Supporting Information for

Effects of Ion Adsorption on Graphene Oxide Films and Interfacial Water Structure: A Molecular-Scale Description

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Graphene oxide monolayer characterization

After spreading the graphene oxide (GO) samples onto each aqueous subphase, we collected a pressure-area isotherm (Figure S1) using a Langmuir trough. All samples show good mechanically stability at both 20 and 30 mN/m, the surface pressures considered in the manuscript. Samples are likely within a condense phase regime¹-³ where GO flakes pinned to the interface can overlap.

![Surface pressure versus area isotherms for prepared graphene oxide monolayers spread over different metal subphases (panels).](image)

The chemical properties of GO strongly affect its adsorption abilities. To understand the monolayer composition, we completed x-ray photoelectron spectroscopy of Langmuir-Blodgett transferred GO monolayers on Si/SiO₂ wafers. An initial survey scan from 0 – 1200 eV using a 1 eV step size revealed 4 elemental regions of interest (Figure S2): carbon, oxygen, sulfur, and silicon. Each region was examined in higher resolution using a 20 eV range and a 0.1 eV step size (Figure S2). We offset the spectra such that the Si 2p peak present from the Si/SiO₂ wafers appeared at 99.4 eV.⁴ We fitted the detected peaks using Gaussians after U 3 Tougaard background subtraction.⁵ The following assignments were made on the fitted peak centers: carbon 1s region, 284.55 eV shows C-C bonds, 286.55 eV shows C-O-C bonds, and
288.72 eV shows O=C=O bonds; oxygen 1s region, 531.95 eV shows O; sulfur 2p region, 167.33 eV shows S; and silicon 2p region, 99.48 eV shows elemental Si, and 103.17 eV shows SiO$_2$. To understand the composition of the sample, we integrated each fitted peak and normalized the areas by the elemental sensitivity factors$^7$ to obtain percent compositions for each element. Because the Si signal is from the substrate, we disregarded these peak areas and their associated oxygen signal areas from additional analysis. The percent compositions for our GO monolayer samples are: 49.4% C-C, 2.98% O=C=O, 5.06% C-O-C, and 42.6% S. The S signal is a common contaminant in GO synthesis.$^8$ These values give a 5.21 carbon : oxygen ratio.

Figure S2. X-ray photoelectron spectroscopy of prepared graphene oxide monolayer on Si/SiO$_2$ wafer for different elemental regions (panels).

To further characterize our GO monolayers, we calculate the approximate number density of the oxygen functional groups. After filtering, the average flake diameter is 0.2 µm, as confirmed using dynamic light scattering. If we assume the hexagonal carbon backbone of each flake remains intact through exfoliation from graphite and subsequent oxidation, we can calculate the maximum number of C-C bonds per flake using the flake area, carbon hexagon area, and number of unique sides per hexagon within a honeycomb pattern. The maximum number of C-C bonds for our sample $1.81 \times 10^6$ C-C bonds/GO flake. Assuming the oxygen functional groups occupy the same space as a C-C bond, a rough approximation that is not strictly true, we use the composition percentages and maximum number of C-C bonds to find 0.285 C-C bonds/Å$^2$, 0.0171 O-C=O bonds/Å$^2$, and 0.0323 C-O-C bonds/Å$^2$. We acknowledge this calculation assumes all GO flakes within the sample are circular and of reasonably similar size and shape, which may not be true given the complex and individualistic structure of GO. However, we report these values to provide additional characterization information about our particular GO sample, as the bonds per area gives more pertinent information than simple carbon : oxygen ratios.
**X-ray fluorescence near total reflection of graphene oxide on 20 mM YCl₃**

Obtained x-ray fluorescence near total reflection (XFNTR) signal for GO compressed to 30 mN/m spread on a 20 mM YCl₃ subphase shows larger than expected intensity values for $Q_z > Q_c$. Given the complex structure of GO in the presence of adsorbed Y³⁺, we speculate additional Y³⁺ are present near the sample hence the increased signal beyond the model prediction.

![Intensity vs. Qz plot](image)

**Figure S3.** Surface-sensitive x-ray fluorescence near total reflection (XFNTR) intensity and fit (solid line) plotted over inverse momentum $Q_z$ for graphene oxide monolayer compressed to 30 mN/m spread on 20 mM YCl₃. Error bars are derived via counting statistics.

