Supplementary Information for Mechanism of Ion Adsorption to Aqueous Interfaces: Graphene/Water vs. Air/Water


Supplemental Materials and Methods

Sample preparation

All glassware was soaked in NoChromix overnight and rinsed vigorously with 18.2MΩ water. Commercial CVD graphene on copper foils (3-5 layers, one sided) was purchased from ACS Material. To ensure quality, all foils were reexamined under a Raman microscope (see Fig. S1A-C). Raman spectra were acquired under ambient conditions with a WiTech alpha300R+ confocal Raman microscope equipped with a 488 nm excitation laser and a 600 lines/mm grating spectrograph operating in 180° backscattering geometry. A Zeiss 50x or 20x objective was used to focus the excitation laser light spot on the samples. The average intensity ratios of the 2D over the G band indicate the graphene has 3 to 5 layers on average (1, 2). The foil was cut into 7x25 mm pieces, then submerged in warm acetone five times to clean up any contamination. This stock graphene was stored in a closed box to avoid new contamination. The stock graphene on copper foil was cut into 7x7 mm pieces and floated on a 30 mL aqueous solution of 10% Na₂S₂O₈ for ~5 hours to etch away the copper. Polyethylene o-rings (cleaned with saturated KOH in ethanol and stored in water) with inner and outer diameters of ~1.2 and ~2.5, respectively, were placed around the pieces (Fig. S2). The o-rings stabilize the water surface so that the graphene pieces are less likely to break during transfers and are more likely to align the laser beam properly. After etching, 200 mL of 18.2MΩ water was added to dilute the etching
solution, then the floating graphene sheet and the surrounding o-ring was scooped into a small cup and transferred into 250 mL water. The solution was stirred slowly to ensure the desorption of any etching product from the graphene and to equilibrate the concentration. The graphene samples were transferred into fresh water three more times and left to float overnight. The next day, the graphene samples were transferred once more into 350 mL water for the last cleaning step. Raman spectra show that the floating graphene is of the same quality as it was on copper (see Fig. S1D-F).

Solutions were prepared volumetrically the day before, using 18.2MΩ water and NaSCN (J. T. Baker, ACS reagent ≥98%) that had been baked at 200°C overnight. Solutions were poured into a large Petri dish and graphene samples were transferred into the dish with a glass scoop. The volume of solution in the scoop was accounted for when calculating bulk concentrations. Once all samples of graphene were in the dish, the solution was stirred to ensure a uniform bulk concentration. The samples were then removed one at a time to be measured in the SHG experiment and replaced in the same concentration solution (see Fig. S2). After all samples were measured, any samples to be reused were transferred to the new concentration. After all SHG measurements were finished, the graphene samples were transferred first to clean water, then to a glass slide to inspect under a Raman microscope. Fig. S1G-K show similar Raman spectra to the original graphene on copper (Fig. S1A-C), indicating that there was no damage of graphene during the SHG experiment. During the experiment, all pieces of graphene continued to float on top of the solution without submerging. Furthermore, when a droplet of water was pipetted onto the floating graphene, it rolled off the graphene and into the bulk solution. This evidences that water is only present on the solution side of the graphene.
Optical design and signal analysis

Femtosecond pulses were generated with a MaiTai oscillator (Spectra Physics, 800 nm, 100 fs, 80 MHz), amplified with a Spitfire amplifier (Spectra Physics, ~805 nm, ~110 fs, 1 kHz), and passed through a TOPAS (Light Conversion, ~9 µJ) to generate 386 nm light. The beam was focused onto the sample with a 100 mm fused silica lens and the reflected light was collected with a 100 mm CaF$_2$ lens. The spot size was about ~100 µm in diameter, much smaller than the graphene samples, even if they broke into smaller pieces. Since the fundamental beam and the SHG beam (193 nm) are collinear, a Pellin-Broca prism was used to separate the wavelengths and send the SHG signal through a monochromator (Acton, SpectraPro 2150i) to a solar-blind PMT (Hamamatsu, R7154PHA). The beam was attenuated to < 1 µJ for graphene samples to prevent damage (3) and to ensure that no more than one photon was generated per pulse. The input intensity was varied with a neutral density filter wheel rotating at 1 Hz and the signal analyzed using a photon counting scheme. The signal was binned according to the input intensity and the average photon count for each bin was calculated using Poisson statistics (4, 5). The average photon count was plotted against input intensity squared and the slope of this line was used as the measurement value. All samples were normalized to the SHG signal from neat water.

