ESRF	**Experiment title:** Microscopic characterization of ionic liquids	**Experiment number**: HD 521
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Report:

Ionic liquids (ILs) are an emerging class of new materials with an extremely wide range of future chemical and industrial applications. They have certain distinct and advantageous properties over other liquids such as low vapor pressures, thermal stabilities and non-toxicity. A vast number of ionic liquids (close to one million binary versions) can be designed by varying the ions. Therefore, for tailoring their macroscopic properties, it is becoming crucial to have a thorough understanding and control of their microscopic behavior. There is a strong need for basic research in order to model and predict the properties of the ILs. Especially, the novel ways to probe the properties, such as Compton scattering experiments, can bring highly important new structural information on these systems. The molecular-level controllability makes ILs very versatile for diverse applications such as drug delivery, as solvents of otherwise insoluble molecules (e.g. cellulose), as novel electrolytes or even as liquid mirrors.

The objective of the project is to find out new sub-nanometer scale geometrical details of ILs in the liquid phase by comparing liquids to crystalline state both experimentally and by theoretical simulations. The project involves the performed experiment, computational parts and interpretation of the results based on structural models. We carried out the measurements according to the plan outlined in the proposal. Temperature was controlled between the room temperature and 170◦C. We used glass capillaries in which the ILs were enclosed. The empty glass capillaries were measured as a reference. We were able to measure datasets from

[mmim]Cl and [bmim]Cl ILs (mmim=methyl-methylimidazolium, bmim=butyl-methylimidazolium). The proper melting of the samples posed some challenges during the experiment. The crystal-liquid transitions were verified by diffraction measurements during the experiment.

The analysis of the measured experimental data continues, and preliminary results can be expected within one month. The computational part of the project is divided into two steps, from which the first part has been achieved (molecular dynamics simulations), and the second part (computation of Compton profiles) is going on. Due to the large number of electrons, only the lightest of the two, [mmim]Cl, is at the moment available from *ab initio* simulations. Dr. Matt McGrath at the University of Kyoto, Japan, is our collaborator in this project concerning the *ab initio* molecular dynamics (MD) simulations. He and his colleagues have performed the MD simulations of liquid [mmim]Cl employing supercomputers and have provided the atomic trajectories in the liquid as a function of time. From this data we are now in the process of calculating estimates for the Compton profiles in the liquid phase. The Compton profile for the crystalline phase can be calculated from published diffraction data. These computational studies have resulted in the preliminary Compton profile difference describing the solid-liquid transition (Figure 1). We used density functional theory and generalized gradient approximation for the molecular dynamics simulations and for the calculation of the Compton profiles.

Figure 1 shows the predicted result on the solid-liquid transition obtained from the *ab initio* MD structures. There is a clear effect upon melting the crystalline ILs, 0.25 % change at the Compton peak, whose origin is the change in the inter- and intramolecular bond lengths. The typical statistical accuracy that is expected in Compton scattering experiments is of the order of 0.02 %-units for the profile differences. Therefore, from this preliminary simulation we can expect that important structural information can be extracted from the experimental data by comparing to the theoretical prediction. The theoretical approach will be further studied to control the effects of parameters used and to get insight into the geometrical changes proper that are responsible for the predicted signal.

The proposed research constitutes the first steps in applying synchrotron inelastic x-ray scattering to understand complex, higher-molecular mass solvents. The project is a new opening towards detecting subtle chemical effects related to molecular topologies and ordering in industrially relevant liquids.Emplying the computations, after completing the analysis of the experimental data, we will be able to publish the project as a scientific article and as presentations in conferences. The possible journals for reporting the project are Journal of Chemical Physics or Journal of Physical Chemistry.

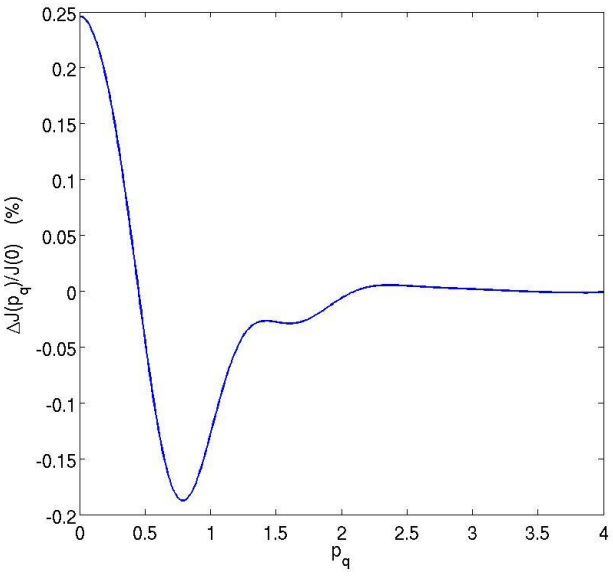

Figure 1. Predicted Compton profile difference between liquid and crystalline [mmim]Cl.