

Article

The Structure of Liquid Water in Aqueous Solutions: A Proposed Model From Near and Mid Infrared Spectroscopy

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Received: June 17, 1996

Espectros no infravermelho médio obtidos num espectrômetro Nicolet 520FTIR com micro-CIRCLE cell (cristal de ZnSe) e espectros no infravermelho próximo obtidos num espectrofotômetro Perkin Elmer Lambda-9 foram usados para investigar a estrutura da água líquida. Foram estudados os espectros de HDO e H₂O entre 5.0 e 55.0 °C e de soluções aquosas de cloretos de alcalinos e alcalinos terrosos, e cloretos e sulfatos de cobre e zinco. Foram estudadas diferenças de espectros tendo como referência o espectro da água a 20 °C (estudo do efeito da temperatura) e o espectro de água pura (estudo das soluções). O efeito da temperatura no espectro da água aponta duas populações de moléculas: água "livre" (detectada em 3650 cm⁻¹) e água "ligada" (3125 cm⁻¹). Outra população foi detectada nos espectros das soluções: água ligada a íons, "água-íon", que é afetada diferentemente por íons, efetivamente por cátions. Cátions com alta densidade de carga fazem interações fortes, com absorção entre 3100 e 3000 cm⁻¹. Cátions com baixa densidade de carga fazem interações mais fracas (3400 a 3350 cm⁻¹). Supõe-se que os ânions não afetam muito esta estrutura porque as interações água-ânion, nos casos estudados, são mais fracas.

Mid infrared spectra acquired using a micro CIRCLE cell with a ZnSe crystal, and near IR spectra were used to study the structure of liquid water in aqueous salt solutions. HDO and H₂O mid IR spectra from 5.0 to 55.0 °C, and near and mid IR spectra for aqueous solutions of alkaline and alkaline earth chlorides and copper and zinc chlorides and sulfates were obtained. Difference spectra were used to detect changes in the water spectrum. The references were the spectrum of water at 20 °C for the temperature effect study and the spectrum of pure water for the solutions study. The temperature effect on the water spectrum pointed to two water molecule populations: "free" water (detected at 3650 cm⁻¹) and "bonded" water at (3125 cm⁻¹). From the solution spectra, another population was detected: "ion-bonded" water, which is affected differently by the different ions, mainly the cations. High charge density cations make stronger interactions, detected from 3100 to 3000 cm⁻¹. Low charge density cations make weak interactions (3400 to 3350 cm⁻¹). Anions do not affect this structure much because their interactions with water are weaker.

Keywords: *structure of liquid water, infrared spectroscopy*

Introduction

Knowledge of the structure of water has increased rapidly during the last three decades but many details are still polemical¹. It is difficult, for example, to describe complex aqueous solutions, such as aqueous systems associated with biological cells and the influence of ions on active membrane transport². These many unknown aspects make water the most studied system in chemistry. Despite all of the present scientific advances, this subject continues

to fascinate chemists, and water is still far from being satisfactorily described on the molecular level³. As a consequence, in many cases, studies of intricate systems start with assumptions of simplified idealized models, followed by optimization of them by comparing observed and predicted results². This reflects the difficulty in providing a structural description which accounts for the ability of water molecules to form structures of a collective character. These structures are the result of the dynamic behavior of the H-bonding ability of water molecules³.

Several models have been proposed to explain the structure of liquid water, and they can be arranged into two main classes according to the interpretation of the vibrational spectra of water: *continuum* and *mixture* models³⁻⁵. *Continuum* models suggest almost completely H-bonded water molecules in a continuous network where the distortion of H-bonds results in a continuous distribution of H-bond distances, angles and energies. The *mixture* models involve an equilibrium mixture of discrete species, differing according to their specific structural arrangements³. In particular, the OH stretching modes, easily detectable in the Raman and infrared spectra, have been topics of much discussion⁶⁻¹⁵ and have been interpreted not only by mixture or continuum models², but also by a fluctuating H-bond model^{16,17}, and by an interstitial model¹, which is a hypothesis very similar to the continuum model.

Mid infrared spectroscopy should be the most powerful technique in the study of the H-bonding character in liquid water¹⁸, but it has been almost absent from studies of water structure³. Probably the main reason for this is the strong absorption of the fundamental OH stretching, giving rise to intense broad bands which makes it impossible to obtain reliable quantitative structural information from this region with standard infrared techniques. This situation has been changed through the use of new techniques such as attenuated total reflection, ATR. Nevertheless, the possibilities of combination modes, and/or the superimposition of vibrational modes of water molecules from 4000 to 3000 cm^{-1} , have usually been invoked to discard any infrared study in this region.

