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Article

Structure of 1-Alkyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)amide Ionic Liquids with Linear, Branched and Cyclic Alkyl Groups

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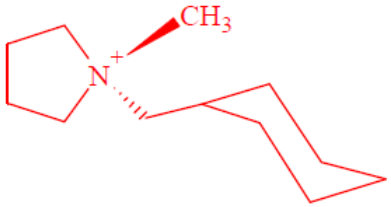
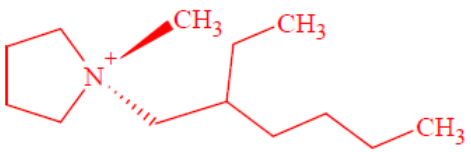
Abstract

X-ray scattering and molecular dynamics simulations have been carried out to investigate structural differences and similarities in the condensed phase between pyrrolidiniumbased ionic liquids paired with the bis(trifluoromethylsulfonyl)amide (NTf 2) anion where the **cationic tail is linear, branched or cyclic**. This is important in light of the charge and polarity type alternations that have recently been shown to be present in the case of liquids with cations of moderately long linear tails. For this study we have chosen to use the 1-alkyl-1-methylpyrrolidinium, Pyrr+1;n with n = 5 or 7 as systems with linear tails, 1-(2-ethylhexyl)-1-methylpyrrolidinium, Pyrr +1;EtHx as a system with a branched tail and 1-(cyclohexylmethyl)-1-methylpyrrolidinium, Pyrr +1;ChxMe as a system with a cyclic tail. We put these results into context by comparing these data with recently published results for the $Pyrr^{+}1,n/NTf^{-}2$ ionic liquids with n = 4, 6, 8 and 10.1,2 **General methods for interpreting the structure function S(q) in terms of q-dependent natural partitionings are described**. This allows for an in-depth analysis of the scattering data based on molecular dynamics (MD) trajectories that highlight the effect of modifying the cationic tail.

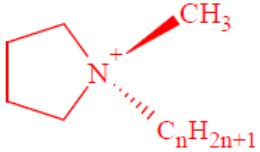
Introduction



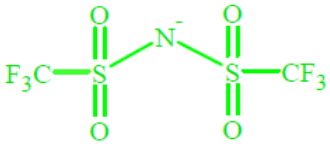
(a) $Pyrr_{1,ChxMe}^{+}$



(b) $Pyrr_{1,EtHx}^{+}$



(c) $Pyrr_{1,n}^{+}$



(d) NTf_2^{-}

Methods

1) X-ray scattering

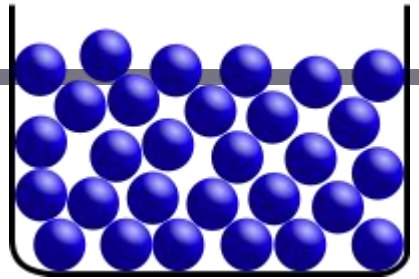
Advanced Photon Source, beamline 11-ID-C

$$S(q) = \frac{I_{coh}(q) - \sum_i x_i f_i^2(q)}{\left[\sum_i x_i f_i(q)\right]^2}$$

2) molecular dynamics simulations

$$S(q) = \frac{\rho_o \sum_i \sum_j x_i x_j f_i(q) f_j(q) \int_0^{L/2} 4\pi r^2 (g_{ij}(r) - 1) \frac{\sin qr}{qr} W(r) dr}{\left[\sum_i x_i f_i(q)\right]^2}.$$

Structure factor (from wikipedia)



