

Introduction

- Ion adsorption near charged electrode surfaces creates an electrical double layer (EDL), a primary site for capacitive energy storage. Full characterization of the EDL structure and associated electrochemical phenomena can enhance efforts to develop advanced energy storage devices.
- Using in-situ high-resolution X-ray reflectivity[1] and resonant anomalous X-ray reflectivity[2], we aim to probe the element-specific interfacial structure of the EDL at a negatively biased graphene-water interface to determine the validity of EDL theories ranging from the simplest diffuse ion profile (Gouy-Chapman[3]) to theories including ion-ion correlations [4].
- Modeling the EDL with computational methods remains challenging due to symmetry breaking at the surface and lack of mathematical model for the dielectric constant at a surface as a function of ion charge and size. Comparisons with experiment is used to validate MD theories and devise a mathematical description of the dielectric constant at an aqueous interface for all-atom and/or coarse-grain molecular dynamics.

Methods

X-ray Reflectivity (XR) Measurements

$$\text{General XR: } R(q) \propto |F(q)|^2 = \left| \int_{-\infty}^{\infty} \rho(z) e^{iqz} dz \right|^2$$

$$\text{Resonant Anomalous XR (RAXR): } R(q_0, E) = |F_{NR}(q_0) + (f'_R(E) + i f''_R(E)) F_{RES}(q_0)|^2$$

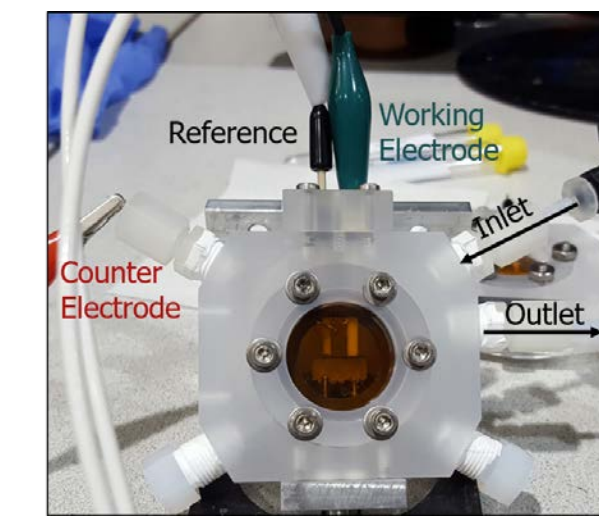
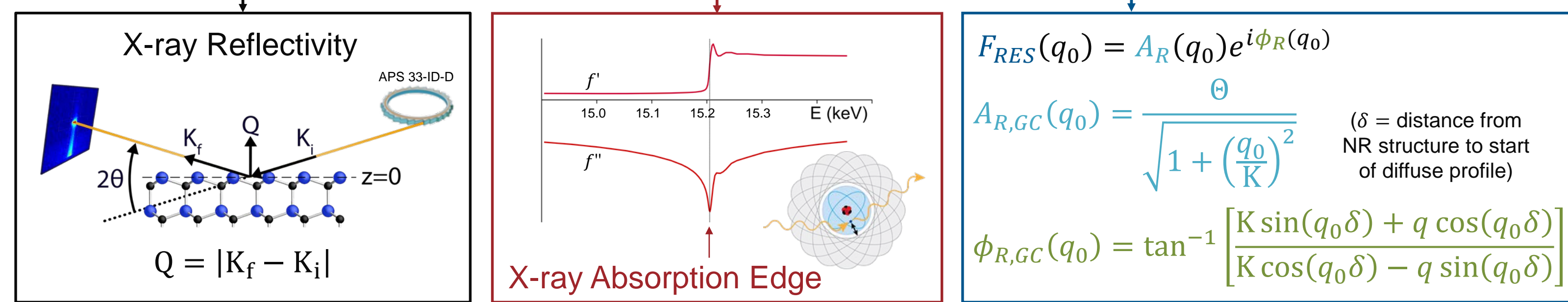


Figure 1. Three-electrode electrochemical cell for in situ XR with graphene working electrode and Pt (or Ag/AgCl) reference.