In contrast to fundamental IR spectroscopy, the overtone spectra, *i.e.* the near infrared region, represent an extremely useful tool for studying the properties of liquid water. The spectra can be easily obtained without the complications mentioned for the mid IR range.

Important considerations can rise from near IR water spectra, such as the study of the efficiency of colloid flocculation of different ionic solutions¹. The addition of different ionic species to water was found to change the electrolyte solutions in a way similar to the effect observed as a result of temperature variation on the pure water spectrum. From these changes, a quantitative definition or ranking for the Hofmeister or lyotropic series can be established, which was empirically described in the nineteenth century. Since this time, colloid chemists have known of special properties of different ions, although ionic solutions were once thought to be dominated by long-range Coulombic forces¹.

The spectrum of HDO molecules has the ν_{OD} stretching mode in a region where no complications are expected. It is related to the properties of the local structure of the liquid in a relatively simple fashion, due to the localized nature of the isotopically decoupled vibrations^{19,20}. The effect of

temperature on this mode shows two populations of HDO molecules in the liquid phase, absorbing in this region. This fact leads us to make an analogy with the ν_{OH} region which assumes a straightforward interpretation.

In this paper we report an ATR study with H_2O and HDO from which some insight about the structure of liquid water can be gained. The results of this study were applied in the interpretation of near and mid infrared spectra of aqueous solutions of alkaline, alkaline earth, copper and zinc chlorides and copper and zinc sulfates. These sets of data, with some reasonable assumptions established through experimental observations, have shown that infrared information about liquid water can be interpreted without a specific cluster model and provides good insight to help understand aqueous salt solutions.

Experimental

Mid IR spectra were recorded on a Nicolet-520 Fourier Transform Spectrometer equipped with a DTGS detector. The displacement of the mirror of the interferometer corresponds to a resolution of 4 cm^{-1} . The spectrum was a Fourier transform of 512 co-added interferograms rationed to air as the background. The ATR accessory was a micro CIRCLE cell from Spectra Tech, with a ZnSe rod nearly 3.9 cm long and a heat-cool jacket. The number of reflections inside the crystal is nearly 12. The temperature of the samples was controlled using a MGK-Lauda RCS-6 water circulating thermostat.

Near IR spectra were recorded on a Lambda-9 UV-visible-NIR Perkin Elmer spectrophotometer. Quartz cells with a 0.1 cm optical path were used, and air was considered as blank. Measurements were carried out at 20 °C with a 2.00 nm spectral band width, 240 nm/min scan speed, 0.5 s response time, and 1 cycle per 0.05 s.

HDO samples were obtained by diluting 99.8% D_2O (Bayer) with distilled water (glass distiller) in a 1:9 ratio. H_2O samples were distilled water (glass distiller).

Aqueous solutions of alkaline, alkaline earth, copper (II) and zinc (II) chlorides, and copper (II), zinc (II) and sodium sulfates were obtained by dissolving the corresponding salts in distilled water, followed by standardization when recommended. The range of concentration varied from 0.0200 to 1.00 mol/L.

The experiments with HDO and H_2O consisted of scanning the spectra from 5.0 to 55.0 °C, in 5.0 °C intervals. The spectra changed smoothly with the temperature. Only the differences in the spectra were studied. Spectral variations due to temperature were studied from plots of the difference between the water spectrum at a determined temperature and the water spectrum at 20.0 °C, used as reference.

The differences between the mid IR solution spectra and the H_2O spectrum (obtained at 20 °C) were plotted in

order to indicate the spectral variations due to the presence of ions. The near IR spectra of these solutions were studied by subtracting the spectrum of pure water from the spectra of aqueous salt solutions corrected by a factor **F**. This correction factor considers the difference in solution densities, responsible for the variation of the number of water molecules in the fixed optical path of the quartz cell. **F** is calculated using the equation below, where ρ is the solution density (g/mL) and C is the concentration in g/L.

$$F = \frac{\rho_{\text{solution}} - C_{\text{solution}}}{\rho_{\text{water}}}$$

A 1 mol/L Na_2SO_4 aqueous solution has pH ~ 8 , and a 1 mol/L CuCl_2 aqueous solution has pH ~ 4 . In order to evaluate the influence of pH on the spectra of water, H_2SO_4 and HCl aqueous solutions down to pH ~ 4 were studied. No detectable change in the spectrum of water was observed. The NaOH aqueous solution, added to reach pH ~ 8 , also gives no change in the observed water spectrum.