Langmuir model

SHG signal is proportional to the square of the input intensity and the square modulus of the second order susceptibility.

\[ I_{2\omega} \propto \left| \chi_{\text{eff}}^{(2)} \right|^2 I_{\omega}^2 \]  

(S.1)

\( \chi_{\text{eff}}^{(2)} \) is a complex quantity and is a sum of the \( \chi^{(2)} \) of all species. Water and graphene are not resonant at 193 nm, so their \( \chi^{(2)} \)'s are purely real. Thiocyanate has a CTTS transition that is
resonant at 193 nm (6, 7), so its $\chi^{(2)}$ is complex. $\chi^{(2)}$ is also proportional to the molecular hyperpolarizability, $\beta$, and number of oscillators. Separating real and complex terms and dividing by the number of waters gives:

$$\frac{I_{2\omega}}{I_\omega} \propto \left( \frac{N_{\text{water}}}{N_{\text{water}}} \beta_{\text{water}}^{\text{eff}} + \frac{N_{\text{graphene}}}{N_{\text{water}}} \beta_{\text{graphene}}^{\text{eff}} + \frac{N_{\text{anion}}}{N_{\text{water}}} \text{Re}\{\beta_{\text{anion}}^{\text{eff}}\} \right)^2 + \left( \frac{N_{\text{anion}}}{N_{\text{water}}} \text{Im}\{\beta_{\text{anion}}^{\text{eff}}\} \right)^2 \quad (S.2)$$

If the anions are allowed to partition between the surface and the bulk, then

$$W_\text{surf} + X^-_\text{bulk} \leftrightarrow W_\text{bulk} + X^-_\text{surf} \quad (S.3)$$

$$K_{\text{ads}} = \begin{bmatrix} X^-_\text{surf} & W_\text{bulk} \\ W_\text{surf} & X^-_\text{bulk} \end{bmatrix} = \frac{\begin{bmatrix} X^-_\text{surf} \\ W_\text{surf} \end{bmatrix}}{\begin{bmatrix} W_\text{bulk} \\ X^-_\text{bulk} \end{bmatrix}} = \frac{\begin{bmatrix} X^-_\text{surf} \\ W_\text{surf} \end{bmatrix}}{\begin{bmatrix} X^-_\text{bulk} \end{bmatrix} - \begin{bmatrix} X^- \end{bmatrix}} \quad (S.4)$$

where $[S_{\text{max}}]$ is the maximum number of surface sites available. Assuming that the water and graphene terms are constant and substituting gives (4–6)

$$\frac{I_{2\omega}}{I_\omega} = \left( A + B \left[ \frac{X^-}{[W]e^{\Delta G_{\text{ads}}/RT}} + [X^-] \right] \right)^2 + \left( C \left[ \frac{X^-}{[W]e^{\Delta G_{\text{ads}}/RT}} + [X^-] \right] \right)^2 \quad (S.5)$$

where the first square term represents the real terms (water, graphene, and thiocyanate) and the second square term represents the imaginary term (thiocyanate).

