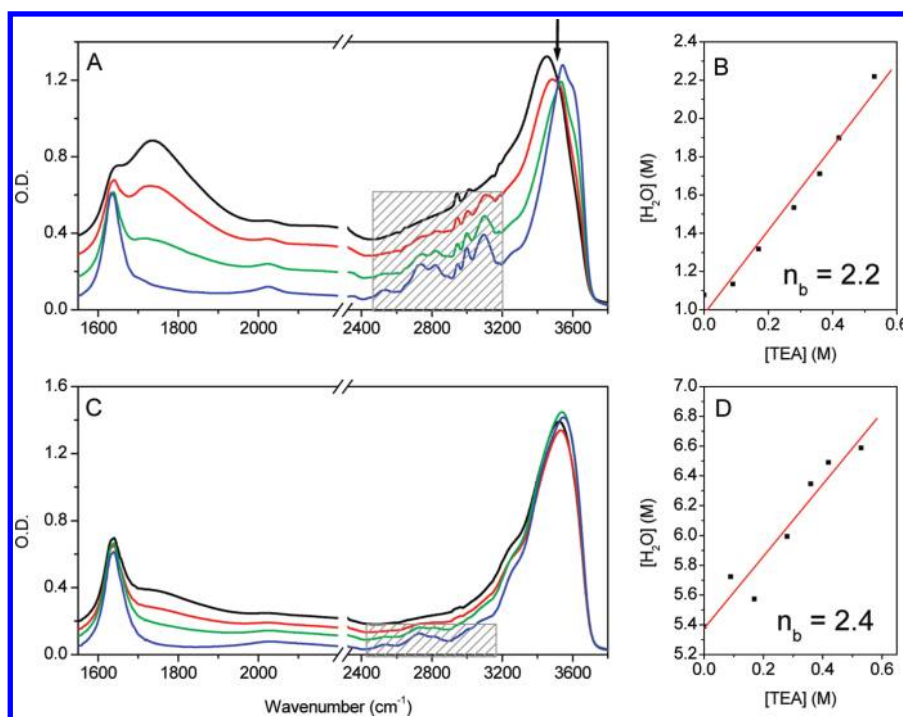


Figure 6. (A) IR spectra (50 μm path length) of 0.56 M HClO_4 and 2.38 M H_2O titrated in acetonitrile with triethylamine base. From top to bottom: 0, 0.18, 0.36, 0.53 M triethylamine. (B) The average number of additional free water molecules per a base molecule added, n_b , contributing to the 1635 cm^{-1} absorption band calculated using the calibration curve of Figure 5. (C) IR spectra (15 μm path length) of 0.56 M HClO_4 and 7.00 M H_2O in acetonitrile titrated with triethylamine base. From top to bottom: 0, 0.04, 0.25, 0.36 M triethylamine. (D) The average number of additional free water molecules per a base molecule added, n_b , contributing to the 1635 cm^{-1} absorption band calculated with the calibration curve of Figure 5.

full dissociation of the acid occurs at slightly higher water/acid molar ratio and reported $n = 1.6$. They also found, using commercially unavailable anhydrous perchloric acid, $n = 1.8$ for perchloric acid in pure water by using the $\nu(\text{Cl}-\text{O})$ absorption of the perchlorate anion at 740 cm^{-1} as the marker transition for proton dissociation. These results are in line with our own findings although very concentrated aqueous solutions of mineral acids are not chemically identical with much diluted solutions of the same acids in acetonitrile/water solutions.

Figure 6 shows the acid–base titration of HClO_4 in acetonitrile in the presence of about 4:1 (A) and about 12:1 (B) molar excess of water, i.e., at $n = 4$ and 12. The acid was titrated by triethylamine. Figure 6 shows enhancement of several IR absorption bands as the titration reaction progressed: these were the water OH stretching vibration of free water in acetonitrile ($3550\text{--}3630\text{ cm}^{-1}$), the triethylamine absorption bands ($2450\text{--}3200\text{ cm}^{-1}$), and the free H_2O band at 1635 cm^{-1} . In contrast, a decrease was observed in the absorbance of the water OH stretching band at lower frequencies ($3200\text{--}3550\text{ cm}^{-1}$) associated with water molecules strongly interacting with the proton. In addition, a decrease was also observed in the amplitude of the 1735 cm^{-1} band and in the absorption of the Zundel continuum between 1000 and 3000 cm^{-1} , the two absorptions that are directly associated with the hydrated proton. An isobastic point was observed at about 3530 cm^{-1} which point to a two-state transition of the OH stretching oscillator, i.e., a transition from free OH oscillators of water molecules not directly interacting with the proton to OH oscillators belonging to water molecules at close proximity to the solvated proton.

