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The Effect of Temperature and LiClO$_4$ in the Water Structure: A Raman Spectroscopy Study

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A method to obtain the components of the broad Raman band assigned to the OH stretching vibrations of liquid water was developed, by considering the subtraction of spectra at several temperatures. From these subtractions a set of six components, that we denominate "basis", was determined corresponding to several water structures. This procedure fixes the number of components in the fitting as well as the values of the frequencies, generating a set of six gaussian bands from which the water spectrum can be calculated at any temperature. With such bands the spectrum of lithium perchlorate was calculated at several concentrations and temperatures. It was verified that the spectrum so obtained was identical to that of pure water at a higher temperature. The presence of an isosbestic point is a proof of the existence of equilibrium between the several structures. The enthalpy and entropy values were determined for the isosbestic point and for pairs of structures corresponding to the gaussian bands.

1 Introduction

Water should be a simple example of molecular structure, with three vibrational normal modes: a bending and the symmetric and anti-symmetric stretching. However its H-bonding ability results in a very complex system until now not completely elucidated [1]. The molecule has two-donation and one acceptor center, originating a network of H-bonding that is temperature dependent; for instance, at low temperature a tetrahedral structure is observed. Increasing the temperature some of the H-bonds are disrupt causing in the Raman spectra a very broad band in the OH stretching vibrations (2700-4000 cm^{-1}) with the shape of its contour depending on the temperature.

The analysis of the Raman band contour of the ν(O-H) vibration usually employs a fit of components by least square method; nevertheless large discrepancy exists in the literature [2-5] about the number of components in the fit. In this work a method to obtain the components of this contour, based on the subtraction of spectra at different temperatures, is described. A set of gaussians bands was derived, corresponding to different structures of water, which allows through a combination to reproduce the spectra of water at any temperature. Also, a combination of these gaussians can be used to reproduce the Raman spectrum of aqueous lithium perchlorate (LiClO$_4$) solution and the spectrum so obtained corresponds to the spectrum of water at a temperature higher than that of the solution.

2 Experimental

The Raman spectra in the region of the ν(OH) stretching were obtained in a Jobin Yvon U-1000 spectrometer, equipped with a RCA C31034A-02 phototube, with a resolution of 4 cm^{-1}. The exciting radiation was the 514.5 nm of an Ar$^+$ Coherent Innova 90 laser, keeping the power at 400 mw.

The sample reservoir was kept in a box connected to a thermostat with temperature control of 1 ^{o}C.

3 Results and Discussion

The broad band in the OH stretching region (2700-4000 cm^{-1}) can be considered as a continuous distribution of hydrogen bonds concerning both energetic and geometric parameters. Such distribution is temperature dependent, since a typical hydrogen bond becomes weaker at higher temperatures. Similar effects occur by the presence of eletrolytes. In the case of LiClO$_4$ the spectra is similar to those of pure water at a higher temperature and the effect is probably enhanced by ionic pair formation.

Figure 1 shows the effect of LiClO$_4$ concentration, at 85 ^{o}C, compared with the spectrum of water at 10 ^{o}C.

In this work a method based on the subtraction of spectra at different temperatures originates a set of frequency values, that we denominate "basis", was developed. Before considering the method it is more convenient to introduce some corrections in the spectra, due to the strong dependence of shape of the ν(OH) band on the temperature. It was observed that increasing the temperature the total integrated area under this contour decreased. This could be

explained by changes in the density and polarizability with the temperature. So, it is convenient to correct the spectra by these two factors.
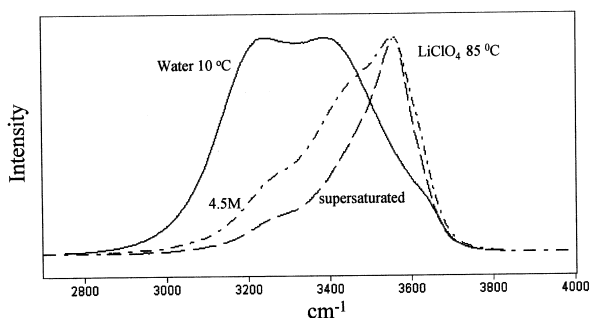

Figure 1. Raman spectra of water and of $LiClO_4$ solution at the indicated temperature and concentration.