Results and Discussion

To evaluate the effect of changes in the index of refraction of water due to temperature variation, we calculated the effective thickness of a film of water using semi-infinite bulk approximation²¹. Allowing for variation of the index of refraction from 5 to 60 °C, the variation of the effective thickness at 3800 cm^{-1} (no absorption) was only about 1%. The variation of the density of water due to the temperature effect was considered in the region from 5 to 20 °C. The expected variation in absorbance due to the density effect was 1/30 of the observed effect.

In conclusion, the temperature effect on the effective thickness and on the density of water can be discarded as an explanation of the observed spectral variation. Similar results can be observed in the literature^{22,23}.

IR spectra of the HDO solution at different temperatures are shown in Fig. 1.

The variation in the HDO spectra caused by temperature is shown in Fig. 2, where the difference between the spectrum at a determined temperature and the spectrum at 20 °C, taken as reference, are plotted. It must be emphasized in the foregoing discussion that in the difference spectra shown in this work, maxima and minima do not represent true IR bands. From 2700 to 2050 cm^{-1} the absorptions are related to ν_{OD} stretching. In this range, two families of curves with opposite behavior can be distinguished with maxima and minima at 2462 and 2615 cm^{-1} , corresponding to ν_{OD} . The plots corresponding to temperatures under 20 °C belong to family A. Family B corresponds to the plots related to temperatures higher than 20 °C. At 2462 cm^{-1} the curves of family A have negative minimum values for the absorbance scale while the curves of family B have a positive maximum. At 2615 cm^{-1} the

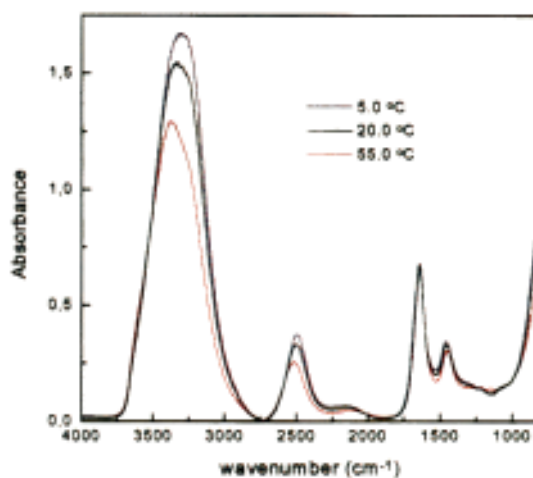


Figure 1. Mid IR spectra of the HDO solution in H_2O at 5.0, 20.0 and 55.0 °C.

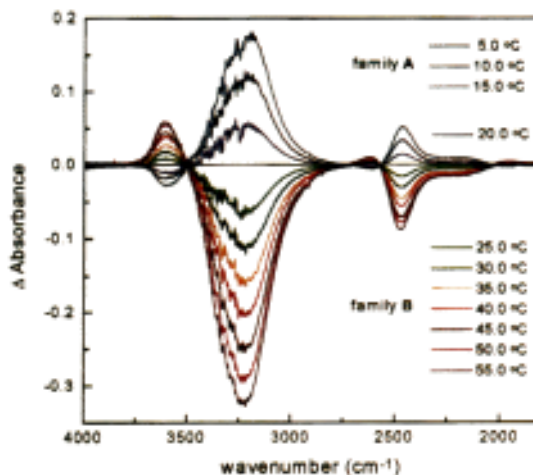


Figure 2. Spectral variations in the mid IR spectra of HDO in D_2O . 1:9 H_2O solution due to the temperature effect from 5.0 to 55.0 °C.

situation is the opposite: a positive maximum for family A and a negative minimum for family B. The isobestic point at 2530 cm^{-1} indicates an equilibrium between two classes of HDO molecules (and two classes of H_2O molecules) also present in solution¹⁵. The relationship of isobestic points to the number of species has been used by other authors to explain their results^{3,22,23}. Walfaren and co-workers¹⁵ associated an isobestic point in the Raman spectrum of the intermolecular vibration of water, at about 128 cm^{-1} , with

the existence of an equilibrium of two species (one linear and the other bifurcated). Studying the effect of temperature on the water spectrum, Libnau and co-workers^{3,22} also assume the equilibrium of two species from the existence of an isosbestic point.

