Hydrophobicity at the molecular scale

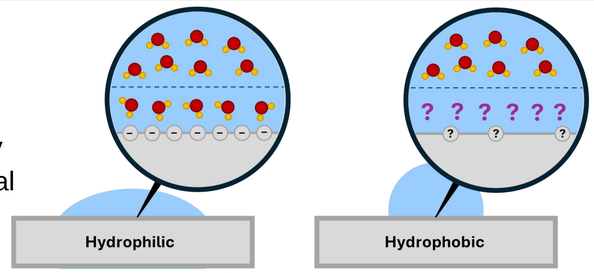
Characterizing the aqueous-polystyrene interface with vibrational sum-frequency generation spectroscopy

Arden Bevington[1], Md. Mosfeq Uddin[1], Dennis K. Hore[1,2]
[1]Department of Chemistry, University of Victoria, Victoria, BC
[2]Department of Computer Science, University of Victoria, Victoria, BC

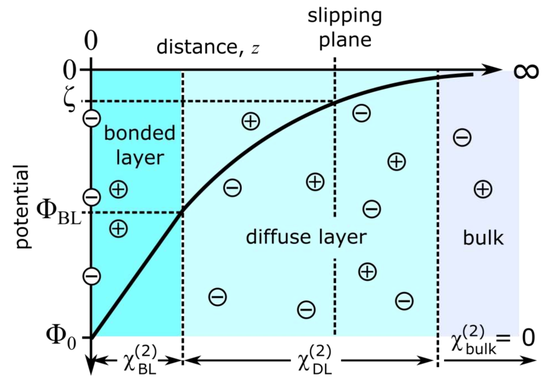
February 20th, 2025

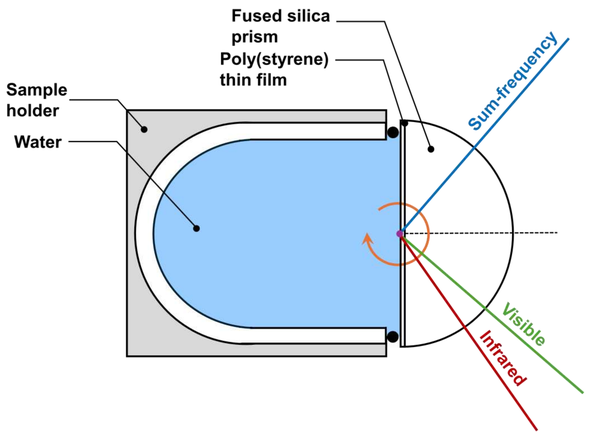
Background

Ever wonder why water forms beads on your plastic water bottle or raincoat? As it turns out, that question has important implications in many scientific fields![1] Hydrophobicity is an important property of polymer materials, but the molecular processes at work are not fully understood. Central among these mysteries is the electrical potential observed at water-hydrophobe interfaces.[2]



Methods





Vibrational sum-frequency generation (SFG) is a spectroscopic technique used to study buried interfaces and other non-centrosymmetric environments by probing second-order susceptibility ($\chi^{(2)}$). By **varying the incident angle** of light on the sample we can separate contributions to $\chi^{(2)}$ from water molecules in the bonded layer (BL) and in the diffuse layer (DL).[3]

$$I_{SFG} \propto \left|\chi^{(2)}_{eff}\right|^2$$

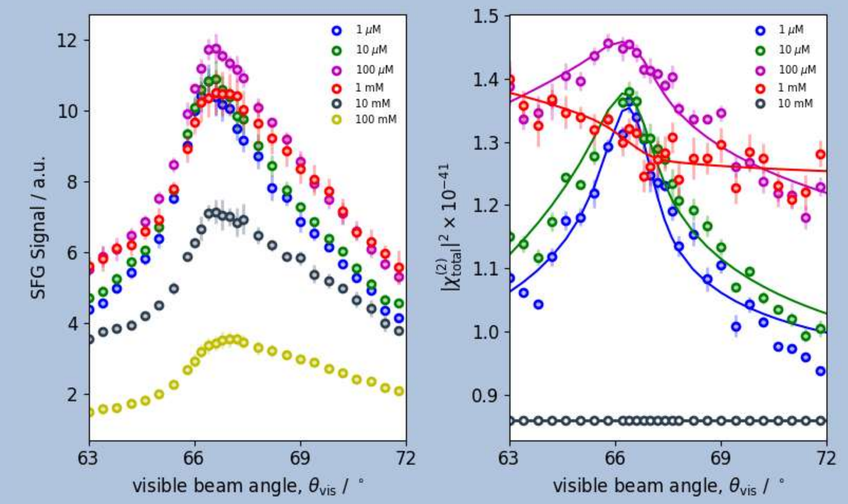
$$\chi^{(2)}_{eff} = L(\theta)\left(\chi^{(2)}_{BL} + \chi^{(2)}_{DL}\right)$$