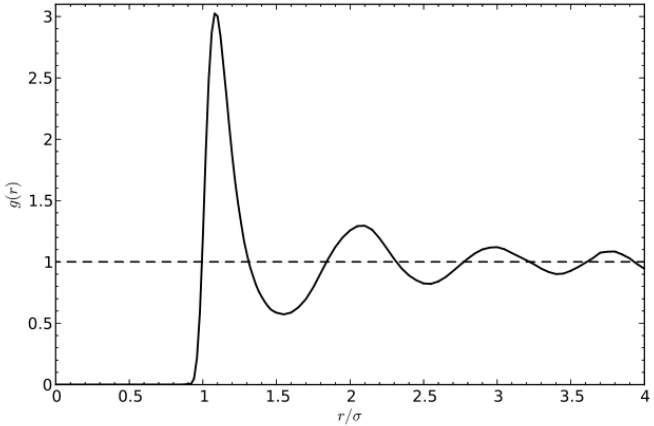
Pair correlation function

1) At short separations (small r), *g(r)* = 0. This indicates the effective width of the atoms, which limits their distance of approach.

2) A number of obvious peaks and troughs are present. These peaks indicate that the atoms pack around each other in 'shells' of nearest neighbors. Typically the 1st peak in *g(r)* is the, strongest feature. This is due to the relatively strong chemical bonding and repulsion effects felt between neighboring atoms in the 1st shell.

3) The attenuation of the peaks at increasing radial distances from the center indicates the decreasing degree of order from the center particle. This illustrates vividly the absence of "long-range order" in liquids and glasses.

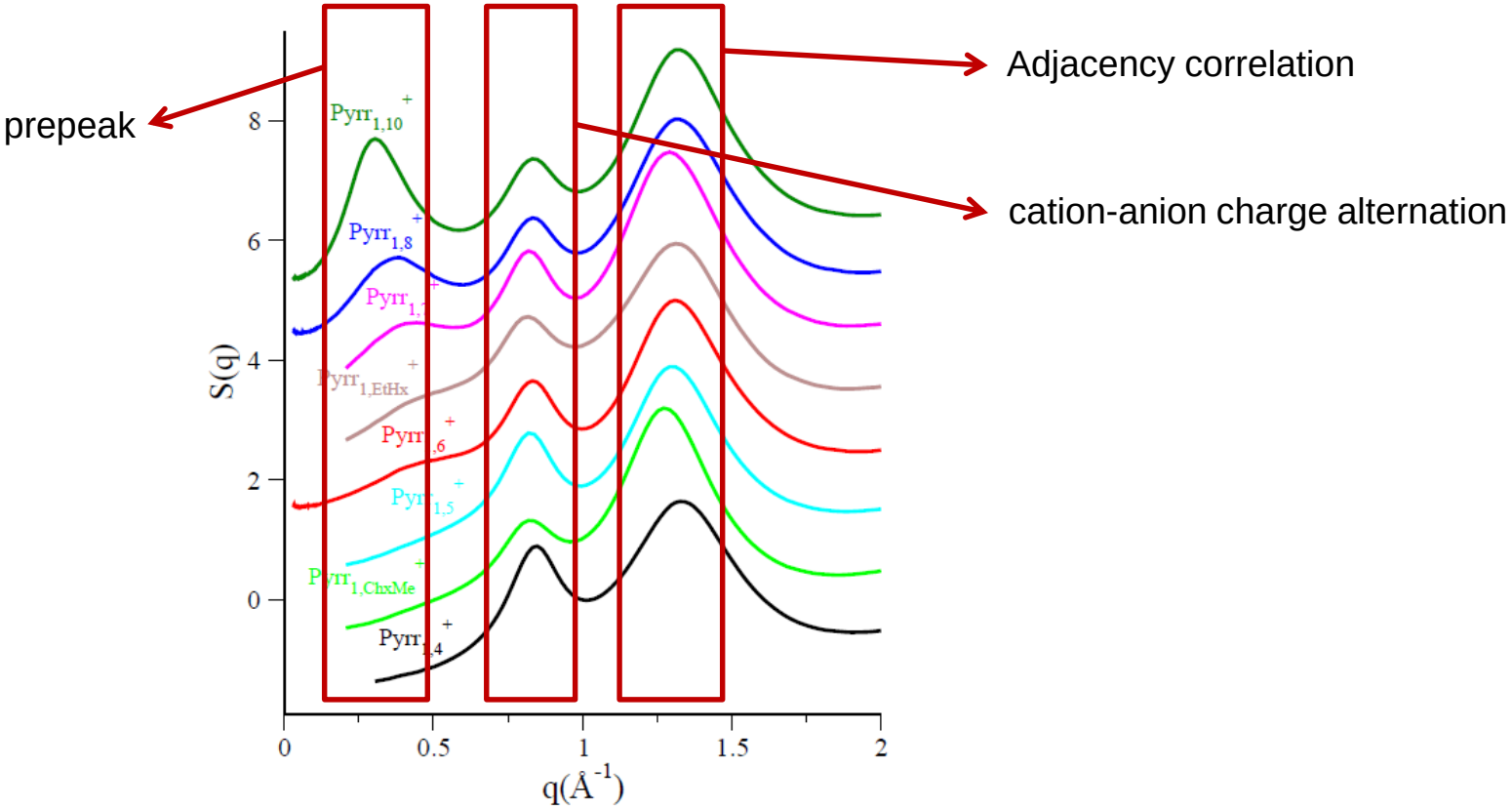
4) At long ranges, *g(r)* approaches a limiting value of 1, which corresponds to the macroscopic density of the material.