Figure 7 shows the titration of 0.60 M HCl with triethylamine base in acetonitrile in the presence of 2.07 M H_2O . An extended

range of the spectrum may be examined with the HCl acid whose solvated anion does not absorb in the $1000\text{--}1300\text{ cm}^{-1}$ range where both the chlorate and triflate anions absorb strongly. With this extended spectral “window” an additional broad absorption associated with the hydrated proton becomes apparent at about 1180 cm^{-1} with a width at half-maximum of about 150 cm^{-1} . This absorption band of the hydrated proton is usually assigned to a proton solvated by two water molecules, the $\text{H}_2\text{O}-\text{H}^+\cdots\text{OH}_2$ grouping which resembles the Zundel cation but is not symmetric about the shared proton. The 1180 cm^{-1} absorption is almost completely diminished and replaced by the absorption of the protonated base when the titration is quantitatively completed after titrating the acid with about an equal concentration of the base (0.57 M). The quantitative analysis of this titration has yielded $n_b = 2.1$ similar but not identical with the value found in the titration of perchloric acid ($n_b = 2.2$ and 2.4).

The titration of triflic acid with triethylamine in acetonitrile in the presence of an equal concentration of water is shown in Figure 8. Both the IR spectrum and the progress of the titration are markedly different from those in the HClO_4 and HCl titration experiments. The IR spectra of the 1:1 hydrated acid exhibit a new very broad and intense absorption band at about 2740 cm^{-1} while the regular OH stretching band at the $3300\text{--}3600\text{ cm}^{-1}$ range is absent. Since the acid is practically completely dissociated in the presence of an equal concentration of water, one can identify in this particular case the stoichiometry of the protonated water solvates as H_3^+O . This is directly corroborated by the appearance of the 2740 cm^{-1} band which is based on gas-phase^{83,124,125} and bulk phase studies^{14,93} and may be assigned in diluted solutions to a single protonated water molecule hydrogen bonded to three molecules of acetonitrile and

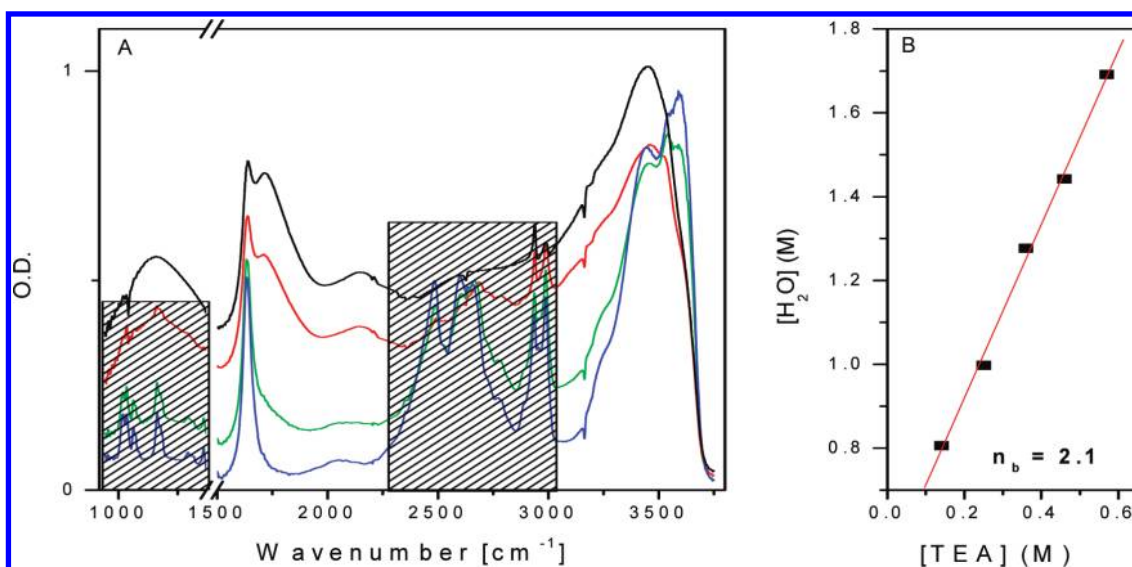


Figure 7. (A) IR spectra (50 μ m path length) of 0.60 M HCl and 2.07 M H₂O in acetonitrile titrated with 98% triethylamine base, from top (black) to bottom (blue): 0.00, 0.14, 0.46, 0.57 M triethylamine. (B) The average number of additional free water molecules in acetonitrile per a base molecule added, n_b , contributing to the 1635 cm⁻¹ absorption band calculated with the calibration curve of Figure 5.