Data were fit to the Langmuir model using the Levenberg-Marquardt algorithm in Python using the lmfit module (8). Data points were weighted by standard deviation, which are the error bars shown in Fig. 1. Temperature was set to 293 K and initial values for the parameters were 1 for A, B, and C and -1000 J/mol for $\Delta G_{\text{ads}}$. This was the only set of initial values that gave a reasonable fit. Parameter errors are the square roots of the corresponding diagonal elements in the variance-covariance matrix. Fit parameters are summarized in Table S1.
Langmuir model with surface potential

Due to the double layer that is most certainly present at the graphene/water interface, the authors attempted to incorporate a term to account for the surface potential. This means that a third, static electric field, dependent on the surface potential, will be present to mix with the SHG signal according to the Eisenthal $\chi^{(3)}$ equation (9)

$$P_{2\omega} \propto \chi^{(2)} E_{\omega}^{2} + \chi^{(3)} E_{\omega}^{2} \Phi_{0}$$

(S.6)

Following a derivation similar to the one above, this gives

$$\frac{I_{2\omega}}{I_{\omega}} \propto (A + B[X_{\text{surf}}^{-}] + \Phi_{0}(A' + D[X_{\text{surf}}^{-}]])^{2} + (C[X_{\text{surf}}^{-}] + \Phi_{0}E[X_{\text{surf}}^{-}])^{2}$$

(S.7)

For concentrations of chloride greater than 0.13M, the surface potential can be described by the Stern model (10). Considering thiocyanate has a greater propensity for the surface than chloride, it is reasonable to assume that the Stern model is appropriate in this case. This means the surface potential is proportional to the surface concentration. Combining that fact with Eq. S.7 and substituting with the Langmuir equation gives

$$\frac{I_{2\omega}}{I_{\omega}} \propto \left( A + B \frac{[X^{-}]}{[W]e^{\Delta G/RT} + [X^{-}]} + D \left( \frac{[X^{-}]}{[W]e^{\Delta G/RT} + [X^{-}]} \right)^{2} \right)^{2}$$

$$+ \left( C \frac{[X^{-}]}{[W]e^{\Delta G/RT} + [X^{-}]} + E \left( \frac{[X^{-}]}{[W]e^{\Delta G/RT} + [X^{-}]} \right)^{2} \right)^{2}$$

(S.8)

The results of the fit are in Table S2 and the correlation matrix for this fit is displayed in Table S3. Initial parameters were all 1, except for $\Delta G_{\text{ads}}$, which was -10,000 J/mol. These parameters gave the most reasonable fit. Notice that the parameter errors are much larger, all correlations are greater than 0.9, and some correlations are ±1. Because of this, these results are
not conclusive and the decision was made to stick with the simpler Langmuir model.

**Supplemental Discussion**

**Analysis of interfacial fluctuations**

To analyze the fluctuations of both the air/water and graphene/water interfaces, we closely followed the methodology outlined in Ref. (7). Specifically, we used the *instantaneous interface* method of Willard and Chandler (11), in which Gaussian mass distributions are assigned to each water oxygen atom. At each point in space, the coarse-grained density field is defined as the sum of all such Gaussian mass distributions, and the interface is taken to be the 2-dimensional manifold where the coarse grained density field is equal to half its bulk value (16 nm⁻³). The Gaussian mass distribution had a width 0.3 nm, and was truncated and shifted at 0.9 nm. In practice, the coarse grained density field is evaluated on a grid, with spacings 0.1014, 0.1036 and 0.0500 nm in the x, y and z directions, respectively.

**Computing the adsorption free energy from the PMFs**

In our simulations, we obtain a PMF, $\Delta F(z)$, for the ion above the graphene surface. In order to compare to experiment, we need to obtain an adsorption free energy, $\Delta G_{ads}$. To do this, we imagine dividing space into small cubic cells of volume $l^3$. Now consider a single solute ‘B’ constrained to an $l \times l \times L$ column, where $L$ is a macroscopic distance. This is shown schematically in Fig. S4. Let us define the following:

- $q_B$, the internal partition function of a cell in bulk containing a solute molecule.
- $q_{B,s}$, the internal partition function of a cell at the surface containing a solute molecule.
- $q_0$, the internal partition function of a cell in bulk with no solute molecule.
- $q_{0,s}$, the internal partition function of a cell at the surface with no solute molecule.