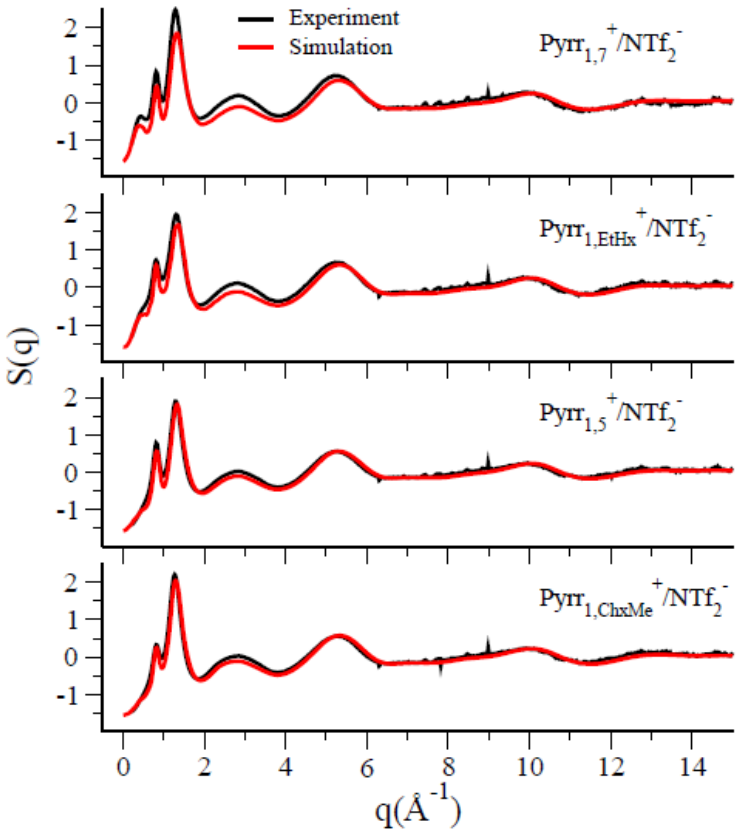
Fourier transformation
-> structure factor

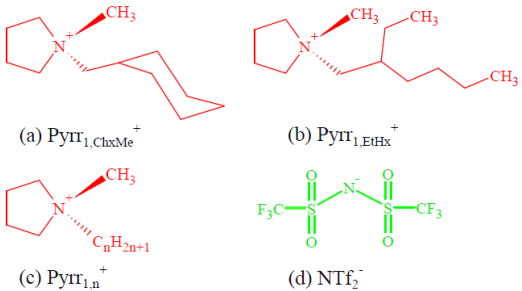
$$S(q) - 1 = \frac{4\pi\rho}{q} \int_0^\infty [g(r) - 1] \sin(qr) dr$$

