ON THE CLUSTER COMPOSITION OF SUPERCRITICAL WATER COMBINING MOLECULAR MODELING AND VIBRATIONAL SPECTROSCOPIC DATA

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I - INTRODUCTION

During the last decade, there has been an increasing interest in the study of the structure and dynamics of water at high temperatures and pressures and in particular in the supercritical domain. This can be explained by the fact that thermochemical properties of sub and supercritical water (SCW) are remarkably different from those at ambient conditions.[1-3] The peculiar behaviour of SCW is related to the change of the hydrogen bond network at high temperatures. Thus, experimental investigations of the intermolecular structure and dynamics provide clues for the understanding of the SCW properties. Numerous experimental and theoretical investigations have been devoted to the study of the structure and dynamics of supercritical water.[4,5] Among the different approaches, vibrational spectroscopies such as near infrared and mid-infrared spectroscopies are particularly well suited due to the sensitivity of the OH stretching vibration to hydrogen bonding.[6,7] However, linking spectral data to structural information at a molecular level such as the degree of hydrogen bonding and the nature and size of hydrogen-bonded aggregates is rather challenging. In order to provide such link, we propose to assume that supercritical water is an ideal mixture of small water clusters (n=1-4) at the chemical equilibrium and that vibrational spectra results from the superposition of the spectra of the individual clusters. Thus, in order to analyse NIR and MIR spectra, we need to determine the spectra of small water clusters. For such task, quantum chemistry calculations have been carried out in the anharmonic approximations (mechanical and electrical anharmonicities) which allow to simulate fundamental vibrational modes as well as combination and overtones modes[8,9] (frequencies and activities). Using this model, we will present in this paper how it was possible to interpret qualitatively the evolution of both mid infrared and near infrared spectra of supercritical water as a function of the density.

II - EXPERIMENTAL AND CALCULATION DETAILS

II - 1 Infrared measurements

The near infrared absorption experiments were performed using a home made stainless steel cell [10] equipped with two cylindrical sapphire windows with a pathlength of 3 mm. The sealing was obtained using the unsupported area principle. The windows were positioned on the surface of a stainless steel plug with a graphite foil placed between the windows and the plug. Flat graphite rings were used to ensure sealing between the plug and the cell body. For mid infrared measurements, because of the strong absorption of water in the OH stretching region, we have used a special stainless steel cell [10] designed in our laboratory in order to obtain a thin film of water at temperatures up to 380 °C and under pressures up to 250 bar. The sealing of the cell is ensured by a graphite ring, which is disposed around the window. The cell was equipped with two sapphire windows separated by a gold spacer ensuring a pathlength varying between 20 and 150 μm. Although the pathlength of the cell is known from the thickness of the spacer, we have usually used the interference technique to get an accurate determination of the thickness of the water layer. Let's emphasise that the data collected over a wide range of densities need to use at least two different spacers with thickness of 20 and 150 μm. We have checked the reproducibility of the data when we have measured water under the same thermodynamics conditions with different pathlengths. The heating of both cells was performed using cartridge heaters disposed in the body of the cells. Two thermocouples were used, the first one located close to one cartridge is used for the temperature regulation and the second one was kept close to the sample area in order to measure the temperature of the sample with an accuracy of about 2 °C. The cell was then connected via a stainless steel capillary to a manual pump (Top Industrie SA) thus allowing to reach pressures up to 25 MPa with an absolute uncertainty of ±0.1 MPa and a relative error of ±0.3%.

The infrared absorption measurements were performed on a BioRad interferometer (type FTS-60A) equipped with dual source capability (a globar and a tungsten halogen source), two different beam splitters (a KBr/Ge and a quartz substrate) and a DTGS (Deuterated TriGlycide Sulphate) detector in order to investigate the spectral ranges of mid (400-6000 cm^{-1}) and near IR (3000-10000 cm^{-1}) respectively. Single beam spectra recorded with a 2 cm^{-1} resolution were obtained after Fourier transformation of 50 accumulated interferograms.