The surface binding probability of a solute that is constrained to reside in the column is:
We can also compute this probability from simulation:

\[
P_{\text{ads}} = \frac{1}{L} \int_0^{z^*} dz' \exp[-\beta \Delta F(z')]
\]

\[
= K / L
\]

\[
K = \int_0^{z^*} dz' \exp[-\beta \Delta F(z')]
\]

where \(z^*\) is a microscopic distance from the interface below which we consider the solute adsorbed, and \(\beta = 1/k_B T\) is the inverse temperature. It immediately follows that:

\[
K = \frac{q_{B,s} q_0}{q_B q_{0,s}} l
\]

Let us denote the probability that a solute occupies a particular site by \(\phi_B\). If there are a total of \(N_B\) solutes, and the total volume of the system is \(V\), which we have also divided into small cubes of volume \(l^3\), we can write:

\[
\frac{\phi_B}{1 - \phi_B} = \frac{Q_{\text{occ}}}{Q_{\text{unocc}}} = \frac{q_{B,s} q_0^{N_B l^3} q_0^{(V/l^3) - N_B} (V/l^3)^{N_B - 1}}{q_{0,s} q_B^{N_B} q_0^{(V/l^3) - N_B} (V/l^3)^{N_B - 1}} \frac{1}{(N_B - 1)!} \frac{1}{(N_B)!}
\]

\[
= \frac{q_{B,s} q_0}{q_B q_{0,s}} \left( \frac{N_B l^3}{V} \right)
\]

\[
= K l^2 \rho_B
\]

where \(Q_{\text{occ}}\) and \(Q_{\text{unocc}}\) are the total partition functions for the system when a particular site is occupied and unoccupied by a solute, respectively, and \(\rho_B\) is the bulk concentration of solute.
molecules. The equilibrium constant for the Langmuir model used to interpret the experimental data is:

\[ K_{\text{ads}} = \frac{\sigma_b \rho_A}{\sigma_A \rho_B} \]  

(S.14)

where \( \sigma_X \) is the surface density of species ‘X’, and the subscript ‘A’ indicates quantities pertaining to the solvent. If the maximum surface density is \( \sigma_{\text{max}} \), and all surface sites are occupied by either solvent or solute molecules we can write:

\[ K_{\text{ads}} = \frac{\sigma_b \rho_A}{(\sigma_{\text{max}} - \sigma_b) \rho_B} \]

\[ = \frac{\phi_b \rho_A}{1 - \phi_b \rho_B} \]

\[ = K_{\text{gra}} \rho_A \]

(S.15)

The adsorption free energy is therefore calculated from the simulation PMF as follows:

\[ \Delta G_{\text{ads}} = -k_B T \ln[(\rho_A l^2)K] \]  

(S.16)

For a liquid-vapor interface, there is a certain degree of ambiguity in choosing the size of an adsorption site \( l \). If we assume that \( l \) is the same for adsorption to the air/water and graphene/water interfaces, then the difference in free energies:

\[ \Delta \Delta G_{\text{ads}} = \Delta G_{\text{gra}}^{\text{gra}} - \Delta G_{\text{ads}}^{\text{vap}} \]

\[ = -k_B T \ln \frac{K_{\text{gra}}}{K_{\text{vap}}} \]  

(S.17)

will be independent of the choice of \( l \). The superscripts ‘gra’ and ‘vap’ indicate quantities calculated for the graphene and air interfaces, respectively. A negative value of \( \Delta \Delta G_{\text{ads}} \) corresponds to more favorable adsorption at graphene than at air. This provides a direct way to compare the simulation and experimental results.
The effect of graphene flexibility

The results presented in the main article have been obtained with a rigid model of graphene. It is possible that allowing the graphene to vibrate could affect water’s interfacial fluctuations and consequently, the propensity of ions to adsorb to the interface. We have therefore performed the simulations using an optimized Tersoff model for graphene (12), which has been shown to predict the harmonic and anharmonic interactions for graphene reasonably well (13). Fig. S5 shows the PMF calculated with $\varepsilon_{C-I} = 0.315$ kJ/mol, both relative to the average height of the graphene surface and the instantaneous interface. While there are some very slight changes in the PMF when computed relative to the average graphene height, these have negligible effect on the adsorption free energies, with $\Delta \Delta G_{ads} = +5.1$ and +4.9 kJ/mol for the rigid and flexible models, respectively. (The PMFs relative to the instantaneous interface give $\Delta \Delta G_{ads} = +5.0$ and +4.7 kJ/mol for rigid and flexible graphene models, respectively.)