**Vibrational sum frequency spectroscopy fitting parameters**

Table S1. Vibrational sum frequency spectroscopy fitted amplitudes for different YCl₃ concentrations.

| [YCl₃] (mM) | $A_{1, \chi(2)}$ (3200 cm⁻¹) | $A_{2, \chi(2)}$ (3400 cm⁻¹) | $A_{1, \chi(3)}$ (3200 cm⁻¹) | $A_{2, \chi(3)}$ (3400 cm⁻¹) |
|------------|-----------------|-----------------|-----------------|-----------------|
| 0          | 404 ± 20        | 319 ± 16        | 50 ± 3          | 50 ± 3          |
| 0.005      | 350 ± 18        | 348 ± 17        | 33 ± 2          | 33 ± 2          |
| 0.05       | 184 ± 9         | 312 ± 16        | 7 ± 1           | 7 ± 1           |
| 0.5        | 58 ± 3          | 205 ± 10        | 1 ± 0.5         | 1 ± 0.5         |

Table S2. Vibrational sum frequency spectroscopy additional fit parameters.

| $\chi$   | $\omega_1$ | $\omega_2$ | $\Gamma_1$ | $\Gamma_2$ | $\gamma_1$ | $\gamma_2$ | $\varphi_1$ | $\varphi_2$ | $\chi_{NR}^{(2)}$ |
|----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|------------------|
| $\chi^{(2)}$ | 3247 ± 4   | 3450 ± 3    | 109 ± 7     | 101 ± 9     | -1.8        | -1.8        | 1.8         | 1.8         | -3.1 ± 0.1       |
| $\chi^{(3)}$ | 3180 ± 5   | 3392 ± 5    | 135 ± 7     | 222 ± 9     |             |             |             |             |                  |

The table shows fitted vibrational amplitudes and frequency parameters for different concentrations of YCl₃. The notation $\chi$ corresponds to the vibrational amplitude, and $\omega$ and $\Gamma$ represent frequency and line width parameters, respectively.
X-ray reflectivity fitting parameters

We model the interface with uniform density slabs sandwiched between air and water and calculate the reflectivity to fit the XR data. We used two slabs for Y samples, and a single slab for Cs and Sr samples. The thickness (d) and the electron density (ρ) of each slab and the roughness between the layers (σ) were let to vary to minimize the merit function:

$$\chi^2 = \sum_{i=1}^{N} \frac{(R_{\text{calc}} - R_{\text{exp}})^2}{\gamma_i^2}$$

where, \(R_{\text{calc}}\) and \(R_{\text{exp}}\) are calculated and experimental reflectivity values, respectively and \(\gamma^2\) is the variance. The best fit parameters are listed in Table S3 and used to plot the electron density profiles in the main text.

Table S3. Model-dependent fit parameters for the XR data provided in the main text Figure 4 (Y) and Figure 6 (Cs and Sr).

| Sample        | \(d_1\) (Å) | \(\rho_1\) (e/Å\(^3\)) | \(d_2\) (Å) | \(\rho_2\) (e/Å\(^3\)) | \(\sigma\) (Å) |
|---------------|--------------|--------------------------|--------------|--------------------------|----------------|
| Y, 0.05 mM, 20 mN/m | 6.8 ± 1.3    | 0.53 ± 0.07              | 16.3 ± 0.5   | 0.06 ± 0.009              | 4.3 ± 0.22    |
| Y, 0.05 mM, 30 mN/m | 5.3 ± 1.4    | 0.54 ± 0.03              | 21.4 ± 1.8   | 0.03 ± 0.002              | 4.5 ± 0.61    |
| Sr, 20mM, 20mN/m  | 7.0 ± 0.6    | 0.43 ± 0.005             | -            | -                        | 4.32 ± 0.02   |
| Sr, 20mM, 30mN/m  | 15.2 ± 0.8   | 0.35 ± 0.003             | -            | -                        | 4.11 ± 0.02   |
| Cs, 0.05 mM, 20 mN/m | 6.8 ± 0.4    | 0.41 ± 0.003             | -            | -                        | 4.25 ± 0.02   |
| Cs, 0.05 mM, 30 mN/m | 15.2 ± 0.8   | 0.36 ± 0.003             | -            | -                        | 4.11 ± 0.02   |

SI-References

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