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Molecular Layering of Fluorinated Ionic Liquids at a Charged Sapphire (0001) Surface

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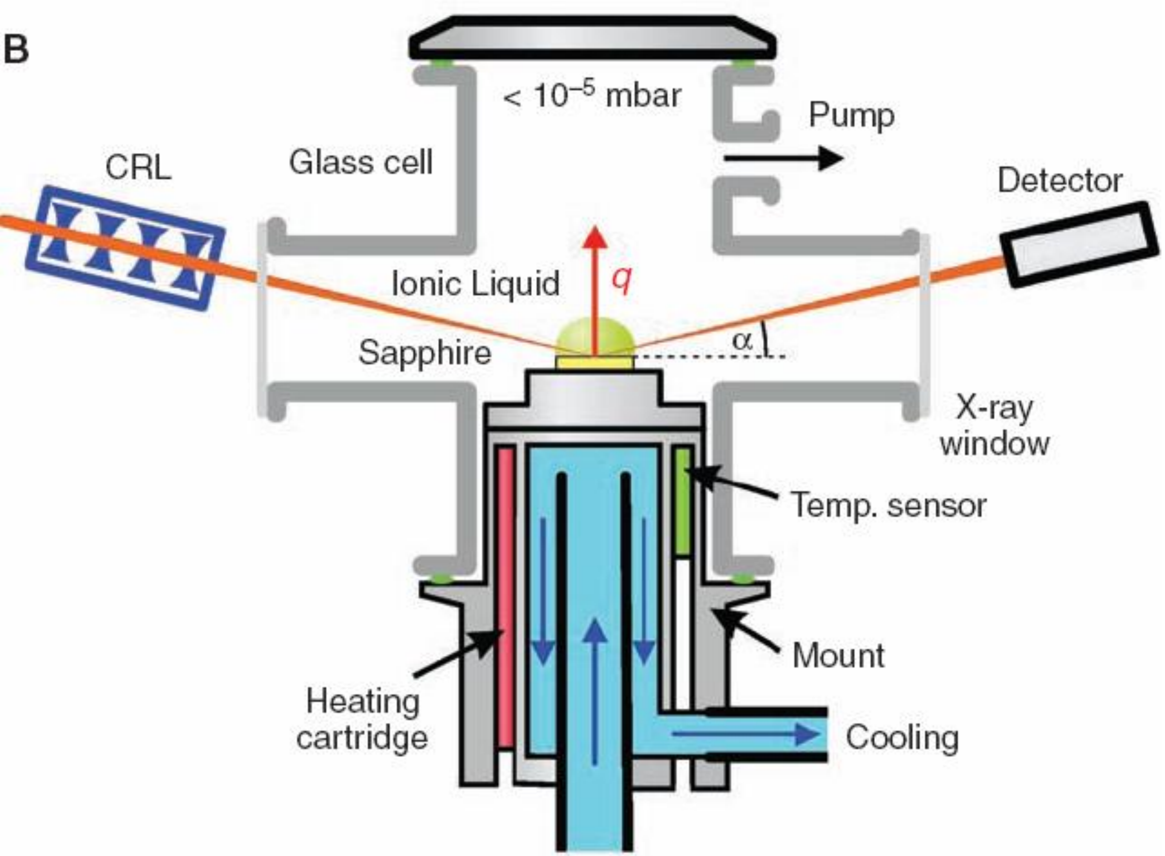
Room-temperature ionic liquids (RTILs) are promising candidates for a broad range of "green" applications, for which their interaction with solid surfaces plays a crucial role. In this high-energy x-ray reflectivity study, the temperature-dependent structures of three ionic liquids with the tris(pentafluoroethyl)trifluorophosphate anion in contact with a charged sapphire substrate were investigated with submolecular resolution. All three RTILs show strong interfacial layering, starting with a cation layer at the substrate and decaying exponentially into the bulk liquid. The observed decay length and layering period point to an interfacial ordering mechanism, akin to the charge inversion effect, which is suggested to originate from strong correlations between the unscreened ions. The observed layering is expected to be a generic feature of RTILs at charged interfaces.