The Raman intensity is proportional to the product of density and polarizability, $I \propto \rho|\alpha|^2$. The water density values as a function of temperature can be found in the literature [6]. Here the Raman intensity is represented by the complete integrated area under the contour in the spectra; so the "total" polarizability ($|\alpha|^2$) can be obtained from this intensity: $|\alpha|^2 = I/\rho$. The spectra can now be corrected by multiplying for these factors to eliminate the dependence of the area with the temperature.

In Table 1 are the correction factors $1/\rho$ and $1/|\alpha|^2$ for which the spectra must be multiplied. The spectra at several temperatures without and with these corrections for density and polarizability are shown in Figs. 2 and 3, respectively.

Table 1. The correction factors $1/\rho$ and $1/|\alpha|^2$ as function of temperature.

T (^oC)	$1/\rho$[6]	$1/|\alpha|^2$
15	1.00090	1.00000
30	1.00437	1.01582
45	1.00983	1.03393
60	1.01707	1.05351
75	1.02581	1.07657
90	1.03594	1.09882

It is noticeable in Fig. 2 the decrease in the area in the region of frequencies lower than *ca.* 3400 cm^{-1} when the temperature increases. At the side of frequencies higher than this value there is an increase of the area but not in the same proportion. For the corrected spectra, show in Fig. 3, the total area remains constant, independent of the temperature. The decreasing of the area in the region under 3350 cm^{-1} is equal to the increasing in the area after this point.
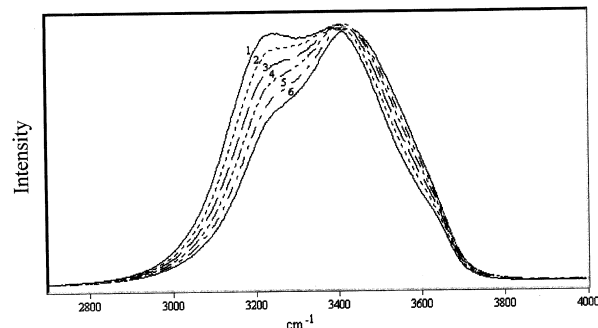

Figure 2. Water spectra without correction at the temperatures: (1) 15 ^oC, (2) 30^oC, (3) 45 ^oC, (4) 60 ^oC, (5) 75 ^oC and (6) 90 ^oC.

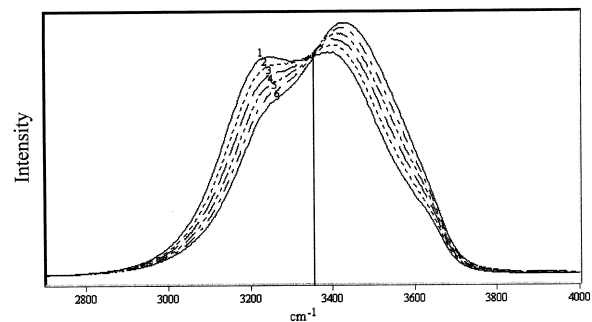Figure 3. Water spectra corrected for density and polarizability, at the temperatures: (1) 15 ^oC, (2) 30 ^oC, (3) 45 ^oC, (4) 60^oC, (5) 75 ^oC and (6) 90 ^oC. The isosbestic point is indicated.

The most impressive fact in the corrected spectra (Fig. 3) is the presence of an isosbestic point (3356 cm^{-1}), which characterizes the existence of equilibrium between several structures of liquid water. As it was mentioned, it is observed in this figure a decrease of area at the low frequencies side and an increase of area at high frequencies side in relation to the isosbestic point. This can be rationalized considering an equilibrium between structures having more H-bonding (OH_{bonded}) and structures having less H-bonding (OH_{free}).