$$F_{RES}(q_0) = A_R(q_0) e^{i\phi_R(q_0)}$$

$$A_{R,GC}(q_0) = \frac{\theta}{\sqrt{1 + \left(\frac{q_0}{K}\right)^2}} \quad (\delta = \text{distance from NR structure to start of diffuse profile})$$

$$\phi_{R,GC}(q_0) = \tan^{-1} \left[\frac{K \sin(q_0 \delta) + q \cos(q_0 \delta)}{K \cos(q_0 \delta) - q \sin(q_0 \delta)} \right]$$

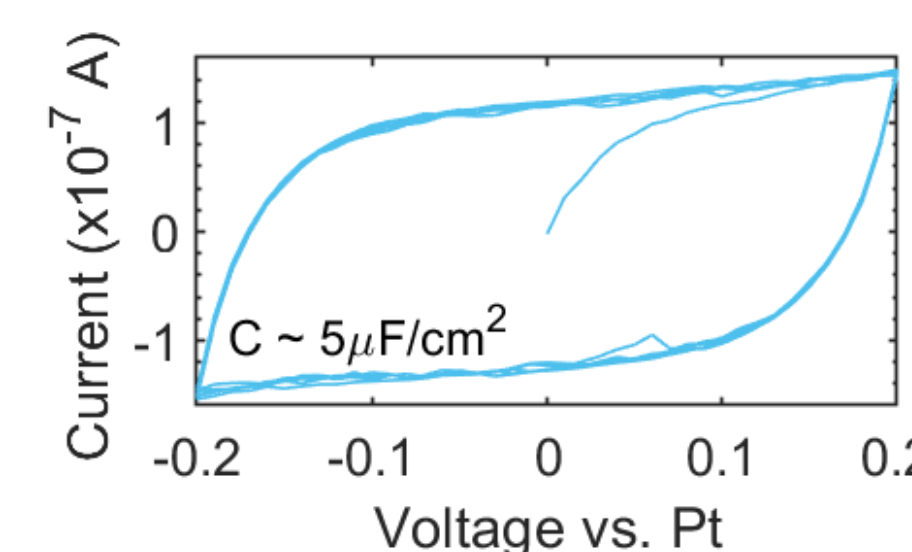


Figure 2. CV for sample EG2 and the measured capacitance.