Seok, Sangjun (11/29/09)

Experimental Setup



◦ Beamline ID15A, 72.5 KeV (Grenoble, France)

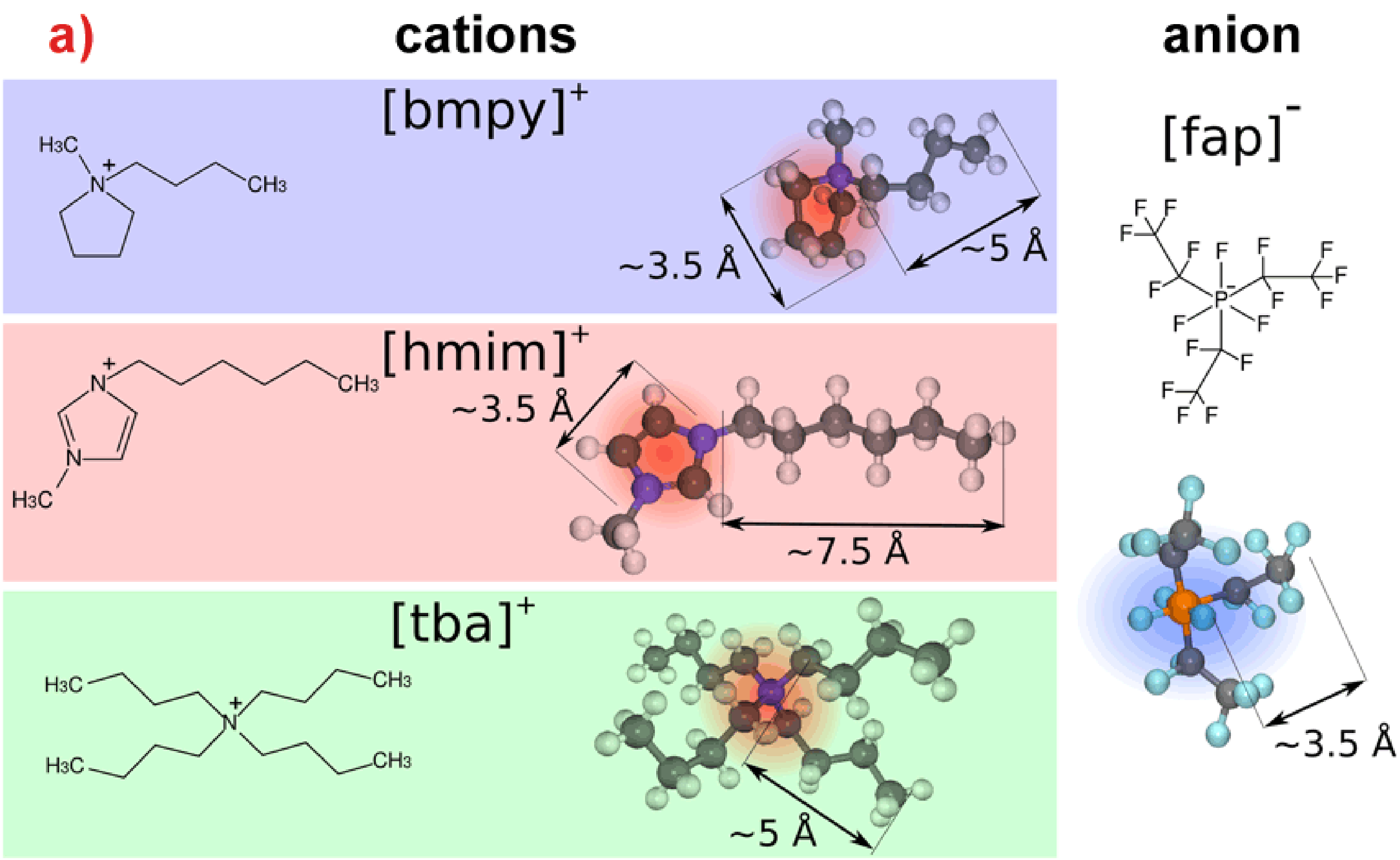
◦ Al_2O_3 substrate
(10 mm by 6 mm by 0.35 mm)
Surface roughness (σ_s) 2 ~ 2.5 Å