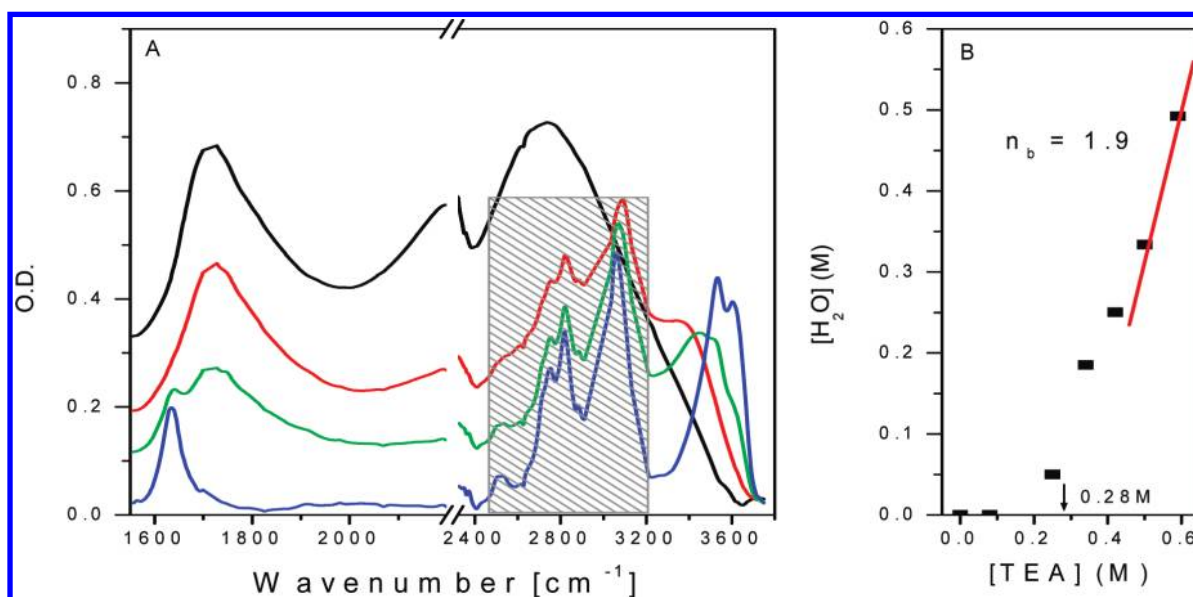


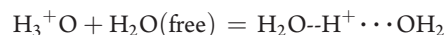
Figure 8. (A) IR spectra (50 μ m path length) of 0.56 M CF₃SO₃H and 0.56 M H₂O titrated in acetonitrile with triethylamine base. From top (black) to bottom (blue): 0.00, 0.34, 0.50, 0.75 M triethylamine. (B) The average number of additional free water molecules in acetonitrile per a base molecule added, n_b , contributing to the 1635 cm⁻¹ absorption band calculated with the calibration curve of Figure 5. The arrow marks the 50% titration point at which half of the acid was titrated.

alternatively in concentrated solutions to the contact ion-pair H₃O⁺⋯O₃SF₃C.⁹³

The progress of the titration corroborates a two-stage titration. In the first stage of the titration the solvated proton mainly exists as H₃⁺O in acetonitrile and each titrated proton frees only one water molecule. However, we do not observe significant emergence of free water molecules until the titration is halfway completed upon the addition of about 0.28 M of base. The following two reactions occur until the midpoint of the titration (see Figure 9)



and



so the water molecules introduced to the acetonitrile solution following the titration reaction are recaptured by the hydronium cation to form the apparently more stable H₂O-H⁺⋯OH₂ grouping. At the midpoint of the titration, the concentration of the hydrated proton is reduced into half of its initial (pretitration) concentration so there are at the midpoint of the titration two water molecules available for solvating the proton, the other half of the initial proton population now protonating the