Molecular Dynamics (MD) Simulations

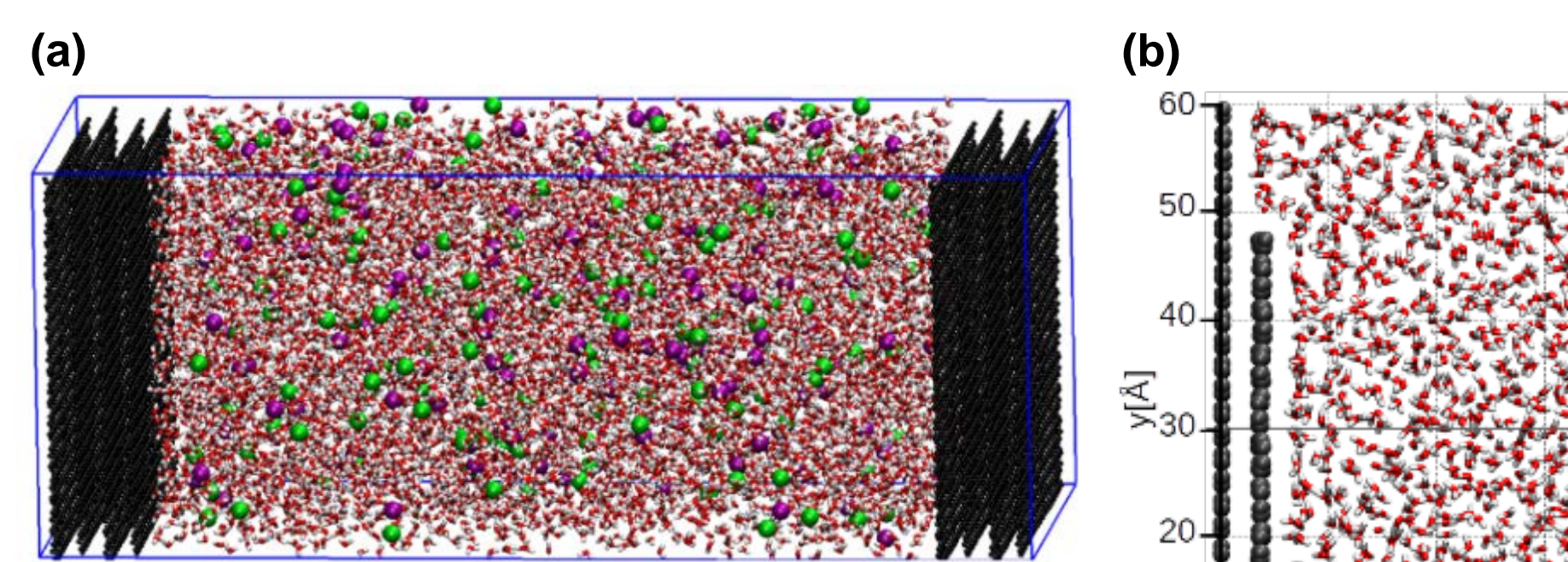