Once obtained the corrected spectra the method of subtraction at different temperatures can now be considered. This can be done more easily through an example, as the one shown in Fig. 4. In this example the spectrum of water at 15 ^oC was subtracted from that at 90 ^oC. The resultant shows two peaks, at 3180 and 3555 cm^{-1}, corresponding to particular components of the "basis". From the spectra at 15 and 30 ^oC these same components and one more, at 3634 cm^{-1}, were obtained. Following this procedure at other temperatures a set of six frequencies, at 3060, 3180, 3240, 3418, 3555 and 3634 cm^{-1}, were obtained. For the 3060 cm^{-1} the subtraction was done between the spectrum of water at –2 ^oC and that for a 4.5M $LiClO_4$ solution at 85 ^oC. These frequencies values constitute the "basis" to be used in the fitting of the contour of the ν(OH) bands at different temperatures. To perform this fitting we have now a fixed number of bands (six) and frequencies values, avoiding the use of an arbitrary number of bands. As a result six gaussian

bands are determined and they will be used to calculate the spectra at any temperature. An important fact is that all the half-widths of these gaussians presented the same value.
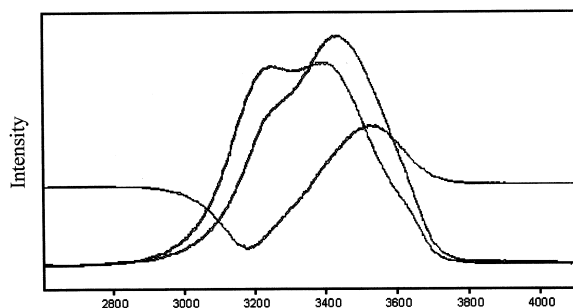

Figure 4. Resulting curve (----) of the subtraction of the water spectra at 15 ^{o}C from the one at 90 ^{o}C; the peaks at 3180 and 3555 cm^{-1} correspond to particular components of the "basis".

It is important to notice that the change in the shape of the contour in the spectra with the variation of temperature (Fig. 3) is only due to equilibrium condition and not to shift of frequencies; an inversion in the order of the intensities with the temperature is observed in the spectra below and after the isosbestic point.

To reproduce the spectra from the considered "basis" it

is necessary to obtain for each gaussian a plot of intensity (obtained in the fit) as function of the temperature. These curves are shown in Fig. 5 and their equations, used to obtain the intensities for each frequency of the "basis" at a given temperature, are shown in Table 2.

From the intensities (areas) of these gaussians for a given temperature the spectra at any temperature can be calculated from the sum of the gaussians.
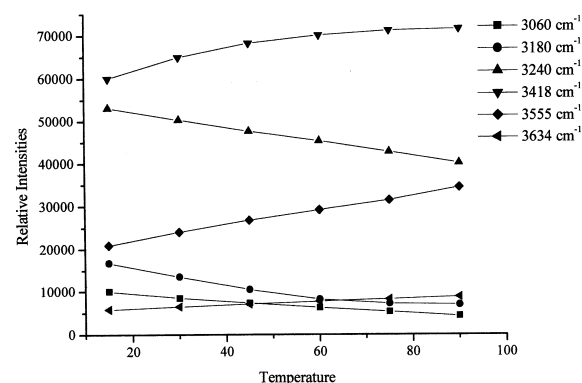

Figure 5. Curves of intensity as a function of temperature (^{o}C) for the six obtained gaussian bands.

Table 2. Equations for the intensities of the six obtained gaussian bands as function of the temperature (^{o}C).