◦ The high-purity grade RTILs degassed at T ~ 70°C in vacuum oven

◦ Before the deposition of the RTIL

1. Substrate was heated to 110°C
2. The cell was evacuated to 10^{-5} mbar
3. After depositing the RTILs

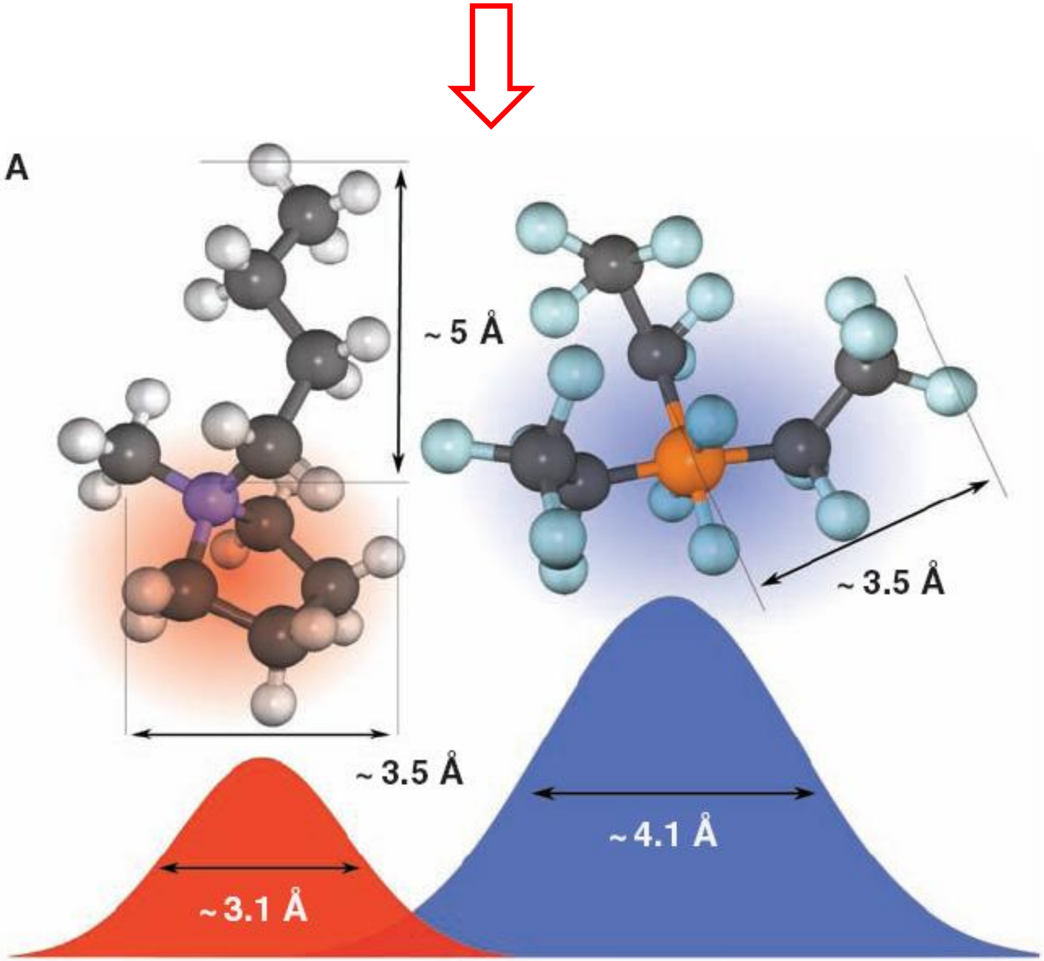
Sample - RTILs



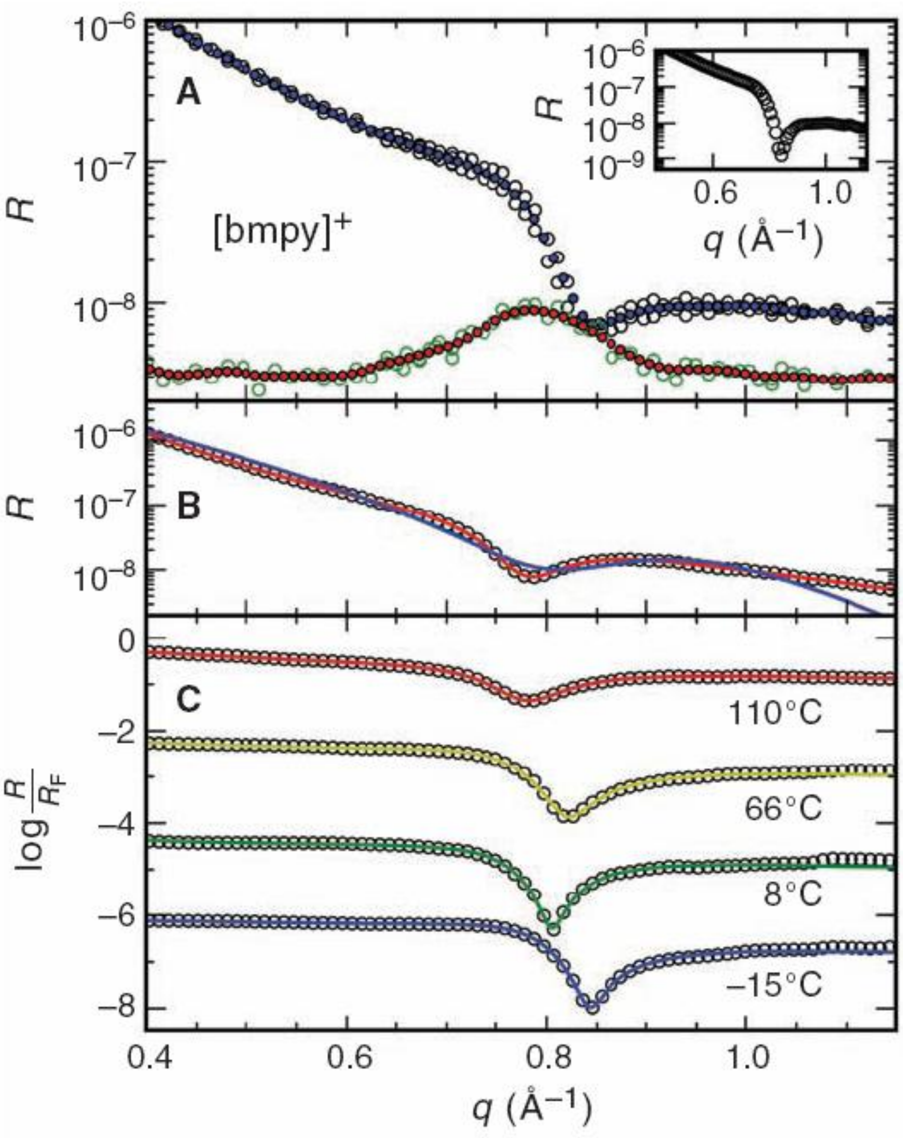
ESRF Synchrotron, Grenoble

The Gaussian electron density profile