The behaviors of families **A** and **B** are strong evidence for the existence of these two water populations, as indicated by the isosbestic points. From 3800 to 2750 cm^{-1} there is the ν_{OH} region, mainly due to H_2O species. Two families of curves can be distinguished with behavior similar to those in the ν_{OD} region. The curves of family **A** appear below 20 $^{\circ}\text{C}$, and of family **B** above 20 $^{\circ}\text{C}$. The maxima and minima of the curves for families **A** and **B** are at 3230 cm^{-1} (analogous to 2462 cm^{-1} for ν_{OD}) and at 3596 cm^{-1} (2615 cm^{-1} for ν_{OD}), respectively. The isosbestic point appears near 3450 cm^{-1} . However, it must be emphasized that the accuracy of this value is strongly affected by the noise level, since the difference spectrum was obtained by subtracting rather strong absorptions.

As expected for pure H_2O , identical behavior on spectral variations due to the temperature effect around $\sim 3300 \text{ cm}^{-1}$ was observed, as shown above for HDO.

These observations are surely the first evidence that spectra in the ν_{OH} region (4000 - 3000 cm^{-1}) are not as intricate as has been reported. The identical behavior of the ν_{OD} and ν_{OH} regions indicates that the latter is not affected by overtones, combination bands or Fermi resonance. It must be noted that there is no need to decide whether the absorptions correspond to ν_1 or ν_3 because this is not important in the present context. The spectra can be interpreted in a straightforward manner. Two different water species co-exist and absorb in this region at different wavenumbers. The highest wavenumber detected in the difference spectra corresponds to species that are favored by increasing temperature and the lowest wavenumber corresponds to the species whose population increases with decreasing temperature. Compared to the spectrum of ice²³, where ν_1 is at 3400 cm^{-1} and ν_3 is at 3220 cm^{-1} , the minima/maxima observed at 3230 cm^{-1} for liquid water can be assigned to OH-bonding more affected by H-bonding. On the other hand, the value at 3600 cm^{-1} in the difference spectra, if compared with that of water vapor²³ (ν_1 at 3657 cm^{-1} and ν_3 at 3756 cm^{-1}), corresponds to weaker H-bonding. The two water structures express different H-bonding characters.

According to the spectral variations studied, it can be considered that there are two water species in the liquid phase, with distinct absorptions corresponding to ν_{OH} . Each family of curves observed in Fig. 2 corresponds to one of these species. The family whose population increases with increasing temperature must be that with less extensive H-bonding, and the family whose population increases with

decreasing temperature must be that with more extensive H-bonding.

The distribution of water molecules in continuous or discrete clusters is always polemical. However, there is an idea common to all models, *i.e.*, two different classes of water molecules are considered. From the above discussion about the infrared spectra, it is possible to recognize these two classes of water molecules. In the difference spectra, the vaporlike molecules (or "free" molecules) are observed at 3596 cm^{-1} , and the icelike molecules (or "bonded" molecules) are detected at 3230 cm^{-1} .

A chemometric approach to resolve the temperature effects on the IR spectra of water directly on the absolute spectra rather than on the difference spectra was used by Libnau *et al.*^{3,24}. Their results also point to two water structures for the liquid phase, distinguished by IR spectroscopy. The "free" molecule spectrum has the ν_{OH} maximum at approximately 3410 cm^{-1} , while the "bonded" molecules have their OH stretching maximum close to 3240 cm^{-1} .

For liquid water, our infrared data clearly show that there are two distinguishable classes of water molecules. Although Libnau and co-workers^{3,24} applied infrared data to establish a closed two-structure equilibrium, we do not believe that our data strictly agree with their proposal, nor do they discredit it.