Small Angle X-ray Scattering (SAXS) Results

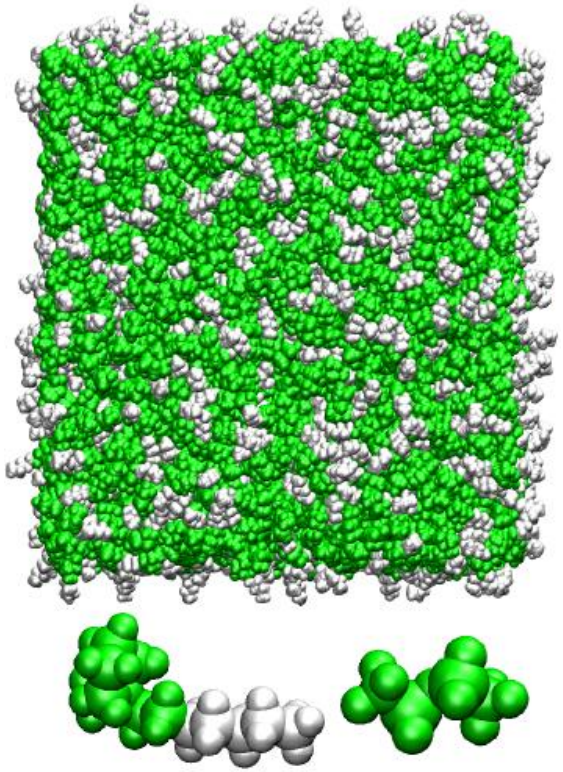


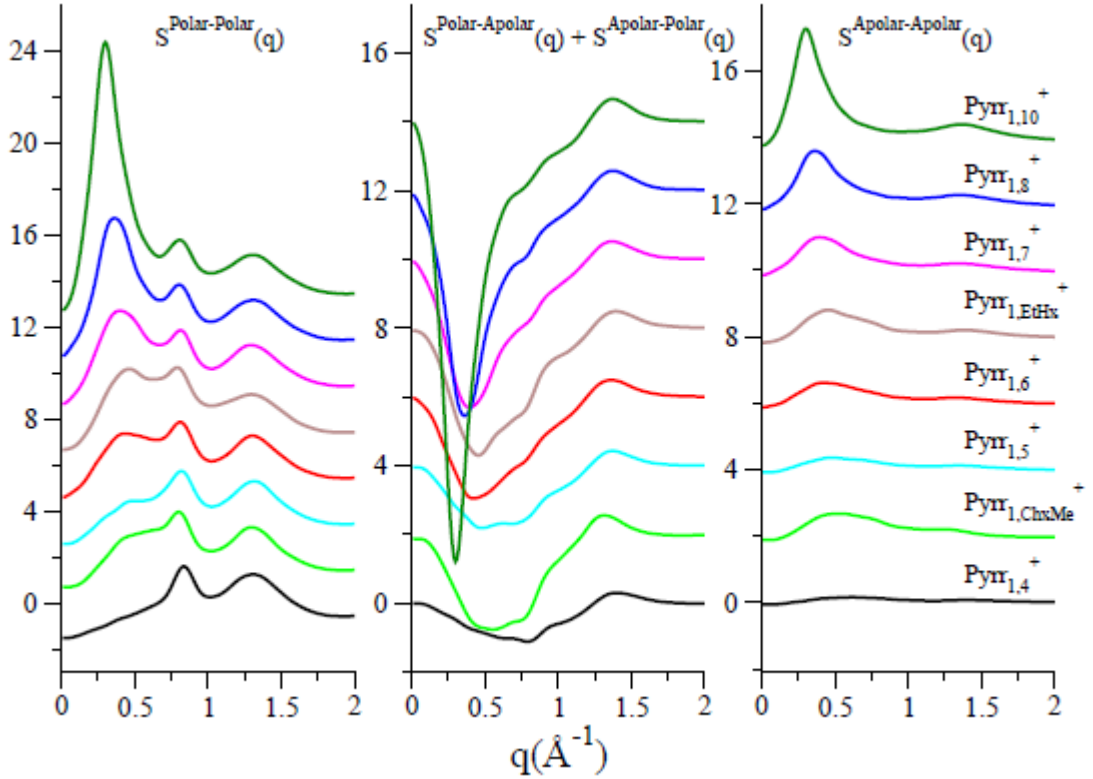
Comparison of SAXS / MD



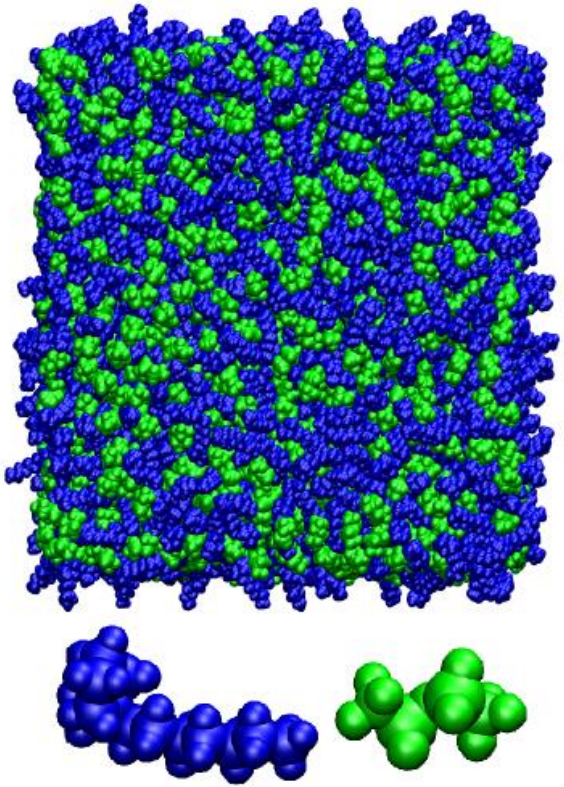