$$\rho(z) = (2\pi)^{-1} \sum_{n=0}^{\infty} \left\{ \frac{\rho_c}{\sigma_n^c} e^{-\frac{1}{2}\left(\frac{d_0 + nd - z}{\sigma_n^c}\right)^2} + \frac{\rho_a}{\sigma_n^a} e^{-\frac{1}{2}\left(\frac{d_0 + (n+\varepsilon)d - z}{\sigma_n^c}\right)^2} \right\} + \sigma_s erf\left(\left(\frac{-z}{\sqrt{2}\sigma_s}\right)\right)$$



Experimental Result for the $[bmpy]^+[FAP]^-$ -Al_2O_3 interface



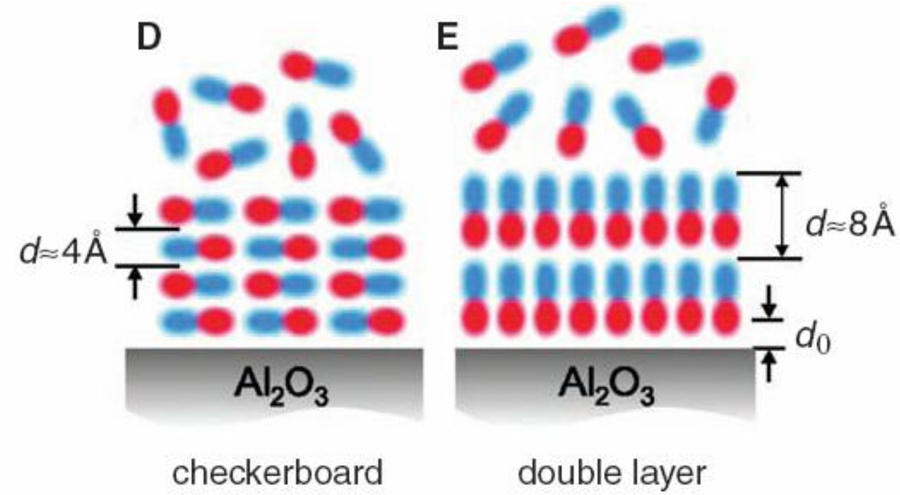
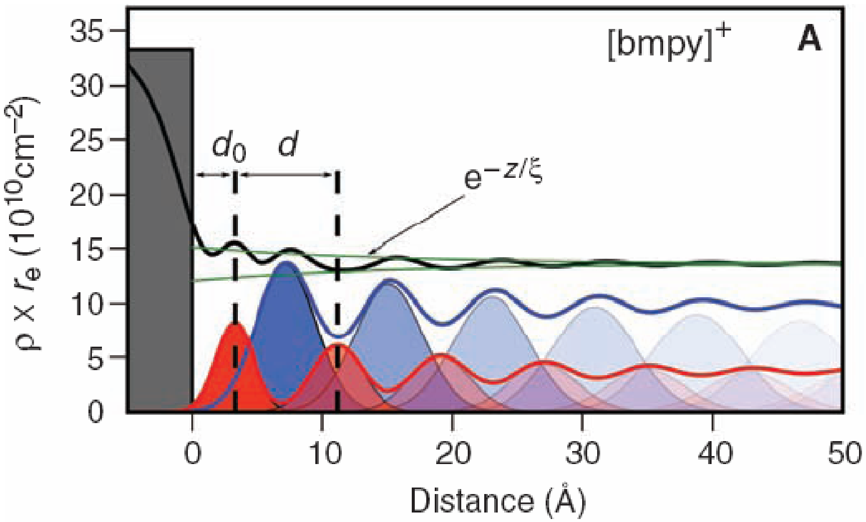