In the foregoing discussion we have tried to show that our data can be correlated with two classes of water molecules: "free" and "bonded" water. At this point we include a discussion of the article by Hagler, Sheraga and Némethy²⁵, where they develop a model to calculate the thermodynamic properties of water, assuming it is constituted of clusters of all possible sizes in equilibrium. They introduce the term "molar fraction of unbroken H-bonds" which can be related to our "bonded" water. Their "broken H-bonds" corresponds to our "free" water. These authors calculated the "molar fractions of unbroken H-bonds" as a function of temperature. We took this quantity as a measure of the molar fractions of "bonded" water. We subtracted the molar fraction at 20.0 $^{\circ}\text{C}$ (reference temperature) from the molar fraction at each temperature, in this way obtaining the "difference molar fraction of bonded water" for each temperature. The "molar fractions of unbroken H-bonds", for which no values were provided²⁵, were calculated by interpolation.

Figure 3 shows, in black, the plot of the differences in the absorbance at 3230 cm^{-1} , which is correlated with "bonded" water, against the difference molar fraction of "bonded" water, calculated as explained above. The linear correlation is quite good. An increase in the intensity of the band with an increase of the "difference molar fraction of bonded water" can be observed. The right ordinate axis in Fig. 3 represents the difference in the absorbance at

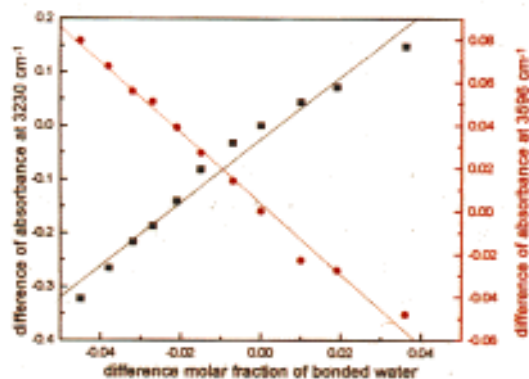


Figure 3. The relationship between the difference of absorbance at 3230 cm^{-1} (■) and 3596 cm^{-1} (●) and the difference molar fraction of “bonded” water.

3596 cm^{-1} . It is correlated to “free” water. The linear inverse relation (in red) is quite good as well.

These results are quite puzzling. Although good correlations were obtained from a “cluster” model, it is not necessary to associate the bands with specific kinds or sizes of clusters.

Infrared data truly show two classes of water molecules. However, there is no direct evidence of whether each class belongs to determined (or identified) clusters, as for instance, octamers and tetramers of water molecules^{3,24}. If a *mixture* model is used to explain the two classes of water molecules, it would be necessary to assume an equilibrium between two polymers of water molecules or among different classes of clusters. How to decide among trimers, tetramers, pentamers, hexamers, octamers, decamers, *etc*? Attempts to explain the thermodynamic properties of liquid water usually claim an equilibrium between discrete species or clusters²⁶, but sometimes a disrupted tetrahedral network, for example, can also be applied²⁷. The two major models for liquid water previously discussed, continuous and mixture models, are often invoked. But we reinforce the idea that it is not necessary to assume any specific cluster model to interpret the infrared data.

We shall use these ideas in studies of aqueous salt solutions, interpreting the way the ions present in the liquid water structure behave when there are “free” and “bonded” molecules. With ions, we assume that new kinds of structured water molecules appear: the molecules that interact more directly with the ions. These species coexist with “free” and “bonded” water.

Mid and near IR spectra of the studied aqueous salt solutions highly resemble the pure water spectrum. Thus, the spectral variations, obtained by subtracting the pure water spectrum from the solution spectra, are more useful for observing the effects of ions on the structure of liquid water than are the absolute spectra. Figures 4 and 5 show

these variations in mid IR spectra for 0.91 mol/L alkaline and alkaline earth chloride solutions. The near IR spectral variations observed for these solutions are shown in Figs. 6 and 7.

Figures 4 and 5 (mid IR) and 6 and 7 (near IR) clearly show different behavior for the MgCl_2 aqueous solution. The effects of this salt will be discussed separately, since with this exception, very similar results for the spectral variations in Figs. 4 to 7 are noted. This similarity is expected because the ν_{OH} is not complicated by combination bands, overtones, *etc.*, as we have shown. The region shown in Figs. 6 and 7 corresponds to the combination²⁸

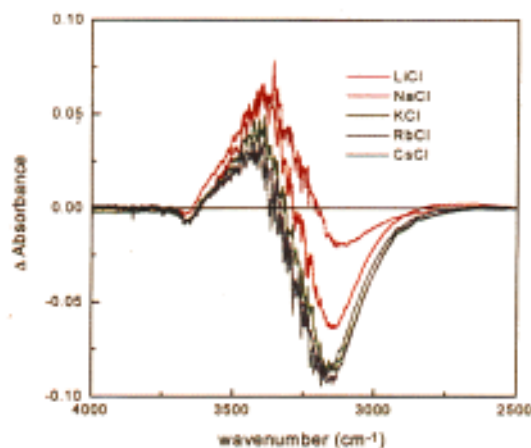


Figure 4. Spectral variations in mid IR spectra of H_2O in 0.91 mol/L solutions of LiCl, NaCl, KCl, RbCl and CsCl.