II - 2 Calculations

DFT calculations on water clusters have been carried out using the Gaussian 2003 program suite.[11] Calculations of geometry, energies, and harmonic vibrational frequencies were performed with the B1LYP [12] functional using the correlation-consistent polarized Valence Triple basis sets (cc-pVTZ) proposed by Dunning and co-workers.[13,14] The frequency calculations in the mechanical anharmanonic approximation were carried out within the perturbation method (initially implemented in the Gaussian program) and using the variational method as developed by Begue et al.[8] Using this method, it was possible to compute all the vibrational modes (fundamental, combinations and overtones) that contribute to the mid and near infrared spectrum of water. In addition, the activity of each mode was also calculated in the electrical anharmonic approximation using a method developed by Baraille et al.[9]

III - RESULTS AND DISCUSSION

III – 1 Infrared absorption

We have reported in figure 1 the evolution of the infrared (IR) spectra of supercritical water at T=380°C as a function of pressure (density) in the range 25-250 bar (0.01-0.43 g.cm^{-3}) in the whole spectral range from the mid IR (3000 cm^{-1}) up to the near infrared region (8000 cm^{-1}).
We emphasize that the experimental spectra have been treated using the beer-lambert law in order to determine the molar extinction coefficient as a function of the wavenumber. The profile observed in the spectral range 3000-4000 cm^{-1} relates to the fundamental OH stretching vibrations whereas the bands observed around 5300 and 7200 cm^{-1} are associated to the OH bending+stretching combination modes and the first overtone of the OH stretching modes, respectively. For each profile, we observe at the lowest density a remnant of the complicated rovibrational structure of the stretching ν_3, the combination $\nu_3+\nu_1$ and the overtone $2\nu_3$ modes centred respectively at 3740, 5350 and 7270 cm^{-1} which qualitatively indicates that under this conditions, water molecules are not hydrogen bonded to other water molecules and rotate almost freely.
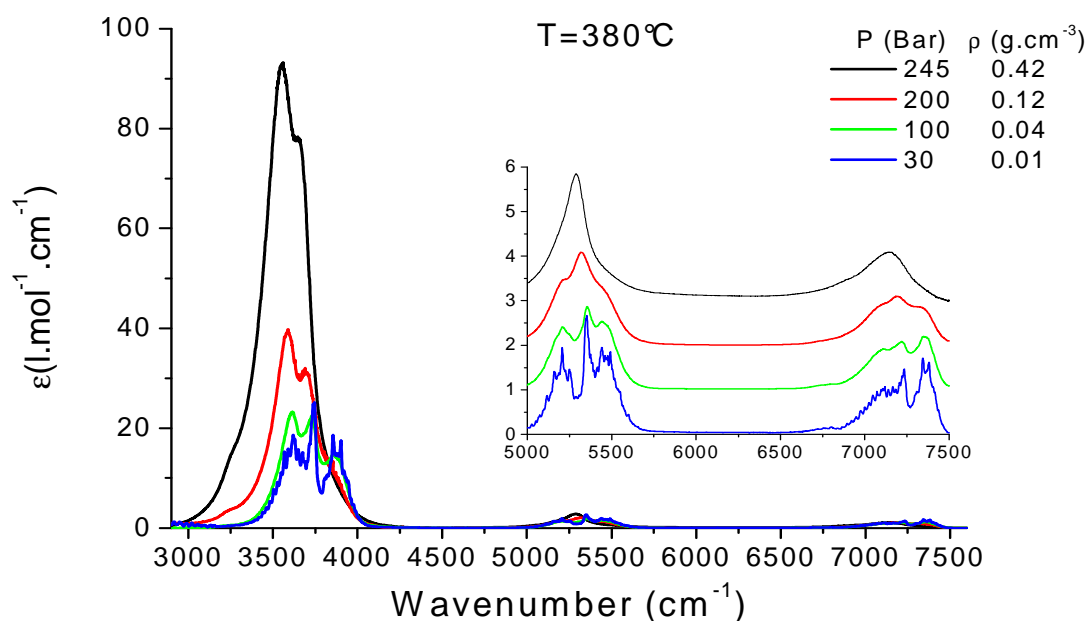

Figure 1: Mid and near Infrared spectra of supercritical water at T=380°C as a function of pressure (density) in the range 25-250 bar (0.01-0.4 g.cm^{-3}).

Concerning the fundamental OH stretching region, the ν_3 mode exhibits a P,Q,R structure (A-type band) as expected for a C_{2v} asymmetric top molecule. Notice that the contribution of the symmetric stretching mode (ν_1) expected at about 3657 cm^{-1} is not observed because its activity is lower by a factor of ten compared with that of the ν_3 mode.[15] The integrated intensity of absorption of water at T= 380°C and P=25 bar in the OH stretching region is about 59 ± 2 km mol^{-1} and found to be in an almost perfect agreement with the value reported by *Bondarenko et al.* [16].