Fig. 2. Experimental results for the $[bmpy]^+[FAP]^-$-Al_2O_3 interface. (**A**) Measured reflectivity (black open circles) and background (green open circles) at $T = -15°C$. The blue and red circles mark the corresponding interpolated data on a regularly spaced grid. (Inset) Background-corrected reflectivity curve. (**B**) Reflectivity at 110°C together with best fits using a checkerboard [blue line and (D)] and a double-layer [red line and (E)] model, respectively. (**C**) Normalized reflectivities (symbols) together with best fits (solid lines) at different temperatures (the curves are shifted vertically for clarity). (**D** and **E**) Different possible layering arrangements of correlated ions at a hard wall with checkerboard-type stacking (D) and double-layer stacking (E).

Experimental Result for the $[bmpy]^+[FAP]^-$ -Al_2O_3 interface



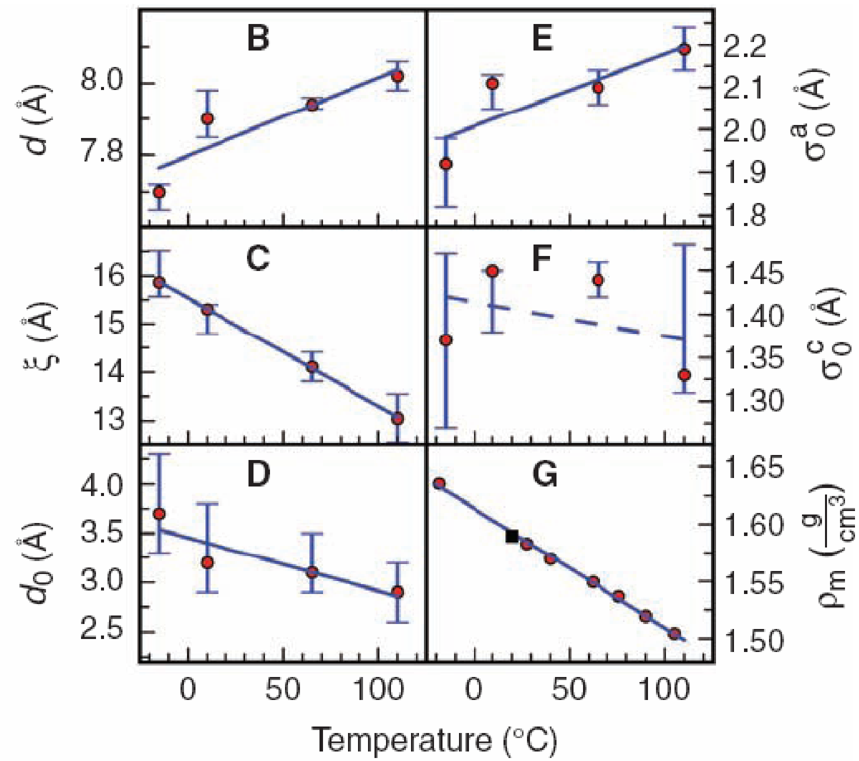


Fig. 3. (**A**) Cation (red), anion (blue), and total (black) electron densities obtained from the best fit at $T = -15°C$. Red and blue lines indicate cation and anion Gaussian distributions contributing to the respective partial electron density profiles; black line, total electron density profile; and gray bar, electron density of the sapphire substrate without roughness. (**B** to **F**) Best-fit values of d, ξ, d_0, σ_0^a, and σ_0^c. Linear fits (blue) are also shown. Error bars were derived from parameter space maps and indicate a 50% decrease in fit quality. (**G**) RTIL mass density ρ_m obtained from bulk density pycnometry (red circles) with a linear fit (blue) and the supplier's room temperature value (black square) (*17*).