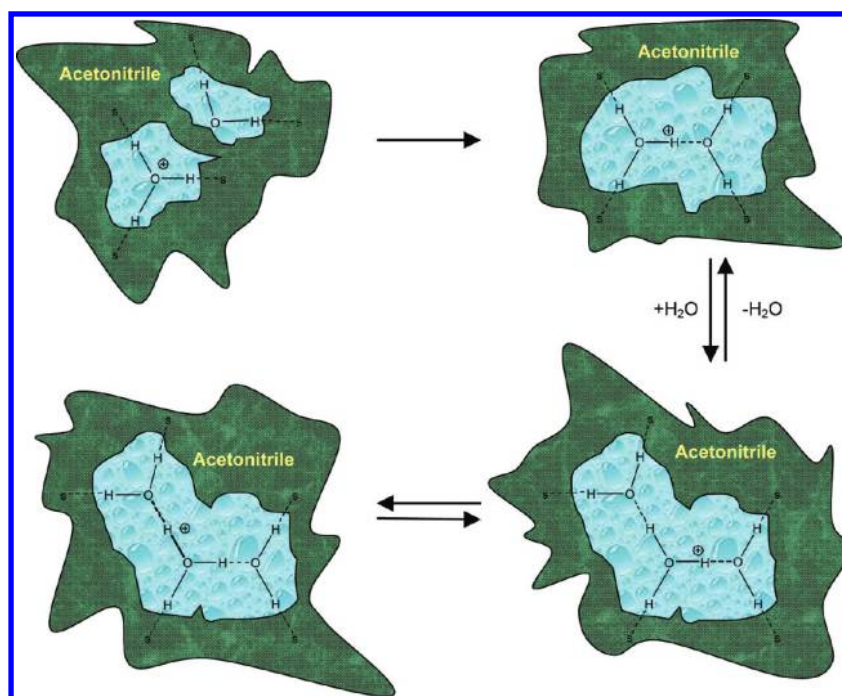


Figure 9. The three smallest protonated water solvates in acetonitrile at high dilution of water in the presence of a strong mineral acid which behaves as a strong electrolyte under such conditions. The average size of the protonated water solvates changes from $n = 1$ to $n = 3$ when $n(\text{H}_2\text{O})$ is gradually increased over that of $n(\text{H}^+)$. For $n = 2$ only one special bond exists while for $n = 3$ the special bond may fluctuate between the two end water molecules and the central water molecule. The arrows indicate the direction of the various spontaneous solvation processes of the hydrated proton in acetonitrile; see the text.

triethylamine base. Only when additional base is added to the solution does the titration progress to its second stage, a stage which we previously have observed with hydrous HClO_4 and HCl where the titration of the (at least) doubly hydrated proton significantly increase the OD of the 1635 cm^{-1} absorption band. In the second stage of the titration of anhydrous triflic acid we have found $n_b = 1.9$ (Figure 8B) closely resembling the outcome of the titrations of HClO_4 ($n_b = 2.2, 2.4$) and HCl ($n_b = 2.1$). These observations point to the existence of two types of protonated water solvates in acetonitrile: The solvated H_3^+O monomer was observed at very low water content and up to equal concentrations of water and a more stable protonated water solvate, most probably the dimer H_5^+O_2 formed at higher water concentrations when two water molecules are available on the average to solvate the proton. At still higher water to acid ratios, a situation which is encountered toward the end of the titration, one expects the presence of higher protonated water solvates; however in contrast to the IR spectra of H_3^+O , which gradually disappears upon further addition of water to acetonitrile when $n = 1$ (equal concentrations of acid and water) the IR spectra of these higher solvates between 1600 cm^{-1} and 1800 cm^{-1} seem to become robust already at about $n = 2.4$ and only slightly changes upon further addition of water to the solution. This dependence of the IR spectra of the solvated proton on water concentration corroborates the outcome of all our titrating reactions as well as the dependence of the proton dissociation rate of protonated aminopyrene photoacid on the concentration of free water molecules in acetonitrile. Considering all our experimental evidence, at least two water molecules are needed to efficiently solvate the proton in acetonitrile. The protonated water dimer core retains its spectroscopic signature when it becomes a part of larger protonated water solvates which are

formed when additional water molecules are added to acetonitrile up to at least 10:1 water to acid ratio. Studies on triflic acid in dichloroethane (DCE) solutions by Stoyanov et al.^{94,95} suggest that in this environment the H_7^+O_3 motif is important, an observation that may suggest an explanation for the slightly higher than 2 values of n that we have found in our titrations. This would have been indeed the case if the spectroscopic signatures between 1600 and 1800 cm^{-1} of the protonated water trimer, H_7^+O_3 , would have been similar to that of the protonated water dimer in acetonitrile solutions; however we cannot justify such a statement nor is such a statement supported by the very detailed gas phase spectra of H_5^+O_2 and H_7^+O_3 taken by Headrick et al.⁸³ which show the two spectra to differ considerably in this energy range.

D. The Harmonic Vibrations of the $\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2$ Grouping with a Mix of HCN –Water Second Solvation Shell. In our B3LYP/cc-pVTZ calculations using the Gaussian 2003 package¹²⁶ we have assumed a core structure of two water molecules sharing the proton, the $[\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{OH}_2]$ grouping. The protonated water dimer interacts with its second solvation shell consisting of four (mixed) solvent molecules, Figure 10.

Figure 11 shows the computed harmonic vibration spectra of the protonated water/ HCN clusters portrayed in Figure 10. In addition, the computed IR spectra of the symmetric H_5^+O_2 and H_9^+O_4 ions, the Zundel and Eigen cations, respectively, are also shown. The computed spectra of the protonated water/ HCN clusters contain three main groups of vibrational transitions between 800 and 4000 cm^{-1} which by comparison with the computed and the experimental spectra of the bare H_5^+O_2 cation may be attributed to vibrations of the $[\text{H}_2\text{O}\cdots\text{H}^+\cdots\text{H}_2]$ core grouping in the $(\text{H}_2\text{O})_n(\text{HCN})_m[\text{H}_5^+\text{O}_2]$ hydrogen-bonding complexes. We