In the combination region, the $\nu_3 + \nu_2$ mode exhibits a P,Q,R structure and the contribution of the $\nu_1 + \nu_2$ mode expected at about 5200 is negligible. [15]

Finally, in the overtone region, the $2\nu_3$ mode exhibits a P,R structure as already reported in a previous investigation of supercritical water in this spectral range. [17]

As the density increases from $\rho = 0.01$ up to $\rho = 0.1$ g.cm^{-3}, we observe in the OH stretching region an enhancement of the intensity of the spectrum and a significant perturbation of the bandshape. This is reflected by a peak situated at about 3600 cm^{-1} superimposed over the envelop of the PQR structure whilst the R branch leads to a shoulder at 3850 cm^{-1}. Finally, upon increasing the density in the range $0.1 < \rho < 0.4$ g.cm^{-3}, we observe a progressive enhancement of its intensity and a shift towards lower frequencies as well as, a broadening leading to a broad band with two maxima at about 3650 and 3550 cm^{-1} at the highest density investigated. The shoulder observed at 3850 cm^{-1} at the lowest density progressively disappeared whereas a new shoulder is observed at about 3250 cm^{-1}. This spectral evolution is in a good agreement with the spectral data reported by Gorbaty et al. [18] in the same density range but at a higher temperature T=500°C.

In the combination and the overtone region, we also observe qualitatively the same bandshape variations as that observed in the OH stretching region. Indeed, we observe a progressive shift towards lower frequencies as well as, a broadening of the rotational lines leading at the highest density investigated to a featureless band with a maximum at about 5280 and 7150 cm^{-1} respectively. However, contrary to the OH stretching region, the intensity of both profiles is almost independent on the density variation. This means that the oscillator strength associated to this two vibrational modes is not sensitive to the state of aggregation of water molecules.

III - 2 Qualitative analysis of Mid and Near IR spectra

The infrared absorption measurements reported above show that the degree of hydrogen bonding increases strongly upon a density increase. These spectral variations can be due to the occurence of small water oligomers as a function of the density. Thus, in order to qualitatively assign our IR experimental findings, we may use the spectra of small water clusters that can be calculated using quantum methods. This has been done by a number of
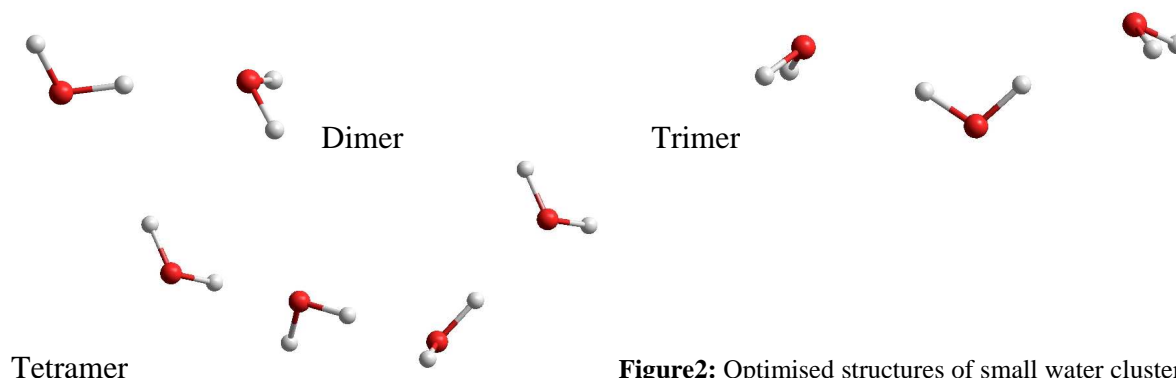

Dimer   Trimer

Tetramer   **Figure2:** Optimised structures of small water clusters

authors for small water clusters (n_{H2O}=2-8) using various level of approximation in the ab initio calculations as well as DFT methods [19-22]. The general trends about optimal structures, binding energies and IR spectra are qualitatively in agreement for all the calculations performed at different levels. However, a complete set of data on vibrational