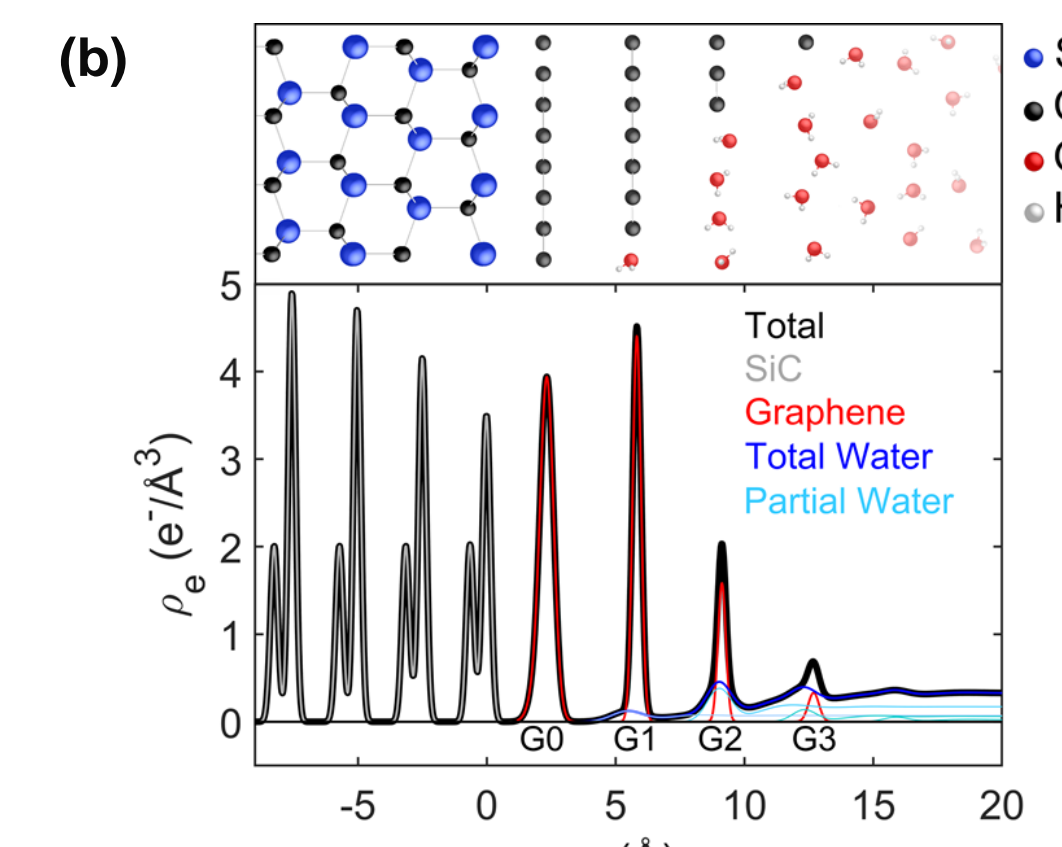
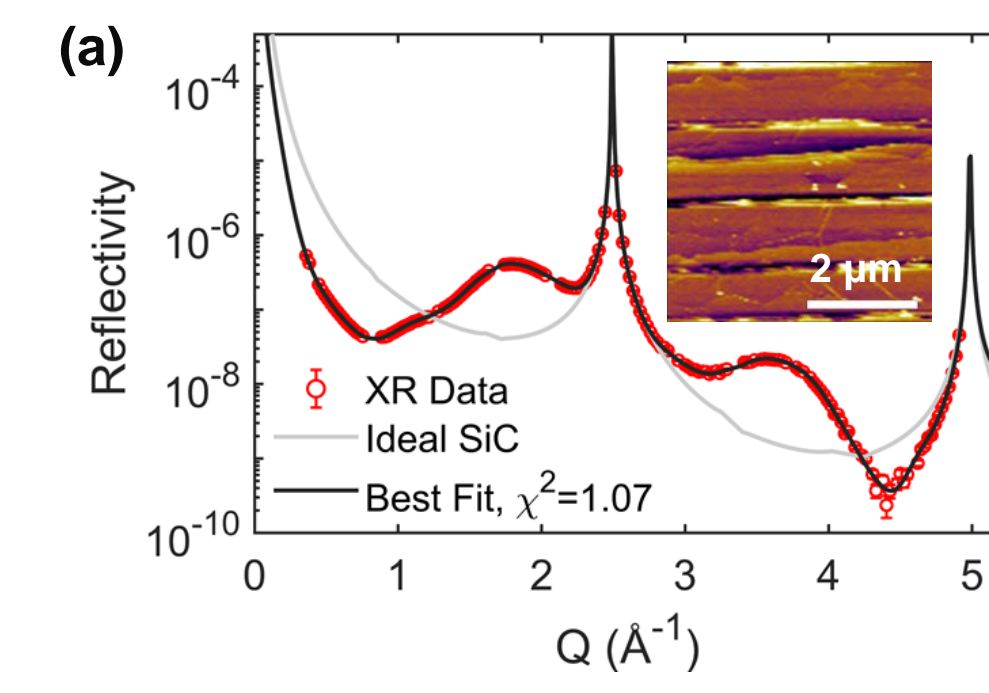