Sensitivity of the potential of mean force to direct interactions between the iodide and graphene

In the main article, we presented results using the Lennard-Jones parameters given in Table S4. To test the sensitivity of our simulation results to the direct interaction between the iodide and the graphene, we also calculated the PMFs using different values of $\varepsilon_{C-I}$. First, we applied the standard Lorentz-Berthelot mixing rules, which gave $\varepsilon_{C-I} = 0.315$ kJ/mol. Second, we used a much stronger interaction with $\varepsilon_{C-I} = 1.046$ kJ/mol. Third, we used an interaction that reproduced experimental results. The adsorption energies for a single iodide at the graphene sheet (no waters) using the different $\varepsilon_{C-I}$ values are presented in Table S5, along with differences in adsorption free energies between the graphene/water and air/water interfaces (see Eq. (S.17)). Adsorption energies in the literature for iodide adsorption at graphene are scarce. Using density
functional theory (DFT), Zhu and Yang (14) report a value of \(-27.0\) kJ/mol for iodide at the center of a \(C_{54}H_{18}\) single layer sheet (19 aromatic rings). Shi et al. (15) report DFT adsorption energies of \(-68.2\), \(-32.2\), and \(-25.1\) kJ/mol for \(F^-\), \(Cl^-\) and \(Br^-\), respectively, suggesting that the adsorption energy of \(I^-\) is weaker than \(-25\) kJ/mol. While it is clear from Table S5 that \(\Delta \Delta G_{\text{ads}}\) is sensitive to \(\varepsilon_{C-I}\), it is reassuring that a value that gives reasonable agreement with experiment also gives a sensible adsorption energy. Furthermore, given the insensitivity of the simulation results to graphene’s flexibility, this suggests that the experimental observation of similar adsorption free energies to the graphene and air interfaces is due to contributions from the direct graphene-solute interaction that offsets a weaker contribution from solvent repartitioning interactions relative to the vapor interface.

**Using the instantaneous interface to compute the PMFs**

In addition to computing the PMF relative to the graphene sheet, it is also possible to use the height relative to the instantaneous interface (16), as shown in Fig. S6. This analysis reveals that at the air/water interface, the ion prefers to reside slightly in the vapor phase, whereas the opposite is true at the graphene/water interface. We also find \(\Delta \Delta G_{\text{ads}} = -1.7\) kJ/mol when these PMFs are used, in good agreement with the value computed with the PMF relative to the graphene sheet (\(\Delta \Delta G_{\text{ads}} = -1.9\) kJ/mol).

**Simulation results using a thiocyanate model**

In the main article, we presented simulation results using a spherical \(I^{0.8}\) ion. Thiocyanate, however, is a linear molecular ion. To investigate the effects of anisotropy, we also calculated the PMF using a molecular model of thiocyanate (6). The details of the calculation were identical to those for \(I^{0.8}\) except for the fact we controlled the height of the ion by constraining the position of the carbon atom, and that a rigid-body integrator was used to
propagate the dynamics of the thiocyanate. The parameters used are shown in Table S6. This procedure allows for averaging over the orientational degrees of freedom of the thiocyanate.