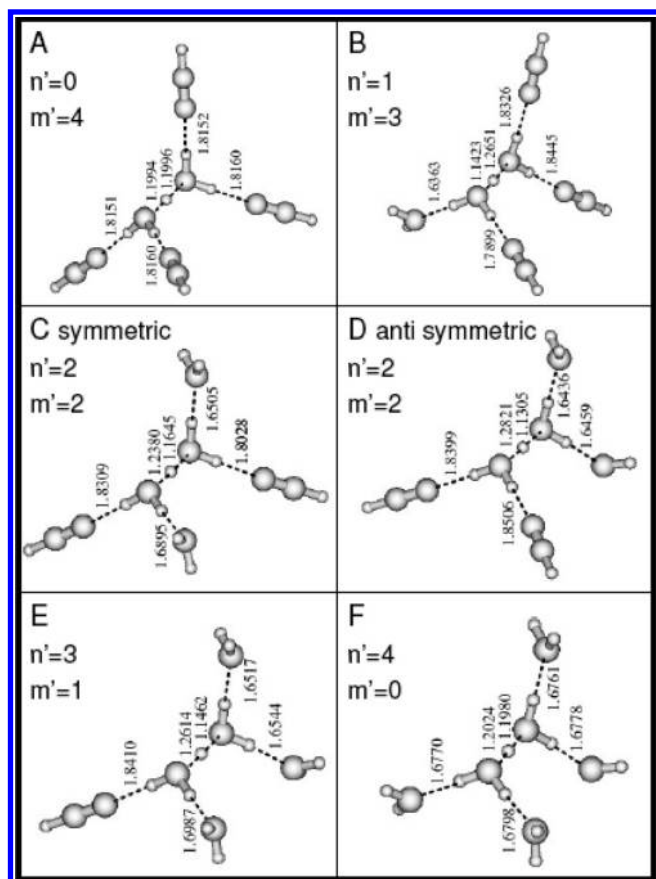


Figure 10. The equilibrium structures and bond lengths of $(\text{H}_5\text{O}_2^+)(\text{H}_2\text{O})_{n'}(\text{CN})_{m'}$ clusters calculated by B3LYP/cc-pVTZ; n' is the number of water molecules in the second solvation shell, $=0-4$; m' , the number of HCN molecules in the second solvation shell, $=4-0$.

have assigned the three main groups of harmonic vibrations as follows: water OH stretching vibrations ($3200-3850\text{ cm}^{-1}$), water-bending vibrations ($1670-1760\text{ cm}^{-1}$), and the shared proton stretching vibration ($900-1250\text{ cm}^{-1}$). An additional fourth group of weak transitions appears in the $1440-1500\text{ cm}^{-1}$ range of the computed spectra but have not been observed in our experiments, presumably because of weak oscillator strengths and the solvent (acetonitrile) strongly absorbing in this spectral range. The above spectral assignments are also in-line with the current analysis of the IR spectra of small protonated (pure) water clusters in the gas phase.

In Figure 11 we have plotted the computed IR absorption spectra of the $[\text{H}_2\text{O}-\text{H}^+\cdots\text{OH}_2]$ grouping as it was modified by varying the composition and the spatial arrangement of the two solvents in the second solvation shell. The calculated gas phase vibrational frequencies of the Zundel cation were not scaled and are observed to be strongly modified by second solvation shell interactions which break the symmetry of the Zundel cation. When four HCN molecules are symmetrically hydrogen bonded to the four dangling hydrogen atoms of the Zundel cation there is little change in the position of the 1740 cm^{-1} band which moves to 1742 cm^{-1} (Figure 11A). In contrast, the water OH stretching band is red-shifted by about 350 cm^{-1} and is slightly split by 15 cm^{-1} . This behavior is in line with the assignment of the 1740 cm^{-1} to a vibrational mode associated with the inner (shared) proton coupled to the bending transition of the two water molecules that directly solvate the

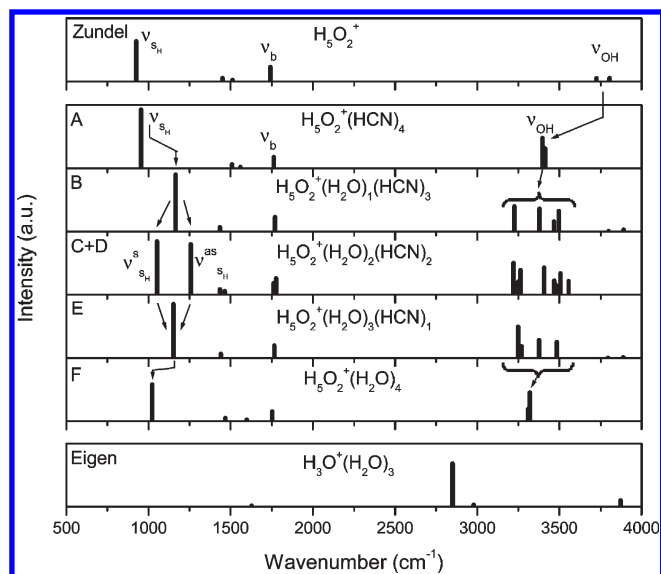


Figure 11. IR absorption spectra of the vibrational modes of the $[\text{H}_2\text{O}-\text{H}^+\cdots\text{OH}_2]$ grouping in different solvation complexes. The harmonic frequencies were calculated with the B3LYP/cc-pVTZ functional. From top to bottom: Zundel, The Zundel cation H_5O_2^+ ; A, $\text{H}_5\text{O}_2^+(\text{HCN})_4$; B, $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_1(\text{HCN})_3$; C + D, $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_2(\text{HCN})_2$ symmetric (s) + asymmetric (as) second solvation shell configurations; E, $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_3(\text{HCN})_1$; F, $\text{H}_5\text{O}_2^+(\text{H}_2\text{O})_4$ and the Eigen cation; Eigen, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$. From A to F, the IR absorption spectra are marked according to the order of their respective cluster configurations portrayed in Figure 10.