Figure 3. Molecular dynamics setup. (a) The simulation box consists of an aqueous phase of thickness $L_w = 22$ nm (11 nm without ions) confined by four complete graphene layers at each side. (b) Partial layers of graphene (G0-G3) were employed to represent the experimental conditions.

- Aqueous solutions (0 and 0.1 M RbCl) were placed between two graphene surfaces separated by a distance L_w (Fig. 3a).
- An electric potential was simulated by placing surface charge densities $\pm\sigma$ on the right/left graphene surfaces.
- The experimental system was mimicked via 4 incomplete graphene layers (Fig. 3b) with coverages determined by the XR best fit:
 - G0: full coverage; G1: 0.784 coverage
 - G2: 0.262 coverage; G3: 0.0749 coverage
- Simulations were run for >100 ns.

Experimental

Non-resonant XR



RAXR

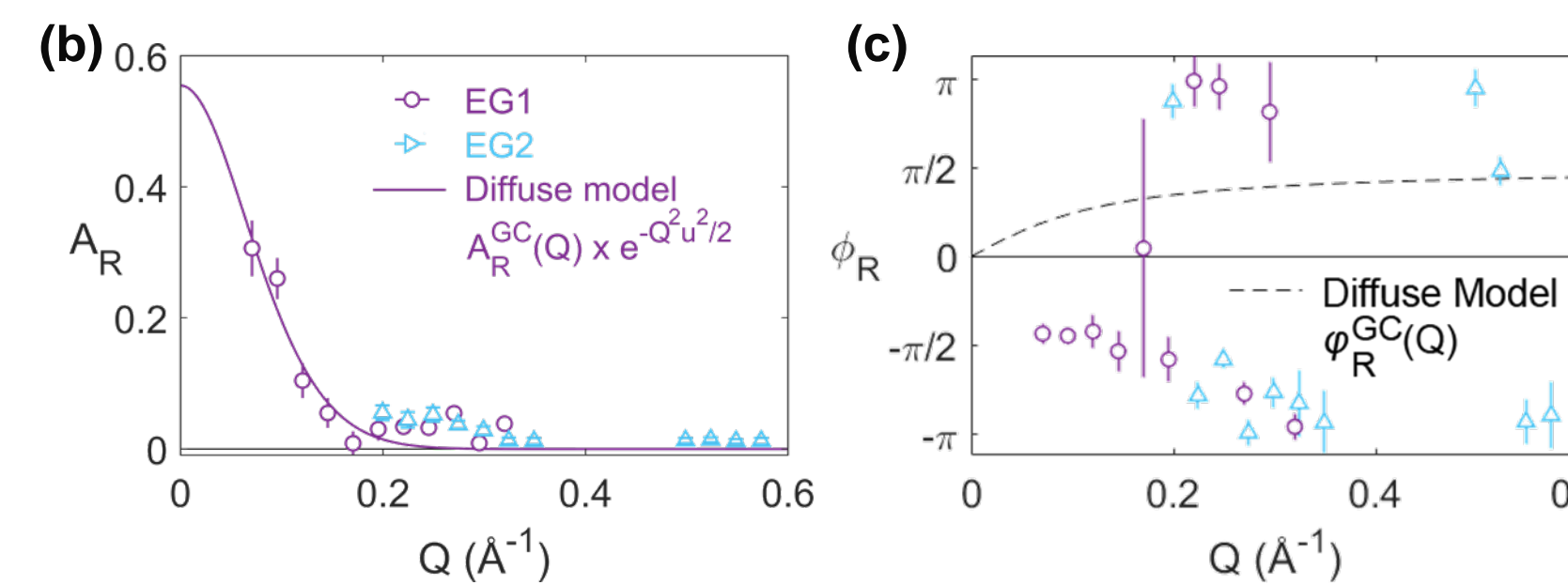
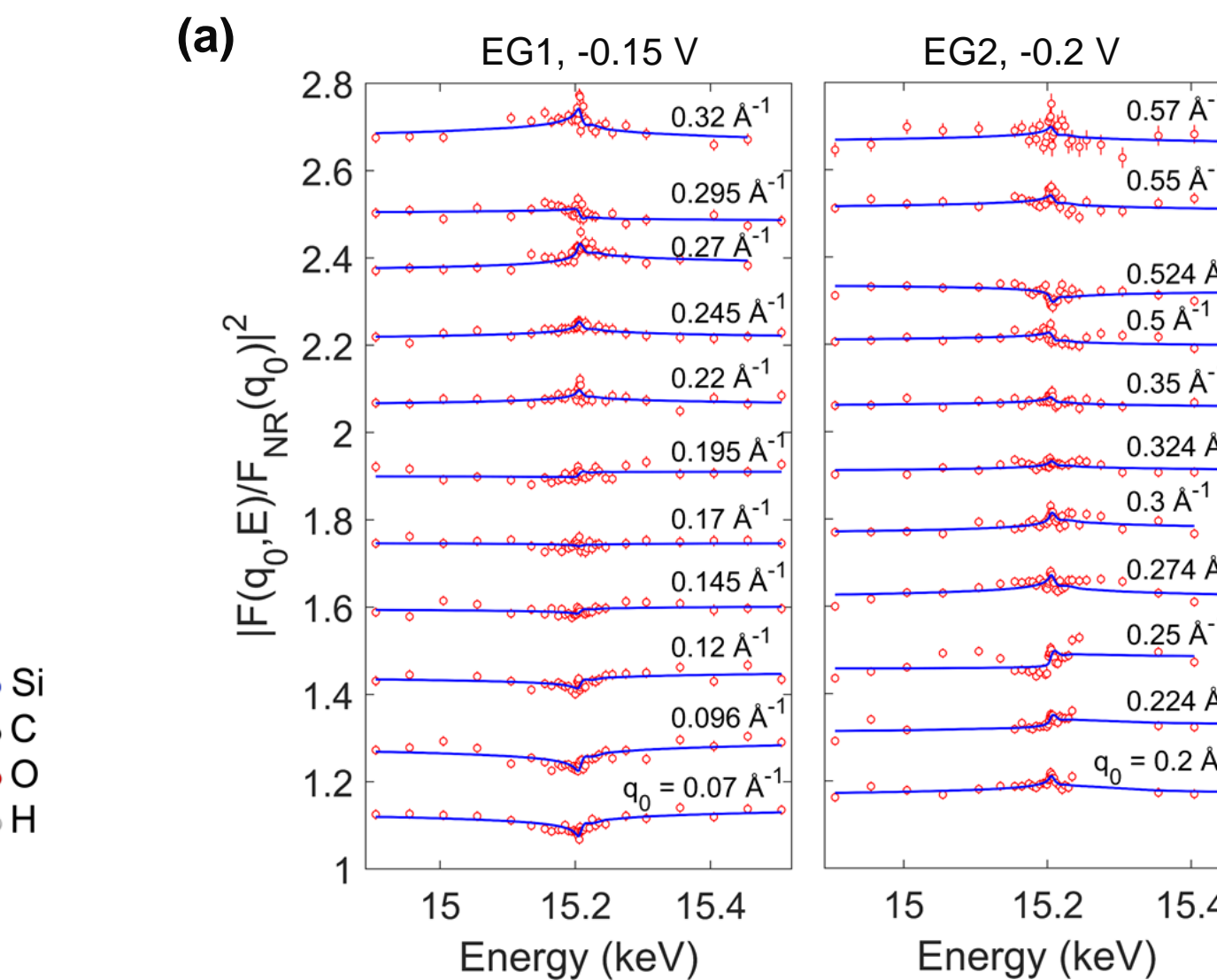


