A combined application of EPR spectroscopy and molecular modelling to nematic and discotic liquid crystals

F. Chami,1 H. Gopee,1 A.N. Cammidge,1 M.R. Wilson,2 and V.S. Oganesyan1,*

1 School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, United Kingdom
2 Department of Chemistry, Durham University, Durham, DH1 3 LE, United Kingdom

Electron Paramagnetic Resonance (EPR) with paramagnetic spin probes (SP) is a particularly valuable advanced spectroscopic method for studying both structure and dynamics of soft matter systems such as liquid crystals (LC). Nitroxide SPs can be readily introduced into LCs to probe the order and dynamics of LC molecules in different phases [1]. EPR is a “fast” magnetic technique which is able to resolve molecular motions of partially ordered systems on the sub-nanosecond timescale. We combine EPR with state-of-the-art molecular modelling approaches and simulate EPR spectra from their outputs. This bridges the gap between theory and experiment allowing unambiguous interpretation of EPR lineshapes and enabling conclusions to be drawn about molecular motions and order in the bulk phase [2,3].

In this presentation we report our recent application of variable temperature EPR spectroscopy combined with theoretical modelling to both nematic and discotic (columnar) LCs.

For nematic LCs structurally variable nitroxide SPs probing different aspects of LC dynamics have been employed resulting in different but highly complementary EPR spectra. Variable temperature EPR spectra of LCs doped with SPs were predicted directly from fully atomistic Molecular Dynamics (MD) simulations using our novel MD-EPR simulation methodology [2]. They show excellent agreement with experiment. Using MD-EPR approach we were able to characterise in detail the dynamics and molecular interactions in different phases of nematic LCs [3-4]. Most importantly, we were able to predict and confirm experimentally dynamic fluctuations between partially ordered and disordered meta-stable states at the phase transition critical points [3-4].

We also present the first application of EPR spectroscopy to columnar discotic liquid crystal (HAT6) using a novel rigid-core nitroxide spin probe designed and synthesized by us for this purpose (see picture below) [5]. EPR spectra measured at different temperatures across three phases show a strong sensitivity to the HAT6 phase composition, molecular rotational dynamics, and columnar order as well as the director distribution. Simulation of the EPR line shapes using a Brownian Dynamics (BD) simulation model gives a numerical estimate of these parameters at different temperatures along both I-Col and Col-Cr phase transitions.

References:

* presenting author; E-mail: v.oganesyan@uea.ac.uk