Gaussian Peak Frequencies (cm^{-1})	Equations (Polynomial Regression)
3060 (G1)	$I = 11456.60 - 105.173\,T + 0.28762\,T^2$
3180 (G2)	$I = 21340.80 - 324.398\,T + 1.81063\,T^2$
3240 (G3)	$I = 55696.10 - 180.231\,T + 0.07611\,T^2$
3418 (G4)	$I = 54633.70 + 409.745\,T - 2.49865\,T^2$
3555 (G5)	$I = 18127.00 + 198.435\,T - 0.21857\,T^2$
3634 (G6)	$I = 5140.60 + 45.2552\,T - 0.05841\,T^2$

As it was mentioned before, the spectrum of LiClO$_4$ solution corresponds to the spectrum of water at a higher temperature. As an example, in Fig. 6 the spectrum of LiClO$_4$ solution, 1.5M at 45 ^{o}C was built with the gaussians obtained from the basis for water at the temperature of 60 ^{o}C. In this way, summing these gaussians (G1+G2+...+ G6) the resultant can be compared to the spectrum of the solution at 45 ^{o}C. In Fig. 6 the experimental spectrum of LiClO$_4$ solution 1.5M at 45 ^{o}C (circle points) shows perfect coincidence with the resultant curve built with the gaussians from water at 60 ^{o}C. This means that the in this solution of LiClO$_4$ the structure of the water as solvent corresponds to that of pure water at 60 ^{o}C.

As it was already mentioned the equilibrium between the structures involving the OH$_{bonded}$ (corresponding to

the gaussians centred at 3060, 3180, 3240 cm^{-1}) and the OH$_{free}$ (corresponding to the gaussians at 3418, 3555 and 3634 cm^{-1}) with the increasing of the temperature is displaced to the structures in the high frequencies side, due to the breaking of H-bonding, according to the equilibrium:

$$\frac{1}{2}\mathrm{OH}_{bonded} \rightleftharpoons \frac{1}{2}\mathrm{OH}_{free}$$
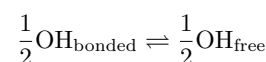
The ratios between the areas at the low frequencies side (A$_l$) and at the high frequencies side (A$_h$), with respect to the isosbestic point, were obtained. Plotting the logarithm of these ratios $\ln(A_l/A_h)$ as a function of 1/T [7-9] (Fig. 7) the enthalpy (ΔH^o= 3.03 kcal.mol^{-1}) and entropy (ΔS^o = 9.81 cal.mol^{-1}.K^{-1}) values were calculated for the isosbestic point.
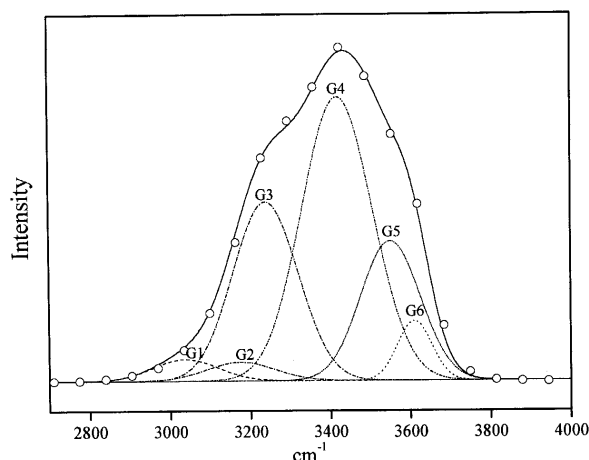
Figure 6. The resultant combination (---) of the gaussians obtained with the basis for water at 60 ^{o}C and spectrum of LiClO$_4$ solution 1.5M at 45 ^{o}C (o).

The obtained gaussians (Fig. 6) suggest that equilibrium between pairs of gaussians should be considered. The equilibrium considered for the isosbestic point could be rewritten as:
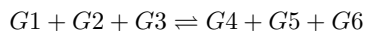
$$G1 + G2 + G3 \rightleftharpoons G4 + G5 + G6$$

Figure 7. Plot of $\ln(A_l/A_h)$ as a function of 1/T (K^{-1}). The slope gives the ΔH^o and the linear coefficient gives the ΔS^o values.