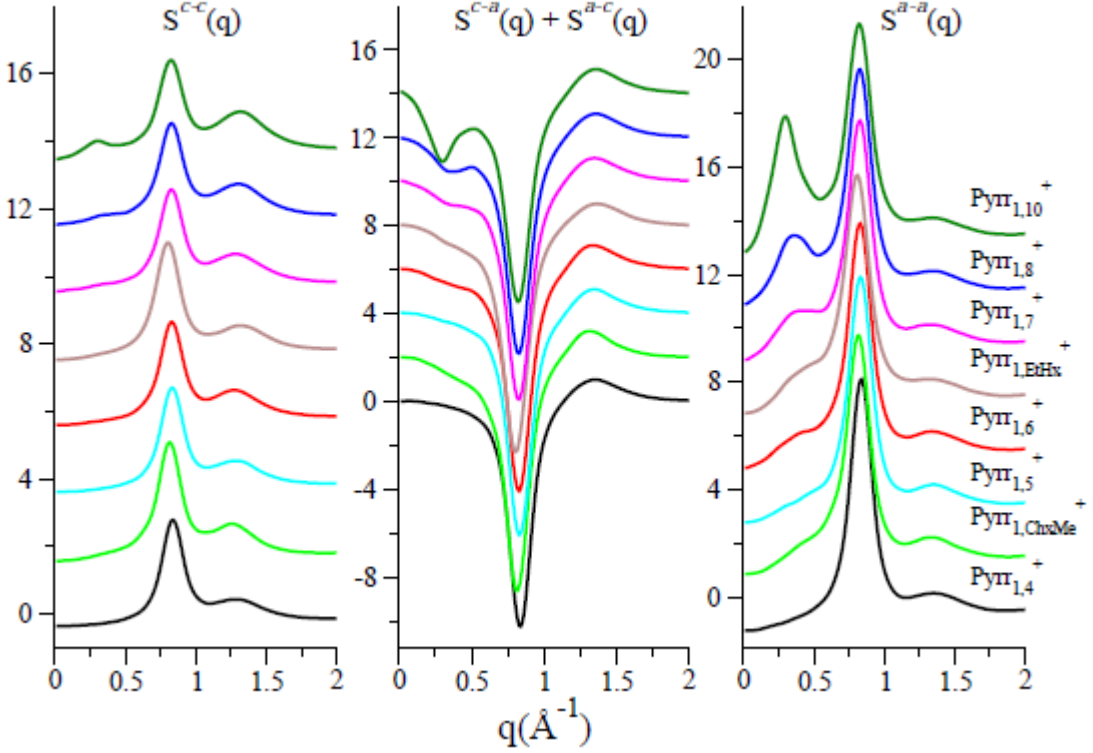
Polarity Partitioning



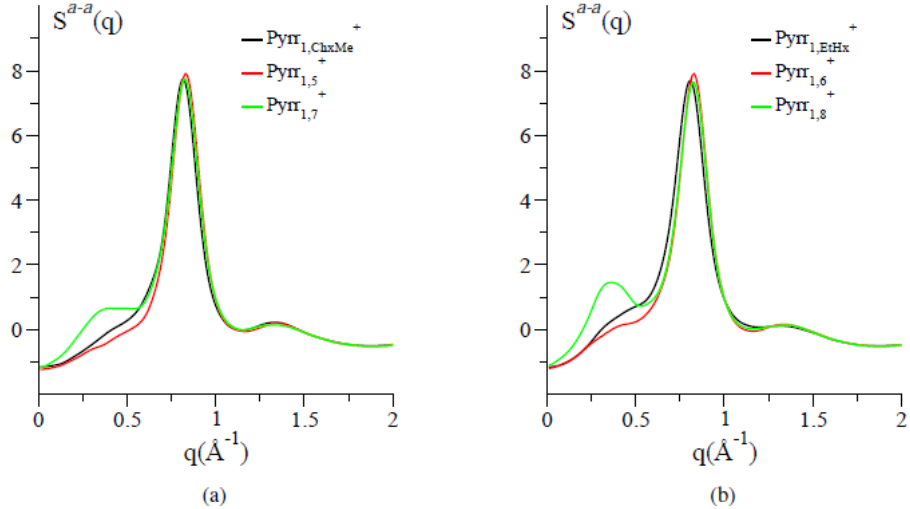


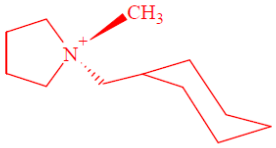
Ionic Partitioning