Figure 4. XR of sample EG2 (AFM image inset) at $E = 14$ keV. (a) A model-dependent best fit to XR data was used to determine F_{NR} for RAXR analysis. (b) The best-fit interfacial electron density profile reveals the surface structure.

Figure 5. (a) Model-independent RAXR analysis (offset for clarity) reveals the (b) amplitude and (c) phase of the resonant spectra. (b,c) The experimental data show behavior distinct from the simple Gouy-Chapman (GC) model.

- XR reveals SiC surface relaxations, 4 graphene layers (G0-G3), and the hydration structure (Fig. 4). The adsorbed Rb⁺ structure was resolved via RAXR and gave an estimated adsorbed Rb⁺ coverage, $\Theta_{Rb} = 0.57 \pm 0.2$ Rb⁺/A_{SiC} (Fig. 5b), corresponding to a surface charge of $|\sigma| \sim 1$ C/m².
- The amplitude data agree qualitatively with a diffuse profile with broadening at the onset, $u \sim 10 \pm 4$ Å, consistent with the total width of graphene. A small oscillation in the data at $Q \sim 0.15$ - 0.35 Å⁻¹ may suggest the presence of a specifically adsorbed layer.
- Phase wrapping between $\pm\pi$ (Fig. 5c) is inconsistent with ϕ of a simple diffuse profile.