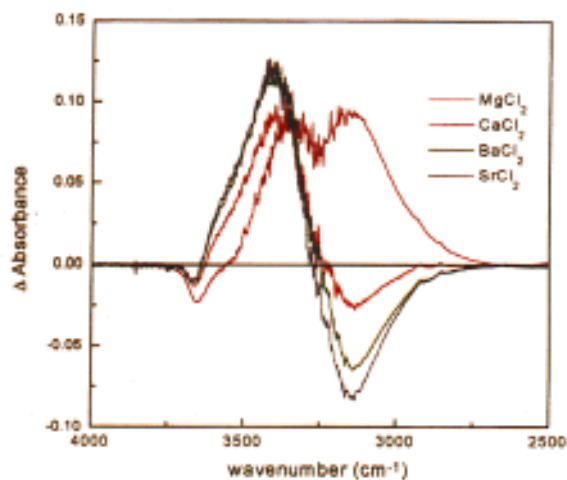


Figure 5. Spectral variations in mid IR spectra of H_2O in 0.91 mol/L solutions of MgCl_2 , CaCl_2 , BaCl_2 and SrCl_2 .

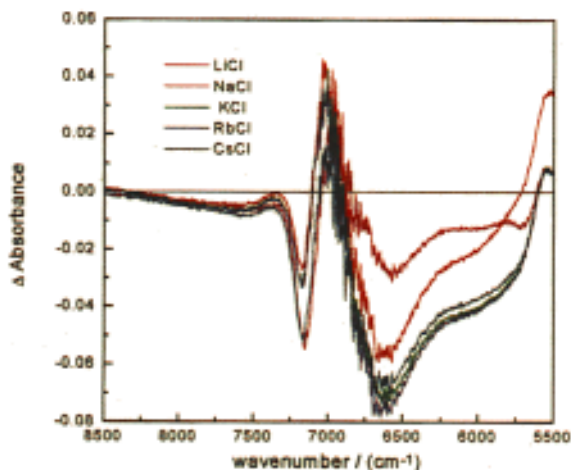


Figure 6. Spectral variations in near IR spectra of H₂O in 0.91 mol/L solutions of LiCl, NaCl, KCl, RbCl and CsCl.

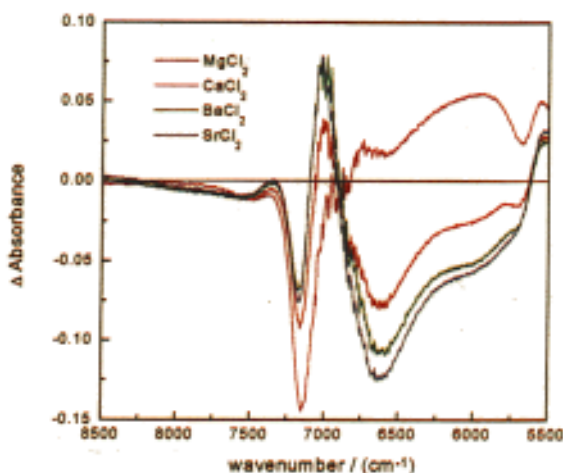


Figure 7. Spectral variations in near IR spectra of H₂O in 0.91 mol/L solutions of MgCl₂, CaCl₂, BaCl₂ and SrCl₂.

$\nu_1 + \nu_3$. In view of our results, it may be more appropriate to say that it corresponds to $2\nu_{OH}$ overtone bands. In the near IR region no complication is expected. In what follows, we compare the same kind of vibrations in the near and mid IR range.

In Figs. 4 and 5 we observe minima at 3180 - 3120 cm^{-1} , and in Figures 6 and 7 the minima appear at 6650 cm^{-1} . It must be remembered that the position of the minima does not represent the position of true bands. The mid IR minima can be assigned to “bonded” water, corresponding to the minima at 3230 cm^{-1} in the spectral variations of pure water due to the temperature effect. Thus, for all salts examined

except MgCl₂ there is a decrease in the population of “bonded” water. By analogy, the ~6650 cm^{-1} minima can be interpreted in the same way.