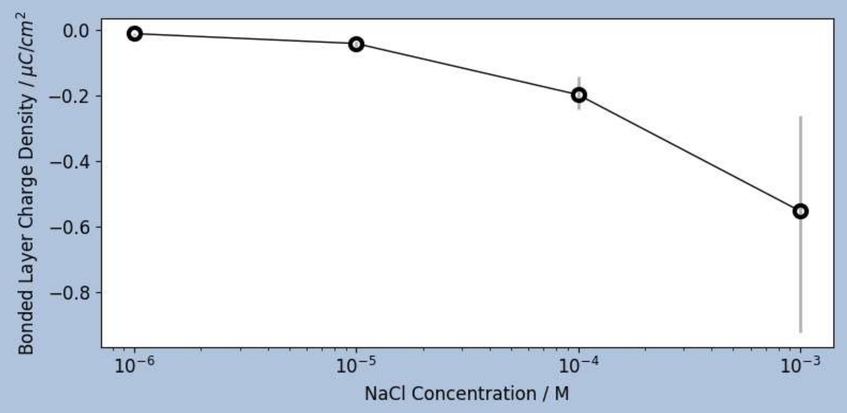
$$\chi^{(2)}_{DL} = \chi^{(3)}\left[\Phi_{BL} - \frac{4ik_BT\Delta k_z}{e}\sum_{n=0}^{\infty}\frac{(tanh(e\,\Phi_{BL}/4\,k_BT))^{2n-1}}{(2n-1)(i\Delta k_z - \kappa(2n-1))}\right]$$

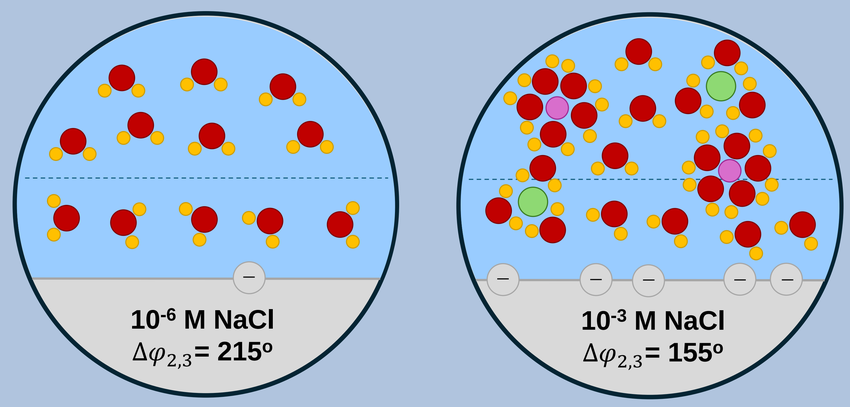
The SFG signal is angle-dependent due to **water molecules in the DL**, and **local field effects.** During the experiment, the ionic strength of the water is increased by adding NaCl. Ions in solution **screen surface charge** and **perturb the interfacial behaviour**, resulting in changes in the SFG signal. Before extracting meaningful quantities from the SFG angle-dependence, a **correction** must be made for the local field effects.

At high ionic strength there is **only** angle dependence due to **local field effects**. By correcting based on the angle dependence at high ionic strength, the angle dependence due to **interfacial water molecules** is **isolated**. Finally, the signal is compared to the signal for α-quartz, which has a known $\chi^{(2)}$ value, **replacing** the relative scale with an **absolute scale**. Nonlinear curve fitting is then used to extract the BL potential (Φ_{BL}), $\left|\chi^{(2)}_{BL}\right|$, and the phase of $\chi^{(2)}_{BL}$ (φ_2), which describe the surface charge and water structure at the interface.

Results and Discussion







Conclusions

- Water molecules are oriented with hydrogen atoms directed towards the polystyrene surface.
  - Similar to water molecules at the hydrophilic silica-water interface.[3]
- Charge density at the bonded layer increases at high ionic strength.
  - Development of charge with ionic strength is different than for the silica-water interface.[3]

References

(1) Foster, J. C. et al. (2020) *ACS Macro Lett.*
(2) Kudin, K. N. et al. (2008) *J. Am. Chem. Soc.*
(3) Uddin, Md. M. et al. (2024) *J. Am. Chem. Soc.*

This research was supported by the Jamie Cassels Undergraduate Research Awards, University of Victoria
Supervised by Prof. Dennis K. Hore