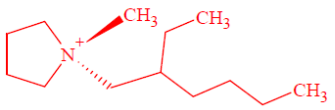


Ionic Partitioning





(a) $Pyrr_{1,ChxMe}^{+}$



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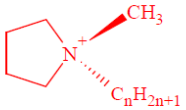
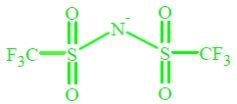
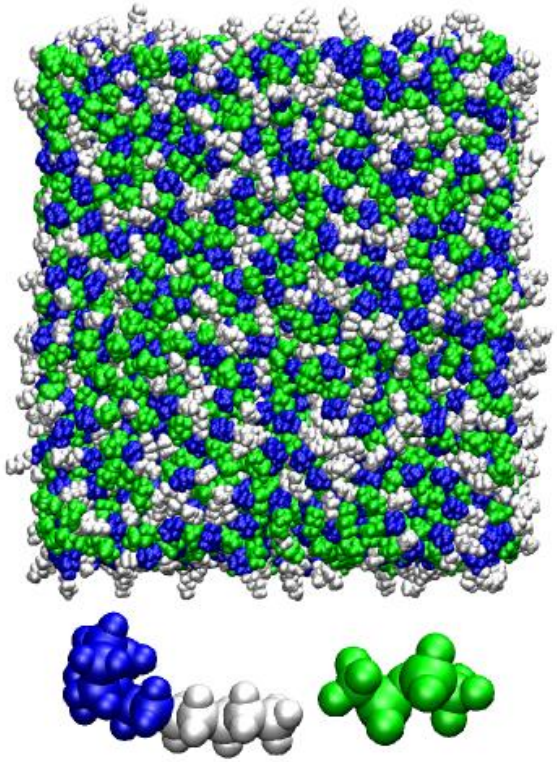


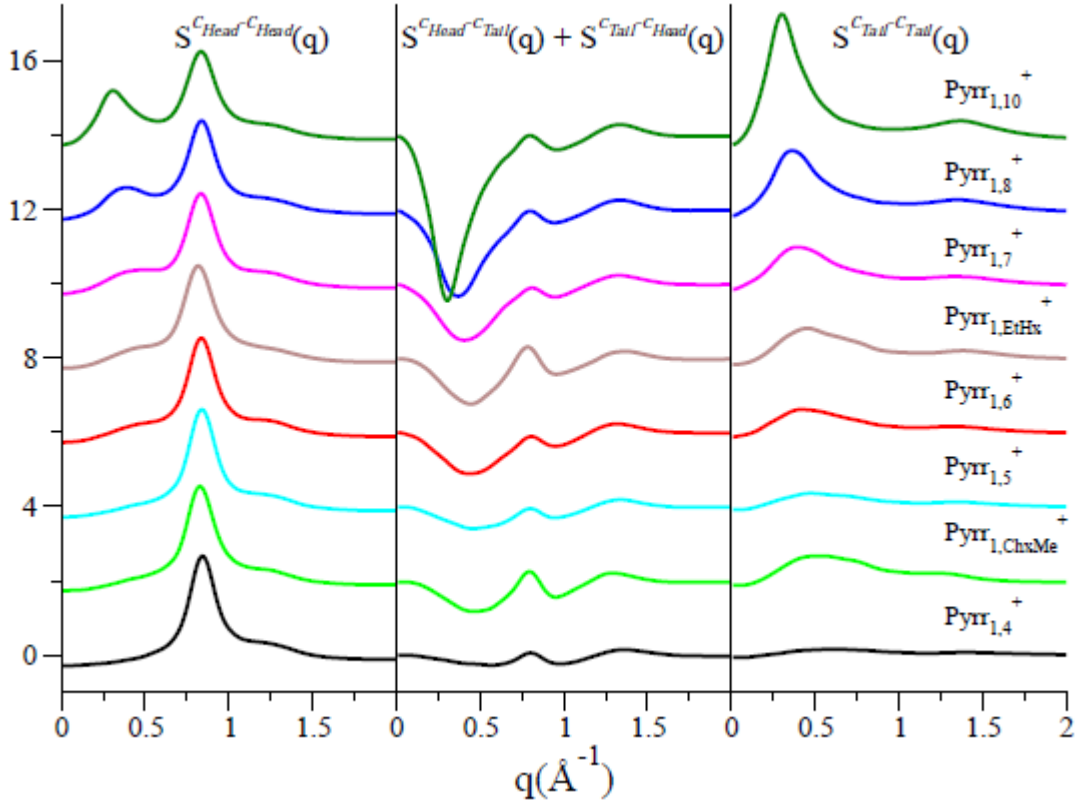
(c) $Pyrr_{1,n}^{+}$



(d) NTf_2^{-}

Sub-Ionic Partitioning





Sub-Ionic Partitioning