Work Plan

The main goal of this STSM will be to work on modelling of the 35/37Cl quadrupolar NMR relaxation parameters of chloride anion in the ionic liquid 1-decyl-3-methyl-imidazolium chloride [C10mim][Cl]. Previous analysis of the MD trajectory of the [C10mim][Cl] ionic liquid has shown that chloride anion is coordinated by the C10mim cations in various ways. The Sternheimer approach based calculations of the nuclear quadrupolar coupling constant of chloride revealed that this quantity is highly sensitive to the structure of the first solvation shell of the ion. These results are important in its own right, yet the reliability of the Sternheimer approach used in herein is to be tested by more accurate quantum mechanics based calculations of the electric field gradients. The QM/MM calculations treating only the selected chloride anions quantum mechanically have shown that the computed electric field gradients can differ from those based on the Sternheimer approach significantly. To assure reliability of the results for electric field gradients, a quantum mechanics based computational approach has to be developed and fully tested.

To develop an efficient computational procedure to compute electric field gradients on quadrupolar anions in the [C10mim][Cl] ionic liquid, the following work plan has been set:

Because nuclear quadrupolar coupling constant of chloride is very sensitive to the structure of its nearest molecular environment, molecular species in the first solvation shell of the anion have to be described quantum mechanically. However, the promotion of the large C10mim cations to the QM region is met with huge computational burden. We will perform a series of DFT based test calculations to find a cost-effective yet reliable computational scheme for the calculation of the electric field gradients on the quadrupolar nuclei of the chloride anions.

The effect of the second and further solvation shells on the electric field gradients of the anion will be evaluated. For this purpose, a suitable classical force field is to be selected to be used in the QM/MM calculations of the electric field gradients. The effect of the polarizable potentials will be investigated.

Computed 35/37Cl quadrupolar coupling constants will be compared to the available experimental data to validate our results.