Results

Computational

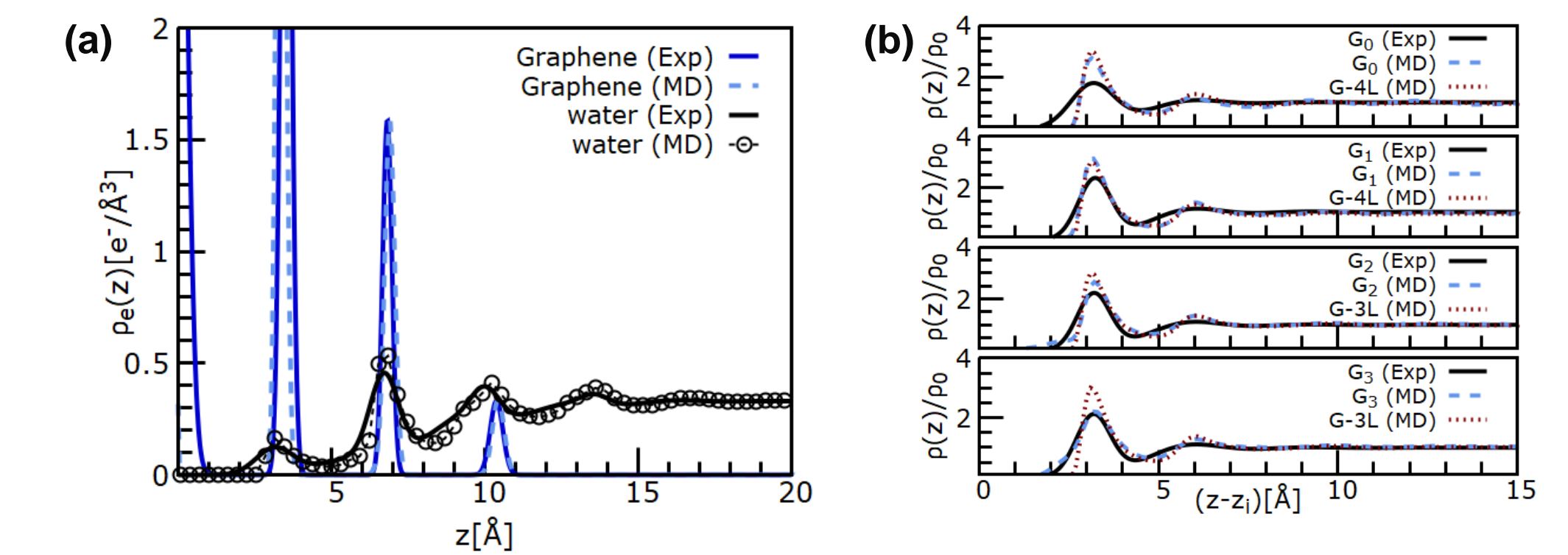


Figure 6. Simulation vs. experimental best fit structures of water on partial coverage graphene layers. (a) Total electron density profiles. (b) Reduced water density profiles above each graphene surface, G_i , for simulations with partial coverage graphene (blue) and complete coverage graphene (red).