Following this statement, maxima at 3400-3350 cm^{-1} in Figs. 4 and 5 and at ~7000 cm^{-1} in Figs. 6 and 7 can be assigned to a new population of water molecules arising from interaction with the dissolved salt. The minima at ~3650 cm^{-1} (Figs. 4 and 5) and ~7150 cm^{-1} (Figs. 6 and 7) correspond to “free” water molecules observed at ~3600 cm^{-1} in the study of the temperature effect on the pure water spectrum.

Summarizing the discussion, for alkaline and alkaline earth aqueous chloride solutions there are at least three populations of water molecules, *i.e.*, the two present in pure water and a third one arising from interactions with the salt. These water molecules will be called “ion-water” species.

To discuss the MgCl₂ interaction, the results for aqueous ZnCl₂, ZnSO₄, CuCl₂ and CuSO₄ solutions are presented. The spectral variations achieved from difference mid IR spectra are shown in Figs. 8 and 9. The maxima at ~3100 cm^{-1} for MgCl₂ in Fig. 4 and at ~3000 cm^{-1} in Figs. 8 and 9 for Cu²⁺ and Zn²⁺ salts stand out. For MgCl₂, a maximum at ~6000 cm^{-1} appears in the near IR range (Fig. 7). These maxima are assigned to “ion-water” species.

The position of these maxima depends on the cation type and suggests that the “ion-water” species is mainly due to “cation-water” species. Further support for this observation comes from the spectral variations for Zn²⁺ and Cu²⁺ solutions in Figs. 8 and 9 where we can note that the maxima at ~3000 cm^{-1} are independent of the anions, Cl⁻ or SO₄²⁻.

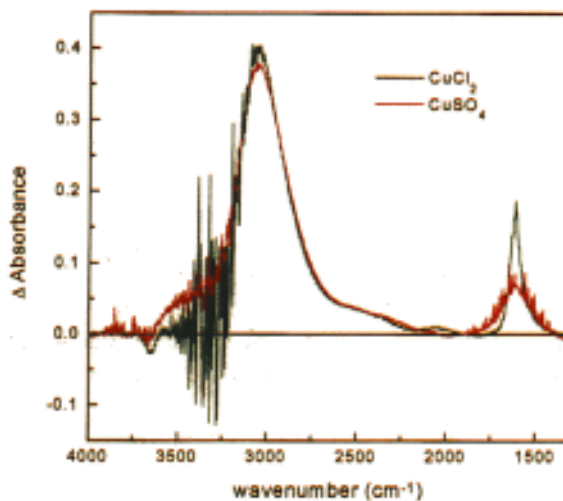


Figure 8. Spectral variations in mid IR spectra of H₂O in 1.00 mol/L solutions of CuCl₂ and CuSO₄.

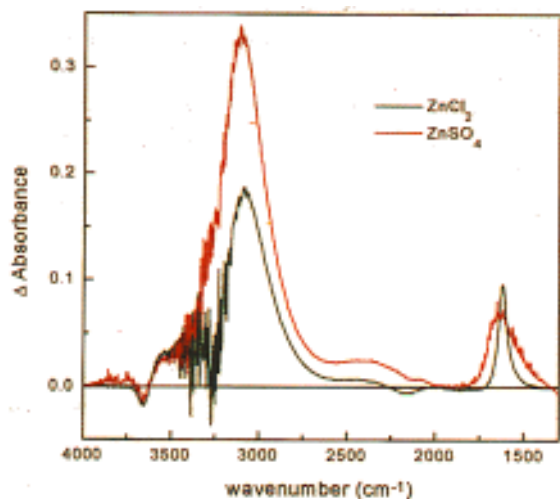


Figure 9. Spectral variations in mid IR spectra of H₂O in 1.00 mol/L solutions of ZnCl₂ and ZnSO₄.

The very different position between the maxima of Mg²⁺, Zn²⁺ and Cu²⁺ (3100 to 3000 cm⁻¹) and that of the alkaline and other alkaline earth cations (3400 to 3350 cm⁻¹) can be accounted for by the higher charge density of Mg²⁺, Zn²⁺ and Cu²⁺. These cations impose a strong polarization on the OH bonding, producing a water population with a very strong H-bonding character.