frequencies with corresponding IR and NIR activities is lacking. Indeed, all the vibrational calculations reported previously in the literature have been performed in the harmonic approximation and do not allow to compute combination and overtone frequencies and activities. Moreover, calculations are generally reported for small cyclic water clusters which are the most stable species at low temperature. However, it has been shown previously by MD simulations that in supercritical water, linear species are expected to be by far predominant in comparison with cyclic structures.[23] In this context, we have carried out new calculations for monomer, dimer, linear trimer and linear tetramer using the DFT method at (B1LYP/cc-pVTZ) level using the Gaussian 03 program.[11] The optimised structures of the water monomer and clusters are reported in figure 2. Their associated fundamental, combination and overtone modes are reported in figure 3 together with the experimental IR of supercritical water at T=380°C and P=250 bar.
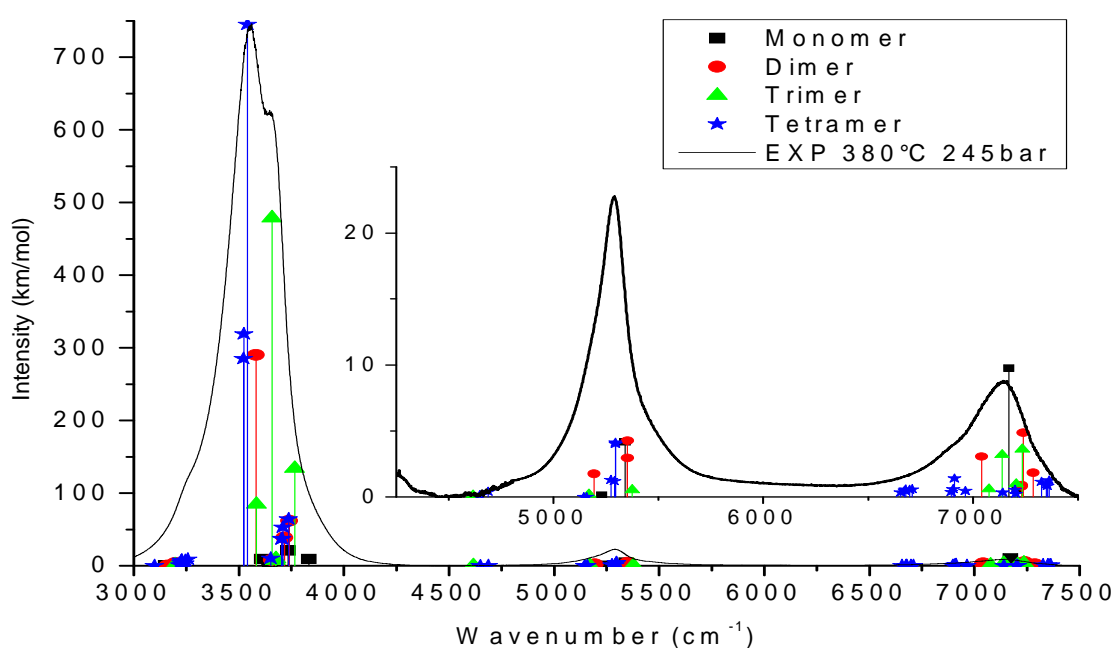

Figure 3: Calculated anharmonic vibrational frequencies and intensities of water clusters using the Density Fonctional Theory (B1LYP-cc-pVTZ). The experimental spectrum of supercritical water at 380°C and 245 bar is reported for comparison.

At a first glance, we observe on figure 3 a nice qualitative agreement between the calculated spectral lines of individual clusters and the experimental spectra which provide support to the present model. Thus, in the spectral range of the antisymmetric stretching mode at about 3650-3700 cm^{-1}, the band associated with the free-OH stretching mode of the oligomers is found to be almost independent of the size of the cluster. At lower frequencies, in the range 3200-3550 cm^{-1}, the characteristic frequencies of the peaks associated with the oligomers hydrogen bonded OH oscillators decrease strongly with the cluster size. Very weak contributions are observed at about 3200 cm^{-1} which are associated to overtones of the bending mode of water. More, the infrared activities of the hydrogen bonded OH mode increases strongly with the size of the aggregates (up to 10 times that of the free OH mode). Although the frequencies of free and bonded OH contributions are well separated in the combination and overtone region, the activity enhancement is not seen for the corresponding combination and overtone activities: the activity of bonded OH modes are close or even

slightly less than that of the free OH modes. Therefore, the contrast effect between the activity of bonded and free OH groups that is clearly seen in the fundamental region is almost negligible in the combination and overtone region.

IV- CONCLUSION

Our study foregrounds that mid and near infrared spectra of supercritical water can be qualitatively considered as resulting from the sum of the individual spectra of small water cluster distribution. Analysis of the mid and near infrared using an Equilibrium Cluster Composition Model is in progress in order to provide a more quantitative picture about the partition of clusters in supercritical water.

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