The resulting PMF is shown in Fig. S7. The PMF, and corresponding energy and entropy changes, at the air/water interface appear to be in good agreement with those reported in Ref. (7). Moreover, the effect on capillary wave fluctuations is the same as that observed for $I^{-0.8}$ (see Fig. S8). At graphene, and in contrast to $I^{-0.8}$, a noticeable decrease in entropy is observed at the free energy minimum. As we can see in Fig. S7, however, the enthalpic change still appears to be dominated by the direct interaction with the graphene. It is important to recognize that the orientation of the thiocyanate affects the direct interaction with graphene, and in Fig. S9 we show binding curves calculated with the thiocyanate “flat” relative to graphene, with its S atom directed toward the graphene, and with its N atom directed toward the graphene. It is clear from Fig. S9 that at the free energy minimum at graphene, only orientations where the thiocyanate is flat are energetically accessible. Moreover, slightly above the free energy minimum it is slightly preferable for the thiocyanate to orient perpendicular to the graphene. The decrease in entropy as the thiocyanate approaches graphene could therefore reflect a loss in orientational degrees of freedom. By considering the distributions $p_z(\cos \theta)$, where $\theta$ is the angle between the vector pointing from S to N and the $z$-axis, we can compute a Gibbs entropy for the ion at a given $z$:

$$s_z = -k_B \int_{-1}^{1} d(\cos \theta) p_z(\cos \theta) \ln[p_z(\cos \theta)]$$  

(S.18)

Distributions for different values of $z$ are shown in Fig S10. By numerical integration we find $T \Delta S = -0.35$ kJ/mol at the air/water interface, and $T \Delta S = -3.23$ kJ/mol at the graphene/water interface (just above the graphene free energy minimum we find $T \Delta S = -0.79$ kJ/mol). For the graphene/water interface, the orientational entropy change is within error of the total entropy change, suggesting that orientational entropy plays a significant role. For the air/water interface,
orientational entropy is clearly not the dominant contribution.

**Cavity formation and electrostatic interactions with the solvent**

The PMF for the neutral cavity presented in Fig. 5 was calculated following the same procedure as that for the charged iodide: All simulations settings were identical except for the charge of the solute. We have also computed the average electrostatic potential at the center of the neutral cavity due to the surrounding solvent molecules, $\langle \phi_{solv} \rangle_0$. Fixing the neutral cavity at the same heights for the analyses presented in Figs. 3B and 4, we find that $\langle \phi_{solv} \rangle_0 = +8.9$, +15.4 and +17.0 kJ/mol-e in the middle of the water slab, at the graphene/water interface and at the air/water interface, respectively, indicating a slightly stronger driving force for anion adsorption to the air/water interface than the graphene/water interface due to $\langle \phi_{solv} \rangle_0$. (We estimate the error in these quantities to be approx. 0.6 kJ/mol-e.) Although the ion’s chemical potential depends upon the full distribution of $\phi_{solv}$, and not simply on its mean, these results for the neutral cavity are nevertheless consistent with the conclusion that driving forces for ion adsorption due to water-water and water-ion interactions are reduced at graphene relative to the air/water interface, and that the direct interaction between the ion and graphene plays a determining role in the thermodynamics of ion adsorption. It is important to note that we have not considered any finite size corrections to $\phi_{solv}$ as, unlike for bulk systems (17, 18), these are not yet well understood for the slab systems studied here. The values presented above should therefore be taken as indicative for how $\langle \phi_{solv} \rangle_0$ may vary through this inhomogeneous system.
References