For those cations the position of the maximum due to "cation-water" prevents the observation of "bonded" water.

To further explore the influence of anions on the "cation-water" species, the spectral variations for NaCl and Na₂SO₄ are shown in Fig. 10, where similar profiles in the difference spectra can be seen. Our observations point to very similar spectra in the 3600-3000 cm⁻¹ region. Apparently, the anions do not affect the strength of the "cation-water" interaction very much. In all difference spectra the major change in going from Cl⁻ to SO₄²⁻ is in the ν₂ region (~1600 cm⁻¹). For all sulfates studied there is a broadening in this band. This broadening can be understood as the anion inducing a more diverse distribution in the H-bonding character. We can assume that anions have only a second order effect on the "cation-water" interaction. This makes the anions more available for other interactions. This observation would explain why some chemical properties of aqueous solutions depend on an anion and not on a cation character.

Conclusions

The study of the temperature effect on the spectra of H₂O and HDO revealed, in the difference spectra, two classes of water molecules. The class with a stronger H-

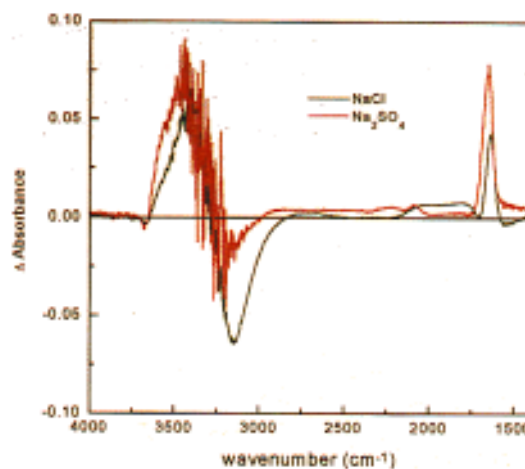


Figure 10. Spectral variations in mid IR spectra of H₂O solutions of 0.50 mol/L Na₂SO₄ and 1.00 mol/L NaCl.

bonding character, detected at 3230 cm⁻¹ (2462 cm⁻¹ for HDO), is identified in this paper as "bonded" water. The class of water molecule detected at 3596 cm⁻¹ (2615 cm⁻¹ for HDO), with a weaker H-bonding character, is identified as "free" water.

Considering the spectra of aqueous chloride solutions of low charge density cations (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ca²⁺, Sr²⁺ and Ba²⁺), from 3120 cm⁻¹ for Li⁺ to 3200 cm⁻¹ for Cs⁺, a minimum analogous to that observed for the "bonded" water is observed, the population of which decreases with increasing temperature. At 3650 cm⁻¹ there is a minimum, indicating a decrease in "free" water. Furthermore, there is a "positive peak" at ~3300-3400 cm⁻¹, indicating a new population of water molecules with no correspondence to the pure water spectrum. This population must be formed by molecules that are interacting directly with the ions. In the near IR range, these observations occur at 6650, 7100 and 7000 cm⁻¹, respectively.

For high charge density cations (Mg²⁺, Cu²⁺, Zn²⁺), spectral variations of two maxima and just one minimum are observed. The "free" water also absorbs at 3650 cm⁻¹ (7150 cm⁻¹ in the near IR range). The population of water molecules interacting directly with the ions appears at 3100-3000 cm⁻¹ (6000 cm⁻¹), much lower than for the low charge density cations. This behavior has been interpreted assuming that Mg²⁺, Cu²⁺, and Zn²⁺ impose a strong polarization on the OH bonding, producing a water population with a very strong H-bonding character.

The dependence of the maxima on the cation nature in the difference spectra led us to propose that high charge density cations make stronger interactions, detected at 3100-3000 cm⁻¹, while low charge density cations make

weaker interactions, and the absorption appears from 3400 to 3350 cm^{-1} . The anions studied (Cl^- and SO_4^{2-}) only slightly modify this interaction.

It must be not forgotten that, in principle, the ability to account for selected experimental data is never sufficient to establish that a model is "correct". Nonetheless, any model which allows previously puzzling results to be rationalized in a straightforward way deserves to be taken seriously.

Acknowledgments

The authors are grateful to the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for fellowships and financial support. We thank Dr. C.H. Collins for the English revision.

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FAPESP helped in meeting the publication costs of this article