

Modelling quadrupolar $^{35/37}\text{Cl}$ NMR relaxation of ionic liquid 1-decyl-3-methyl-imidazolium chloride using molecular dynamics/quantum mechanics approaches

WORK PLAN

The aim of this STSM is primarily to provide extra momentum for the collaboration project between computational chemistry groups lead by Prof. Francesca Mocci at University of Cagliari and by Dr. Kęstutis Aidas at Vilnius University in the field of multi-scale modelling of quadrupolar NMR relaxation. This project in particular concerns the modelling of the $^{35/37}\text{Cl}$ quadrupolar NMR relaxation parameters of chloride anion in the ionic liquid 1-decyl-3-methyl-imidazolium chloride, [C10mim][Cl]. We will tackle this problem by using an integrated molecular dynamics/quantum mechanics approach, which has previously been shown by us to be very promising in terms of accurate modelling of quadrupolar NMR relaxation parameters. First, classical molecular dynamics simulations of the system under study are performed. This allows modeling structural and dynamical features of the ionic liquid at particular thermodynamic conditions, paying particular attention to the behavior of the chloride anions. In addition, molecular trajectories recorded during the molecular dynamics runs are used as input for quantum mechanics based calculation of the electric field gradients at the site of the nucleus of the chloride. Quantum mechanics/molecular mechanics approaches are used for this purpose. The electric field gradients computed along the molecular trajectory are then used to evaluate the $^{35/37}\text{Cl}$ quadrupolar coupling constant. We are in this manner aiming to assess the performance of our computational scheme, but also to provide new and unique insight into the structure and dynamics of ionic liquids on the molecular level. Our project is thus completely within the lines of scope of Working Group 1 "Energy-Resolved Methods" as it contributes to the development of computational algorithms for accurate prediction of spectroscopic parameters.

So far, extensive classical molecular dynamics simulations of the [C10mim][Cl] ionic liquid have been carried out along with some structural analysis primarily at the University of Cagliari. Meanwhile at Vilnius University, careful quantum chemical benchmark calculations of the electric field gradients have been performed. We are thus in the position where our efforts have to be combined. The work plan of this STSM is thus as follows:

1. The recorded MD trajectories of the [C10mim][Cl] ionic liquid will be analyzed in order to in order to classify the most recurring coordination patterns of chlorine anions and their evolution on the relevant time scales. Imidazolium ionic liquids are known to be heterogeneous systems, particularly those with long alkyl chains. This structural analysis is thus mandatory as local environment of the anion has direct influence to its quadrupolar coupling constant.
2. A series of QM/MM test calculations of electric field gradients felt by the $^{35/37}\text{Cl}$ nuclei will be performed in order to assure reliable estimate of the quadrupolar coupling constant. We will thus consider the convergence of the computed coupling constants on the size of the considered molecular systems and the spacing between molecular snapshots along the trajectory. The type of the classical potential – polarizable or non-polarizable – will also be considered. Different schemes for derivation of the force field parameters to used in the QM/MM calculations will be investigated. These steps are necessary to take as conclusions reached for the ordinary molecular liquids may be invalid for the case of ionic liquids due to the complex nature of intermolecular interactions governing their behavior at molecular level. Therefore, test calculations on chloride anions in both aqueous solution and ionic liquid will be considered.
3. Computed $^{35/37}\text{Cl}$ quadrupolar coupling constants will be compared to the available experimental data [Spectrochim. Acta A, 132 (2014) 879] to validate our results.

4. Based on the conclusions reached so far, different QM/MM based strategies for evaluating the $^{35/37}\text{Cl}$ correlation time of electric field gradient fluctuations will be considered.