Fig. S1. Raman characterization of the graphene samples used in the experiment before etching, after etching, and after exposure to the laser beam. (A) Optical image of the graphene on Cu with Cu grain boundary (dark line). (B) Spatial map of 2D/G intensity (peak height) ratios over the area marked in A. (C) Average spectrum of area marked in A (without background subtraction). (D) Optical image of the graphene on clean water after Cu etching. (E) Spatial map of Raman spectra of graphene and water in the area marked in D. (F) Average spectra of area with and without graphene covered on water. (G) Optical image of graphene on glass after SHG measurement. (H) Spatial map of 2D/G intensity ratios over the area marked in G. (K) Average spectrum of area marked in G, and spectrum of glass substrate.
Fig. S2. Preparing samples of graphene floating in sodium thiocyanate solution for SHG experiment. (A) CVD 3-5 layer graphene on copper foils. The polyethylene o-rings are outlined in red for clarity. (B) 3-5 layer graphene confined inside the o-rings after cleaning. (C) Each graphene and the o-ring are scooped in a small cup for SHG measurement. The red and blue lines represent the fundamental and SHG beam paths, respectively. Beam colors are for clarity and do not correspond to the experimental wavelengths.
**Fig. S3. Average heights for the interfaces and three iodide positions.** The average height of the air interface (top) and the graphene interface (bottom) for iodide positioned at the graphene interface (0.4 nm, red triangle), in bulk (1.2 nm, blue x), and at the air interface (2.0 nm, cyan diamond). The graphene center corresponds to 0.0 nm on the y axis. Neat simulations without the iodide are shown with black circles for comparison.
Fig. S4. Schematic of the model used to calculate the adsorption free energy. We imagine that a single solute ‘B’ is constrained to a column above the surface. The dimensions of the column are $l \times l \times L$ and we imagine that it has been divided into small cubes of volume $l^3$. The probability that the solute is adsorbed to the surface is given by Eq. (S.9).
Fig. S5. PMF for an iodide above rigid and flexible graphene models, with $\varepsilon_{C-I} = 0.315$ kJ/mol. The introduction of graphene flexibility has little effect. The air/water interface is in blue and the graphene/water interface is in red. (A) The PMF relative to the average graphene position. Graphene is centered at 0.0 nm. (B) The height relative to the instantaneous interface. Graphene is centered at 0.0 nm and negative values for the height correspond to the liquid phase. Note the change in the x-axis between A and B.
Fig. S6. PMFs for an iodide computed relative to the instantaneous interface. The air/water interface is in blue and the graphene/water interface is in red. A height of 0.0 nm corresponds to the appropriate instantaneous interface. Negative values for the height correspond to the liquid phase.
Fig S7. PMF for a thiocyanate above graphene with energy and entropy contributions. The qualitative trends at the air/water interface are the same as those observed for I$^{-0.8}$ (see Fig. 2). In contrast I$^{0.8}$, a noticeable decrease in entropy is observed at the free energy minimum at graphene. Unlike at the air/water interface, this is primarily due to a decrease in orientational entropy of the thiocyanate (see Figs. S8 and S10).
Fig. S8. Variance of the height fluctuations of the instantaneous graphene- (left) and air-water (right) interfaces in the presence of a thiocyanate ion. Results are shown for the thiocyanate ion positioned at the graphene- and air-water interfaces, and in bulk. Neat simulations (no ion) are also shown. The inset shows the fluctuations at the graphene interface on a larger scale.
Fig S9. Contributions of the direct interaction between thiocyanate and graphene to the total potential energy (PE). The total PE (red) of the thiocyanate in solution and the direct interaction energy of a single thiocyanate at the graphene sheet (no waters). The direct interaction (blue, purple and orange) was calculated with the thiocyanate in three different orientations shown schematically on the right. Graphene is centered at \(z_{\text{ion}}=0\) nm. The total PE has contributions from ion-graphene, water-ion, and water-water interactions.
Fig S10. Distributions of $\cos \theta$, where $\theta$ is the angle between the vector pointing from the sulfur to the nitrogen atom of the thiocyanate, and the $z$ axis (perpendicular to graphene), computed for the ion at different heights. The solid lines are guides to the eye. Close to the graphene, it is clear that the thiocyanate is constrained to lay flat to the surface ($\cos \theta \sim 0$).
Table S1. Values for the fitting parameters obtained from the Levenberg-Marquardt algorithm for the simple Langmuir model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>B</td>
<td>-5 ± 2</td>
</tr>
<tr>
<td>C</td>
<td>-8 ± 3</td>
</tr>
<tr>
<td>ΔG</td>
<td>-8.5 ± 1.1 kJ/mol</td>
</tr>
</tbody>
</table>

Parameter errors are standard errors calculated from the square roots of the corresponding diagonal elements in the variance-covariance matrix.
Table S2. Values for the fitting parameters obtained from the Levenberg-Marquardt algorithm for the Langmuir model with surface potential.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value ± Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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<tr>
<td>B</td>
<td>-30 ± 90</td>
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<tr>
<td>C</td>
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<tr>
<td>D</td>
<td>0 ± 2e5</td>
</tr>
<tr>
<td>E</td>
<td>0 ± 8e5</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>-13 ± 5 kJ/mol</td>
</tr>
</tbody>
</table>

Parameter errors are standard errors calculated from the square roots of the corresponding diagonal elements in the variance-covariance matrix.
Table S3. Correlation matrix for the fit to the Langmuir model with surface potential.