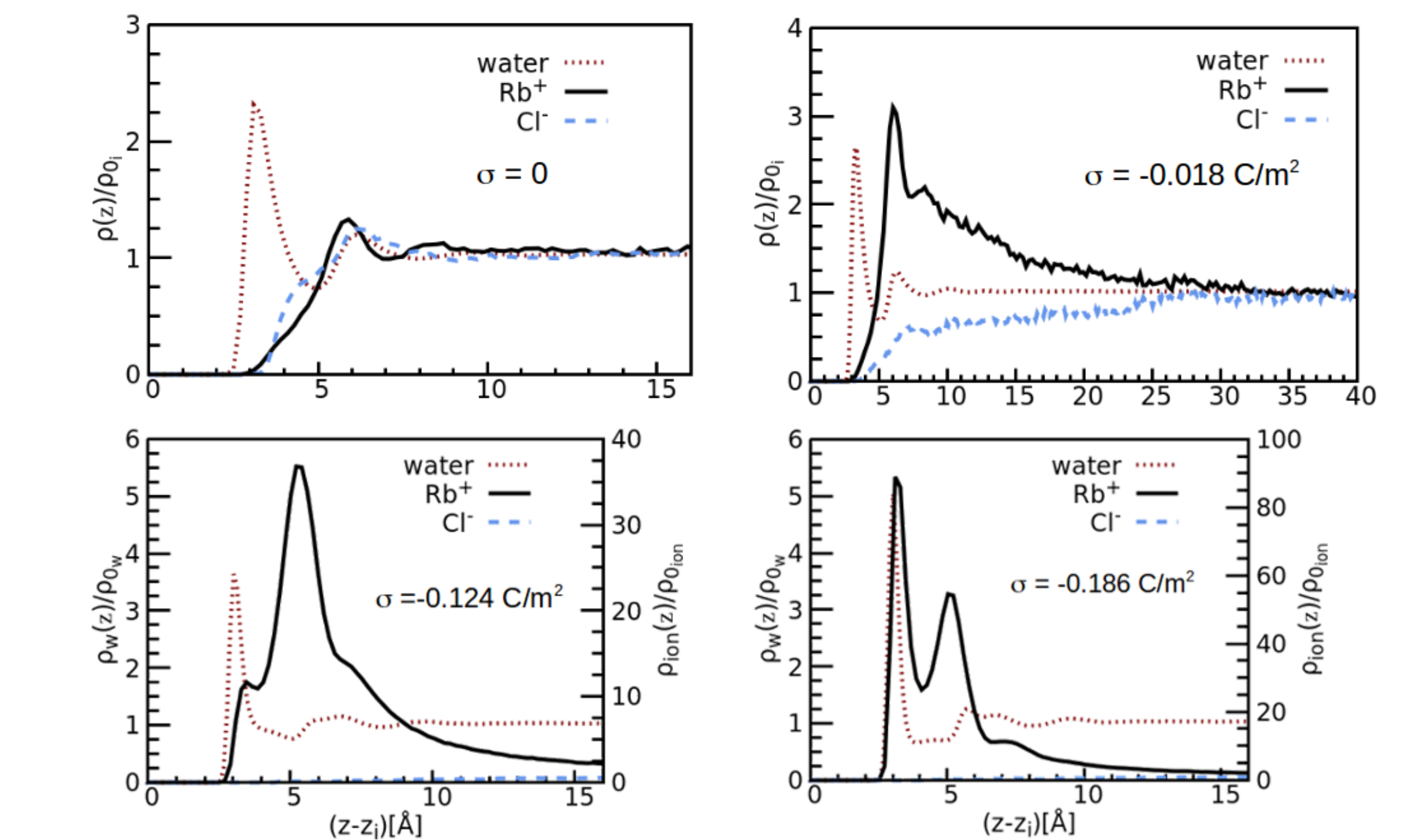


Figure 7. Reduced density profiles of water, Rb⁺, and Cl⁻ from MD simulations containing a 0.1 M RbCl solution confined between two oppositely charged graphene surfaces. The surface charge density is $|\sigma| = 0, 0.018, 0.124, 0.186$ C/m². Only the results from the negative surface are shown.

- MD simulations of the partial coverage graphene system agree with the experimental best fit model of the water-graphene interfacial structure.
- MD reveals significant changes to the water and ion structure as a result of electrode surface charge. Rb⁺ develops a two-peak profile with increasing surface potential.

Conclusions and Future Work

- RAXR data reveal an EDL structure more complex than a simple GC diffuse ion profile. Additional structure in the amplitude and phase data requires further investigation but may indicate ion-ion correlations or over-charging of the electrode surface.
- Consistent results from both samples suggest the EDL structure at these experimental conditions is electrode-independent. This agrees with the assumption of GC theory that the EDL structure depends only on solution ionic strength.
- MD simulations reveal layering of Rb⁺ with increasing surface charge. An underlying decay behavior may be qualitatively consistent with GC theory and experimental observation.

- Predicted water and ion structures from MD will be compared directly to experimental data via sensitive χ^2 quality of agreement [5] to quantify the accuracy of the simulated structures.
- New theoretical methods are required to correctly account for ionic correlations and the dielectric mismatch at the interface.
- Experimentally applied potentials are 5x the maximum surface charge from the MD simulations and will need to be taken in account during quantitative analysis.
- RAXR measurements have been done for 0.01 M RbCl and 0.05 M RbCl and will be analyzed to further elucidate the validity of different levels of theory.

References and Acknowledgements

[1] Fenter, *Rev. Mineral. Geochem.* (2002). [2] Park and Fenter, *J. Appl. Cryst.* (2007). [3] Gouy, *J. Phys. Theor. Appl.* (1910); Chapman, *Philos. Mag. Series 6* (1913). [4] Howard et. al., *J. Phys. Chem. B* (2010). [5] Harmon et. al., *submitted* (2018).

This work was supported by the Midwest Integrated Center for Computational Materials (MICCoM, Department of Energy, Office of Basic Energy Sciences). KH gratefully acknowledges support from the Department of Defense (DoD) through the National Defense Science & Engineering Graduate Fellowship (NDSEG) Program and from the Ryan Fellowship and the Northwestern University International Institute for Nanotechnology. X-ray reflectivity measurements were performed at Sector 33-ID-D at the Advanced Photon Source (APS) at ANL, a U.S. DOE Office of Science User Facility operated by ANL under Contract No. DE-AC02-06CH11357.