proton.^{62,73,77} Finally, the s_{H} stretching band of the shared proton is blue-shifted by only 29 cm^{-1} , which indicates that the complex retains its overall symmetry about the shared proton. The symmetry of the $\text{H}_5^+\text{O}_2(\text{HCN})_4$ complex (Figure 10A) is broken when one HCN molecule is replaced by one water molecule (Figure 10B). The four inner OH oscillators are now split by about 270 cm^{-1} (Figure 11B). In addition, there is a large blue shift in the absorption of the shared proton of about 130 cm^{-1} compared with the 4-HCN complex, but the position of the 1740 cm^{-1} absorption band only blue shifts by additional 16 cm^{-1} .

Replacing a second HCN molecule by water may be done in several not-equivalent ways, the two limiting structures symmetrywise are the ones that are shown in Figure 10C and Figure 10D where the two water molecules are either at the same side of the complex making it antisymmetric about the shared proton (Figure 10D) or one at each side of the complex keeping partial symmetry about the shared proton (Figure 10C). The introduction of partial symmetry to the structure of the solvation complex of the proton shifts s_{H} back to the red toward the absorption of the fully symmetric Zundel cation while the four OH oscillators are almost equally split over about 300 cm^{-1} range indicating the great sensitivity of the OH oscillators to their heterogeneous local environment. The opposite trend, a very large blue shift in the s_{H} transition of the shared proton to 1257 cm^{-1} , is observed for the antisymmetric 2:2 complex. The four OH oscillators are split unevenly into two groups, differentiating between second-shell solvation by water and by HCN. In contrast to these considerable spectral changes, the 1740 cm^{-1} transition still remains almost unaffected by the second-shell interactions and blue shifts by only 15 cm^{-1} as compared with the

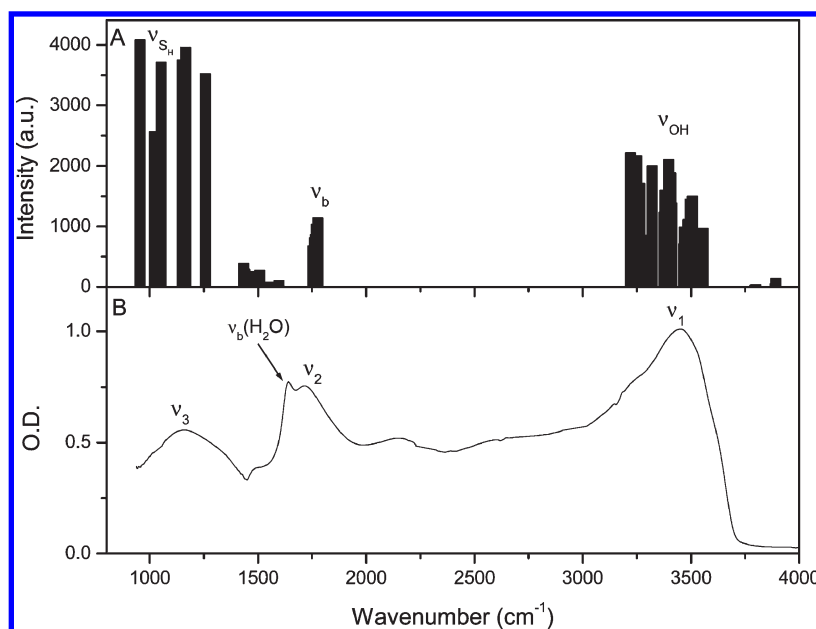


Figure 12. (A) Overlaid computed IR absorption spectra of 6 $(\text{H}_5\text{O}_2^+)(\text{H}_2\text{O})_{n'}(\text{HCN})_{m'}$ complexes calculated on the B3LYP/cc-pVTZ level, whereas $n' = 0-4$, $m' = 4-0$, $n' + m' = 4$. (B) IR absorption spectra of concentrated 37% HCl diluted to 0.6 M HCl in acetonitrile, $[\text{H}_2\text{O}]/[\text{HCl}] = 3.5$.