As example of the equilibrium between a pair of structures involving the OH$_{bonded}$ and the OH$_{free}$, the equilibrium G1 $\rightleftharpoons$ G4 can be considered. The slope of the plot of *ln* of the ratio of the intensities of G1 and G4, $ln(I_{G1}/I_{G4})$, as function of 1/T gives the value of the enthalpy for this particular equilibrium. The values of enthalpy calculated for the pairs of the considered structures are in Table 3. In the table the values of enthalpy are in decreasing energy order.

Table 3. Equilibrium between pairs of structures and the correspondents ΔH^o (kcal.mol^{-1}) values.

Equilibrium	ΔH^o	Equilibrium	ΔH^o
G1 $\rightleftharpoons$ G4	46.34	G1 $\rightleftharpoons$ G2	4.67
G2 $\rightleftharpoons$ G4	45.21	G3 $\rightleftharpoons$ G4	3.56
G1 $\rightleftharpoons$ G5	23.58	G5 $\rightleftharpoons$ G6	2.37
G2 $\rightleftharpoons$ G5	22.52	G3 $\rightleftharpoons$ G5	2.24
G1 $\rightleftharpoons$ G3	20.88	G4 $\rightleftharpoons$ G5	0.62
G2 $\rightleftharpoons$ G3	19.44	G3 $\rightleftharpoons$ G6	0.52
G1 $\rightleftharpoons$ G6	6.56	G4 $\rightleftharpoons$ G6	0.19
G2 $\rightleftharpoons$ G6	5.76	*G1+G2+G3 $\rightleftharpoons$ G4+G5+G6	3.03

* Equilibrium for the isosbestic point.

The temperature variation is directly related with the structures existent in liquid water. Consequently this variation affects the enthalpy values corresponding to the breaking of H-bonding. As is shown in Table 3, there is a coherent sequence between the equilibrium and the calculated enthalpy values: large values of ΔH^o are related to equilibria involving G1 and G2 with the structures in the order G4>G5>G3>G6; it follows the equilibrium G1$\rightleftharpoons$ G2, G3 $\rightleftharpoons$ G4, G5$\rightleftharpoons$G6 and the lower values of ΔH^o for the equilibrium of G3 and G4 with G5 and G6.

A deeper analysis of these results may help in the understanding of models related to the possible structures of water in condensed phases.
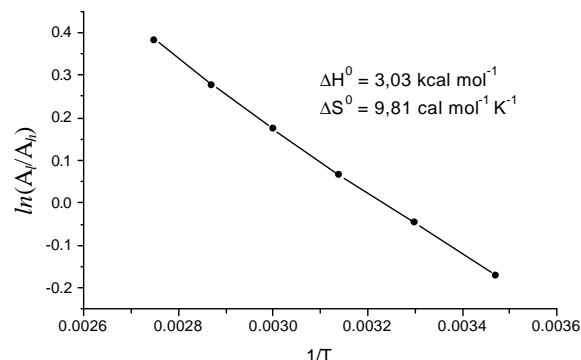
4   Conclusions

To avoid the incertitude existent in the literature about the number of components to be used in the fitting of the contour of the O-H stretching vibrations in the Raman spectra of liquid water a different method was introduced. It considers a "basis" established by subtraction of spectra at different temperatures. This "basis" corresponds to predominant structures in the water and allows obtaining a set of six gaussians bands. With a combination of these bands it is possible to reproduce the spectra of pure water or of LiClO$_4$ solutions at any temperature.

Making some corrections in the spectra an isosbestic

point was determined, indicating the existence of equilibrium of the several structures in the water. Through area measurements in the spectra values of enthalpy and entropy were calculated at the isosbestic point and for the equilibrium between the several structures corresponding to the obtained gaussians.

Acknowledgments

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