$[hmin]^{+}[FAP]^{-}$ -Al_2O_3 and $[tba]^{+}[FAP]^{-}$ -Al_2O_3 interface

d =7.7Å
d_0 = 2.7Å
ξ = 7.7 Å

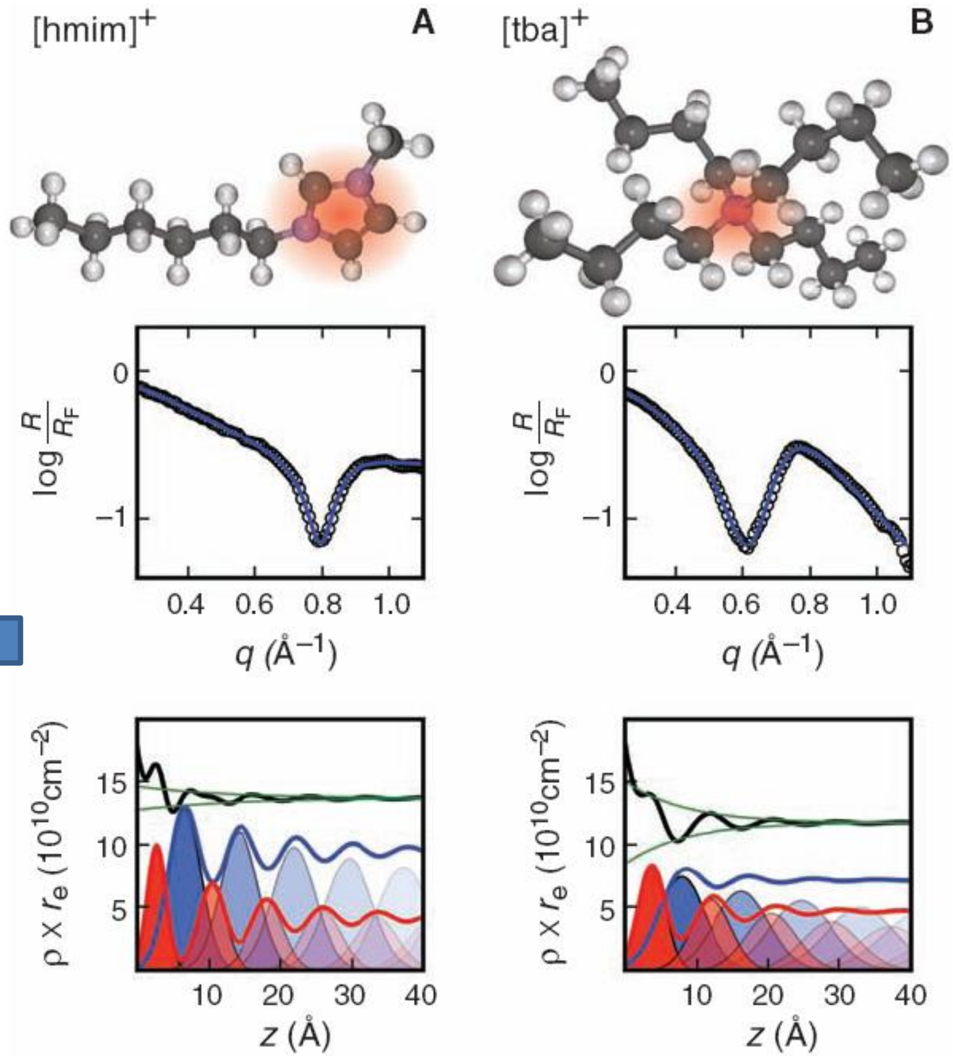


Fig. 4. Molecular layering at the $[hmim]^{+}[FAP]^{-}$-Al_2O_3 interface (**A**) and $[tba]^{+}[FAP]^{-}$-Al_2O_3 interface (**B**). Each column displays a sketch of the corresponding cation; the normalized reflectivity (open circles) measured at $T = -34°C$ (A) and $T = 56°C$ (B), including the best fit (solid line); and the cation (red line), anion (blue line), and total (black line) electron densities obtained from the best fit.

d =8.4Å
d_0 = 3.7Å
ξ = 8.1 Å