symmetric 2:2 complex (Figure 11C,D). This again points to the 1740 cm^{-1} transition being a relatively isolated mode of the inner solvation complex of the proton not being so sensitive to second shell interactions. Replacing a third HCN molecule by water (Figure 10E) makes the IR spectrum of the complex (Figure 11E) appear similar to the spectrum of the $3\text{HCN}:\text{H}_2\text{O}$ complex, Figure 11B. The substitution of the fourth and last HCN molecule by water makes the environment of the shared proton symmetric again (Figure 10F) and purely aqueous with the OH oscillators of the two inner water molecules converging back to almost a single absorption line which is red-shifted by about 100 cm^{-1} compared with the situation pertaining with a full (symmetric) HCN second solvation shell (Figure 11F). This outcome shows the hydrogen bonding interactions of the protonated water dimer being the strongest with water fully occupying the second solvation shell around the shared proton. The s_{H} transition of the fully hydrated complex, $\text{H}_{13}\text{O}_6^+$ is blue-shifted as compared both with the Zundel cation, H_5^+O_2 and with the symmetric 4HCN complex. This shows a second type of solvent effect which may be ascribed to a type of a cavity effect due to second-shell water molecules promoting partial delocalization of the proton charge. Finally, we have included for the comparison the computed spectrum of the fully symmetric Eigen cation, H_9O_4^+ . Clearly, and as noticed before both experimentally and computationally,⁸³ the main feature of the symmetric Eigen cation is the strong absorption around 2850 cm^{-1} (not scaled) with all other absorptions being much weaker. Very noticeably, the absorptions around 1000 cm^{-1} and around 1740 cm^{-1} which we have associated with the shared proton in the solvated $[\text{H}_2\text{O}-\text{H}^+\cdots\text{OH}_2]$ complexes are completely missing from the IR spectrum of the Eigen cation. This makes the motif of the symmetric Eigen cation highly unlikely to significantly contributing to the protonated water complexes probed in our computations, a conclusion which is easily verified by inspecting the geometry of the structures A–F, Figure 10, where no 3-fold symmetry around a H_3^+O center is observed to exist.

We have overlaid the spectra A–F appearing in Figure 11 along a single energy axis, Figure 12, and by doing so we have

attempted to very crudely estimate the effect of a fluctuating mixed-solvent environment around a robust $[\text{H}_2\text{O}-\text{H}^+\cdots\text{OH}_2]$ grouping in acetonitrile/ H_2O solutions. While our analysis only resulted with the harmonic vibrations of a small number of gas phase complexes, the outcome of overlaying all the computed spectra on one energy axis does show considerable visual resemblance to the measured IR spectrum of 37% concentrated HCl diluted in acetonitrile solutions, Figure 12.

The visual resemblance between the computed and measured IR spectra shown in Figure 12 provides some rationalization to why the measured spectra of strong acids in various acetonitrile/water solutions is so robust. Clearly, the IR spectra of the $[\text{H}_2\text{O}-\text{H}^+\cdots\text{OH}_2]$ grouping is not very sensitive to second-shell solvation interactions with the mixed solvent. Much larger sensitivity of the IR absorption spectra of the hydrated proton core to second-solvation shell variations are expected when the protonated water hydrate forms ion pairs with its counterion as was observed in low-polarity solvents^{92–96} or when the acid concentration is very high. This is not the case at relatively low concentration of acids in the much more polar acetonitrile solvent.

The existence of the $\text{H}_2\text{O}-\text{H}^+\cdots\text{OH}_2$ grouping in aqueous solutions has been extensively discussed in the literature and is often termed a special pair interaction.^{32,34,35,39,42–44,46,47,71} Unlike the symmetric Zundel cation^{20–25} which only exists as a stand-alone complex in the gas phase or alternatively as a transient (limiting) structure in the liquid the solvated $\text{H}_2\text{O}-\text{H}^+\cdots\text{OH}_2$ grouping is inherently asymmetric. The inner proton does not interact equally with the two oxygen atoms and is not located at the exact center of the grouping. This may be described as a situation where the proton interacts very strongly with one water molecule while forming an additional strong but weaker bond with a second water molecule. A special bond is likely to exist not only when only two water molecules are available to solvate the proton but as part of large protonated water solvates. The existence of such a configuration between the proton and two water molecules was predicted theoretically,

