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Study of Structural organization in Ionic Liquids by Hyper-Rayleigh Scattering and DFT calculations

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In this study, we investigate the local structure for a series of imidazolium Ionic Liquids (IL) involving different anions (namely, $[BF_4]$, $[PF_6]$, [TFSI], [SCN] and $[(CN)_2N]$) using Hyper-Rayleigh Scattering (HRS). In particular, we show that the scan polarization profiles of the harmonic scattered light provide well-defined signatures due to 'transient' ion clusters probed within the observation time of the HRS technique (10^{-14}-10^{-12} s). Combined with DFT calculations from differently sized ion clusters, the multipolar analysis of the HRS measurement reveals mainly the octopolar character of the hyperpolarisability associated with the elementary scattering structure in IL. In this framework, the calculated HRS 'spherical' invariants ($|\beta_{J=1}|$ and $|\beta_{J=3}|$) converge towards values approaching the experimental ones especially for the calculated structures involving a number of neighbors leading to form at least a well-defined a first solvation shell around a central ion (<1nm). We emphasize that this octopolar contribution to the HRS response originates (at the expense of the dipolar one) from the strong correlations and non additive interactions (cooperative effects) taking place between ion species in IL. Such cooperative effects lead indeed to an interaction-induced mechanism which reinforces the HRS coherent scattering intensity (moment of zero order) [1]. This finding is consistent with conclusions reported in previous studies especially by OHD-RIKES and low-frequency Raman spectroscopies invoking the collective nature of the intermolecular motions between ionic species in ILs from the analysis of the measured spectral densities in the spectral range 10-200 cm^{-1} [2-4].

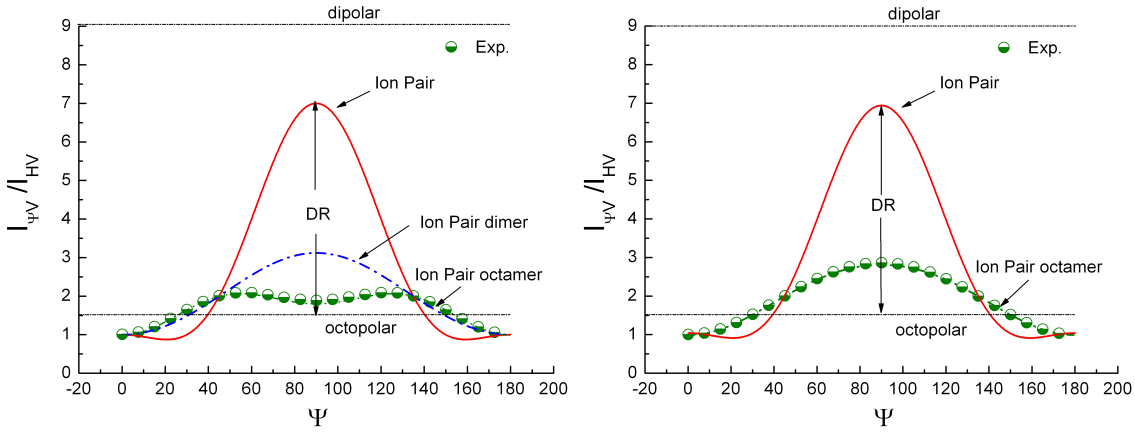

Fig. 1: Comparison between the experimental elliptical polarization scans (circles) and the corresponding profiles calculated from the different ion pair structures (IP, IP2 and IP8) involving [BMI] with $[BF_4]$ (left) and [EMI] with $[N(CN)_2]$ (right**).**

References

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