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>G</th>
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<tr>
<td>A</td>
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<td>0.985</td>
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</tr>
<tr>
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<td>-0.989</td>
<td>0.979</td>
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<tr>
<td>C</td>
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<td>-1</td>
<td>0.940</td>
<td></td>
<td></td>
</tr>
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<td>-0.940</td>
<td></td>
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</table>

Notice that all of the correlations are greater than 0.9 and some are even ±1.
Table S4. Lennard-Jones parameters used in the iodide simulations.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$\varepsilon_{ij}$ (kJ/mol)</th>
<th>$\sigma_{ij}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-O</td>
<td>0.650</td>
<td>0.3166</td>
</tr>
<tr>
<td>C-O</td>
<td>0.392</td>
<td>0.3190</td>
</tr>
<tr>
<td>$I^{\delta 8}$-O</td>
<td>0.521</td>
<td>0.4145</td>
</tr>
<tr>
<td>$I^{\delta 8}$-C</td>
<td>0.708</td>
<td>0.4169</td>
</tr>
</tbody>
</table>

The water-water parameters were taken from Ref. (19), the water-carbon parameters from Ref. (20) and water-iodide parameters from Ref. (21). The iodide-carbon $\varepsilon_{ij}$ was chosen to obtain agreement with experiment, and the obtained absorption energy of a single iodide at the graphene sheet (no waters) is in reasonable agreement with literature values obtained with density functional theory (14, 15).
Table S5. Adsorption energy of a single iodide to the graphene sheet (no waters) for different values of \( \varepsilon_{C-I} \), and differences in adsorption free energies between the graphene/water and air/water interfaces (\( \Delta\Delta G_{\text{ads}} \)).

<table>
<thead>
<tr>
<th>( \varepsilon_{C-I} )</th>
<th>Adsorption energy (kJ/mol)</th>
<th>( \Delta\Delta G_{\text{ads}} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.315</td>
<td>-6.9</td>
<td>+5.1</td>
</tr>
<tr>
<td>0.708</td>
<td>-15.4</td>
<td>-1.9</td>
</tr>
<tr>
<td>1.046*</td>
<td>-22.8</td>
<td>-8.9</td>
</tr>
</tbody>
</table>

*These simulations were performed with the flexible graphene model.
Table S6. Lennard-Jones parameters used in the thiocyanate simulations.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$\varepsilon_{ij}$ (kJ/mol)</th>
<th>$\sigma_{ij}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-O</td>
<td>0.650</td>
<td>0.3166</td>
</tr>
<tr>
<td>O-C$_{gra}$</td>
<td>0.392</td>
<td>0.3190</td>
</tr>
<tr>
<td>O-C$_{ion}$</td>
<td>0.526</td>
<td>0.3463</td>
</tr>
<tr>
<td>O-S</td>
<td>0.995</td>
<td>0.3733</td>
</tr>
<tr>
<td>O-N</td>
<td>0.449</td>
<td>0.3658</td>
</tr>
<tr>
<td>C$<em>{gra}$-C$</em>{ion}$</td>
<td>0.317</td>
<td>0.3487</td>
</tr>
<tr>
<td>C$_{gra}$-S</td>
<td>0.600</td>
<td>0.3757</td>
</tr>
<tr>
<td>C$_{gra}$-N</td>
<td>0.271</td>
<td>0.3682</td>
</tr>
</tbody>
</table>

The charges on the C$_{ion}$, S, and N atoms on the thiocyanate are +0.49, -0.75, and -0.74, respectively.