ESRF	**Experiment title:** Structure and dynamics of hydrogen bonds in water and aqueous solutions	**Experiment number:** CH-1924
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Report:
This constitutes the final report on a long-term project ending in February 2007. The experiments reported here have been carried out during the periods 15-26/04/2005 (1st semester), 1-10/12/2005 (2nd semester), 14-23/06/2006 (3rd semester) and 14-23/02/2007 (4th semester). The main motivation for the proposal is developing the Compton scattering technique for structural studies on molecular liquids.

The general aims of the proposal and their fulfillment: **(1)** *Developing practical instrumentation for Compton scattering studies on liquids in different conditions.* This objective has been carried out by studies using different sample cells, developing an acid-proof chamber suitable for studies on (possibly corrosive) aqueous solutions and commissioning partially perforated diamond anvil cells for high-pressure Compton scattering experiments. In particular, these systematic studies, pushing the detection limit of the technique, have proved indispensable for the present and future experiments on molecular liquids. As one of the most important outcomes, a very small statistical inaccuracy (0.02% at the Compton peak) necessary for these studies is now routinely obtained.

(2) *Acquiring new structural information about the short-range molecular order.* Significant new structural information on water was obtained.

1st semester: (i) By comparing data acquired from water and polycrystalline ice Ih, a correlation between the intra- and intermolecular structures was for the first time demonstrated by Compton scattering and compared to ab initio quantum mechanical calculations [1]. (ii) Unique data for the subtle structural isotope effect in liquid water was obtained,[2] awaiting high-level simulations. The technical improvements related to these experiments included systematic studies on the

experimental sensitivity and commissioning of different sample cells.

2nd semester: (iii) Hydrogen bonding in aqueous solutions of hydrocloric acid (i.e. protonated water) was studied, following a recent methodological study on ion hydration [3]. This experiment provided relevant information and important experience on sample environments for the planning of future studies on aqueous solutions. The instrumentation development related to this experiment included the planning, production and commissioning of an acid-proof sample chamber for aqueous samples utilizing glass capillaries.

3rd and 4th semester: (iv) Pressure effects in water were studied up to 1.0 GPa utilizing both partially perforated diamond anvil cells and a Paris-Edinburgh large-volume cell. These represent important high-pressure Compton scattering experiments, including the planning and commissioning of different partially perforated diamond anvil cells, the use of which improves the signal-to-noise ratio in the experiments. Although high-pressure Compton scattering experiments continue to be very demanding, the aforementioned experimental improvement should facilitate future experiments on both liquids and solid-state materials. (v) Effect of microwave radiation on water was considered based on achievable experimental conditions. With the achievable x-ray intensities and detection systems, the simultaneous breaking of H bonds by microwaves and probing by X-rays was found to be at present too inefficient.

(3) *Collaboration with theoretical groups.* The long-term project has been extremely fruitful in establishing new theoretical contacts, tools and ideas. The collaboration includes groups from the universities of Dortmund (Germany), Stockholm (Sweden), Oulu and Helsinki (Finland). The computational supercell method, for the first time used for liquids during this project [2], will continue to be crucial for future experiments.

To conclude, the long-term project has been prolific from both experimental and theoretical points of view. Two papers were published exclusively from the measured data [1,2], four invited talks were given at the most important international conferences of the field. The experimental techniques and the sample environments developed within this project are still in use at the beamline and have been further utilized by our and other research groups in successive liquid Compton experiments. The related computational schemes have also had important further use. The project constituted the core of the PhD thesis of K. Nygård and the MSc. thesis of T. Pylkkänen. The expertise gathered will be crucial in the subsequent work [see, for example, 4]. Based on the international response, the technique is seen as truly complementary, thus eventually enriching the field of Compton scattering.

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[2] K. Nygård, M. Hakala, T. Pylkkänen, S. Manninen, T. Buslaps, M. Itou, A. Andrejczuk, Y. Sakurai, M. Odelius, and K. Hämäläinen, J. Chem. Phys. **126**, 154508 (2007).

[3] K. Nygård, M. Hakala, S. Manninen, K. Hämäläinen, M. Itou, A. Andrejczuk, and Y. Sakurai, Phys. Rev. B **73**, 024208 (2006).

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