



	<b>Experiment title:</b> Compton scattering study of supercritical water	<b>Experiment number:</b> HE-1678
<b>Beamline:</b> ID15B	<b>Date of experiment:</b> from: April, 7th                      to: April, 16th	<b>Date of report:</b> 02.18.2005
<b>Shifts:</b> 21	<b>Local contact(s):</b> Thomas Buslaps	<i>Received at ESRF:</i>
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**Report:** Singular properties of supercritical water (SCW), when compared to water at ambient conditions, are observed at all levels :

- from a macroscopic point of view, scwater shows the decrease of dielectric constant (this allows dissolution of non polar substances), the decrease of viscosity which means an increase of molecular mobility, and the increase of compressibility.
- from a mesoscopic point of view, the major effect is the Local Density Inhomogeneities (LDI) : zones with higher density than global liquid density are observed. As a consequence, « high » and « low » density zones coexist in scwater.
- from a microscopic point of view, change in the tetrahedral water network is observed, and a controversy still exists. Postorino et al (Neutron diffraction) assumed that H-bonds mainly disappear in sc conditions, whereas other neutron studies conclude that the H-bonds exist in sc state even if the tetrahedral structure collapses. X-ray diffraction studies or other techniques (infrared spectroscopy, RMN, molecular dynamics) mostly agree with this last result. The number of H-bonds per water molecule which is about 3.5 in the liquid state would decrease to about 1.8 in dense scwater ( $\rho = 0.73 \text{ g/cm}^3$ ). In SCW at low density only monomers are assumed to be present, whereas dimers and eventually trimers form as density increases.

Our Compton study addresses the following questions: what are the changes in the H-bond network ? What is the structure of subcritical and supercritical water ? This study, which is the first study of momentum space electronic density modification of water under high pressure and temperature conditions, seeks to apply the sensitivity of Compton scattering to chemical bonding to this problem.

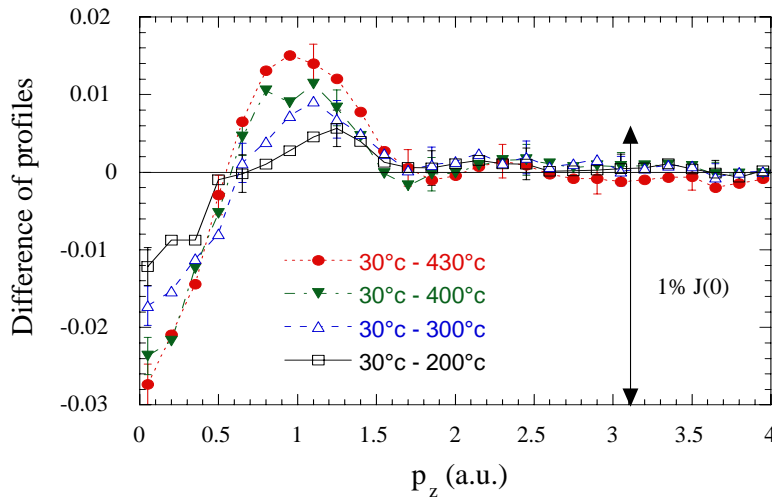
We used the 56 keV experimental set-up at ID15B, and the high pressure cell designed in the supercritical fluids team of the Laboratoire de Cristallographie (Grenoble) especially for this study, using back-scattered photons in order to obtain Compton profiles detected by a Ge-detector. We measured 5 temperature points along isobaric curve  $P = 300 \text{ bars}$  :

- $T = 30^\circ\text{C}$  : as reference point

- T = 200°C : in order to start getting the effect of hydrogen bond breaking and collapse of tetrahedral arrangement
- T = 300°C : idem than 200°C, but more pronounced effect
- T = 403°C : on the critical isochore, in the supercritical zone, density fluctuations are maximal. Here critical density is 0.322 g/cm<sup>3</sup>
- T = 430 °C : region with local density inhomogeneities and fluctuations

Room temperature and ambient pressure point has also been measured as a second reference point.

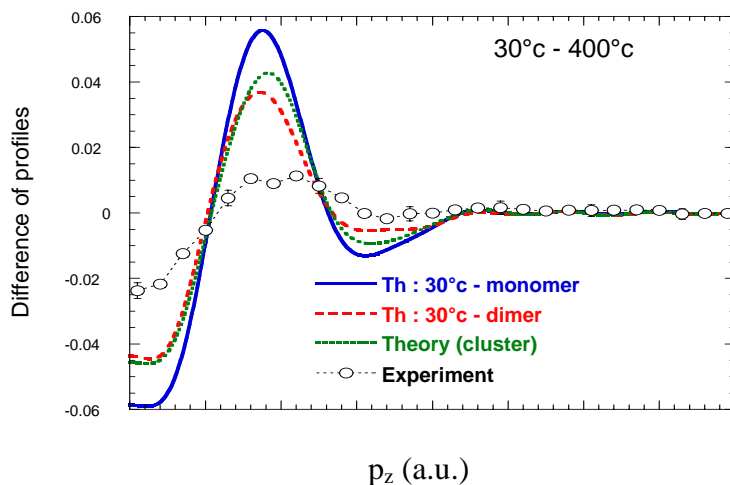
Figure one shows differences between the 30°C/300 bars reference profile and profiles measured at other temperatures defined above:



**Fig. 1 :** On the isobaric 300 bars curve, difference between reference profile measured at 30°C and profiles measured respectively at 200°C, 300°C, 403°C, 430°C.

The differences are all negative at  $p_z = 0$  a.u., and positive at around 1 a.u., the oscillation being due to the normalisation of the profiles to the same area. The high temperature Compton profiles are higher and narrower than reference profile at low  $p_z$ . This means that valence electrons are more localized in momentum space, i.e. delocalized in charge space when temperature increases. In other terms, as the structure of water tends towards smaller clusters, the Compton profile becomes narrower due to increased delocalization of valence electron in charge space.

Figure 2 compares the experimental difference between reference profile and profile measured at 400°C with Car-Parrinello Molecular dynamics calculations for supercritical water at the DFT-PBE level:



**Fig. 2 :** Comparison between experimental difference measured at 30°C and 400°C, and corresponding theoretical difference, namely “theory (cluster)”. The theoretical differences including monomeric and dimeric water are also shown.

Calculations are for 30°C, 200°C and 400°C. Comparison between theory and experiment for 200°C results shows a good agreement, i.e. a very similar trend in phase and magnitude. But, as visible in Fig.2, one can notice a clear difference in magnitude when comparing experimental and theoretical results at 400°C. Our results indicate that clustering is still significant at 400°C with clusters larger than dimers at least in part and is underestimated by theory which allows for essentially dimer formation. As a consequence, simulations seem to describe H-bond behaviour better at low temperature than at high temperature.

Calculations are still under progress for 430°C and 300°C. These results will lead to a quantitative comparison between experiment and theory which may give indication as to the structure of supercritical water (% distribution of dimers, trimers etc.).