and the second exceptionally strong bond of the proton with water was termed a “special bond”.^{32,35,44,45} The special bond was first described by Tuckerman et al.³² who characterized it as a very strong hydrogen bond along the $\text{OH}^+ \cdots \text{O}$ axis which is shorter than 1.3 Å. Interestingly, a similar length criterion may be used to describe the outcome of our own gas-phase computations where the longest “special bond” in the $[\text{H}_2\text{O} \cdots \text{H}^+ \cdots \text{OH}_2]$ groupings was found to be 1.28 Å (Figure 10). The possible existence of special bonds in protonated water solvates was also discussed in great computational and theoretical detail by Vuilleumier et al.^{44,45} and Staib et al.³⁵ using an extended valence bond model for the excess proton in water. The special bond was predicted to be affected by solvent fluctuation and to fluctuate between partners but to exist long enough to carry its own vibrational spectra. Recently, it was proposed that in bulk water a special bond may fluctuate in an orderly fashion around a H_3^+O center hydrogen bonded to three additional water molecules.^{79,99,100} Although not previously described in the context of a mixed solvent environment, we propose that the terminology of a “special bond” is applicable whenever a shared proton hydrate bearing spectroscopic resemblance to the Zundel cation is observed in any solution containing water. We also suggest that special bonds give rise to the robust spectral features we have observed in the IR spectra of hydrous acids in acetonitrile solutions. Gas phase measurements on protonated water clusters suggest that the Eigen and Zundel motifs alternate when the second shell solvation is not symmetric and small fluctuation around the central protonated water Eigen or Zundel motifs may alter the overall symmetry between a localized Eigen-like H_3^+O and the more delocalized Zundel-like motif. When water is present in large excess over the proton, the second shell of the hydrated proton is expected to be fully aqueous. Interestingly, the IR spectra of the fully hydrated Zundel motif, i.e., $(\text{H}_2\text{O})_6\text{H}^+$ as measured in the gas phase using Ar tagging⁸³ and as predicted by several computational studies strongly resembles the IR spectra of the hydrated proton in acetonitrile with excess of water as well as of the IR spectra of HCl in pure water.^{13,100} A clue to why this is so may be found in two recent computational studies.^{99,100} Xu et al.¹⁰⁰ have shown that a central H_3^+O motif which alternately forms a special bond with one of its water ligands gives rise to IR absorption spectra having many features in common with the experimental IR spectra and with the calculated spectra of a fully hydrated (distorted) Zundel motif. A second study by Livshits et al.¹²⁷ on the water dimer and water pentamer cations, $(\text{H}_4\text{O}_2)^+$ and $(\text{H}_{10}\text{O}_5)^+$, has resulted in a computed vibrational spectrum (harmonic) very similar to that of the Zundel cation whenever a special pair was found to be thermodynamically stable. This was so although the electronic structures of the cationic water complexes which are formed by removing one electron from the cluster were considerably different from that of the corresponding protonated water clusters. These studies point to the robustness of the vibration spectrum of the hydrated special pair motif whenever a protonated two-water center is formed in a protonated water hydrate.

IV. SUMMARY AND CONCLUSIONS

We have found that the stoichiometry of acid–base reactions in acetonitrile/water solutions may be described as $2(\text{HX})_s + (\text{B})_s + 2(\text{H}_2\text{O})_s = 2(\text{X}^-)_s + (\text{BH}^+)_s + [(\text{H}_2\text{O})_2\text{H}^+]_s$ where s is any composition of the mixed solvent

solution in conditions where the concentration of water is at least twice the concentration of the acid but low enough to be considered a much diluted solute in acetonitrile solutions. We were able to verify this stoichiometry up to several moles per liter of water. In addition, we have found the IR spectra of strong mineral acids considerably diluted in acetonitrile to be relatively insensitive to solvent composition in the 1600–1800 cm^{-1} spectral range once there were at least two water molecules available for proton solvation. We attribute the IR absorption in this range to two water molecules solvating the proton by a special (strong) hydrogen bond of the form $\text{H}_3^+\text{O} \cdots \text{H}_2\text{O}$ while hydrogen bonded to either acetonitrile or to additional water molecules.

We have undertaken computational studies of gas-phase clusters where we have assumed the first solvation shell of the proton to be made of two water molecules and varied the composition of the second shell. This resulted with the inner hydrated proton always forming strong special bonds with a second water molecule shorter than 1.3 Å regardless of the solvent composition of the second solvation shell. Summarizing on the overall merit of using B3LYP/cc-pVTZ computations for capturing the essential properties of the IR absorption of the hydrated special pair in the gas phase, we can repeat the statement made in ref 128 that “it is as good as can be expected from a method of its relatively modest computational cost”.¹²⁸

We conclude that all our experimental and computational findings are consistent with the motif of the hydrated $[\text{H}_2\text{O} \cdots \text{H}^+ \cdots \text{OH}_2]$ grouping being the main core solvate of the proton in solutions of strong acids in acetonitrile/water solutions. This motif may be part of a larger protonated water solvate such as formed by the proton solvated by three (distorted H_7^+O_3) or four (distorted H_9^+O_4) water molecules. From a more general point of view one may conclude that in aqueous solutions at any given instance the proton is strongly solvated by at least two water molecules that form its first solvation shell. The hydrated proton may fluctuate and exchange water molecules by a “special-pair dance”^{99,100} but on a slower time scale than the characteristic vibration times of the protonated special-pair core. Finally, we conclude that the ionization of strong acids in acetonitrile should be greatly enhanced upon the addition of water in concentrations which are higher than twice the acid concentration. This means that small concentrations of many strong acids could be appreciably deprotonated in acetonitrile in presence of only traces of water.

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