

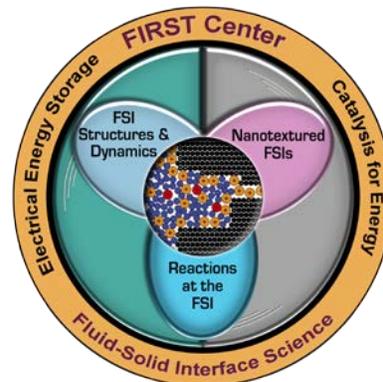
FIRST Center Research Perspective:

Nonlinear optical approaches for elucidating interfacial fluid and sorbed species structures and dynamics

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Research Summary: We have worked to optimize nonlinear optical techniques, specifically vibrational sum frequency generation (SFG) and second harmonic generation (SHG), to investigate the structure, orientation, adsorption, and electrostatics of various fluid interfaces over carbon materials and single layer graphene. Over the variety of systems studied, we have determined that the underlying support substrate for the graphene film often regulates the electrostatic field at the interface. The presence of single-layer graphene between an aqueous or organic fluid phase and the solid phase has little or no influence on adsorption free energy, electrostatics, or other energy relationships in the electrical double layer.

Technical Details: Sum frequency generation (SFG) and second harmonic generation (SHG) are ideal techniques for providing interface specific information on the structure and electrostatics at carbon interfaces with high surface-selectivity, *in situ*, without the need of labels and without damage to the carbon substrates. The combination of these two surface selective techniques allows for the study of a variety of fluid solid interfaces, and allows us to focus on many fluid/solid interactions relevant to the FIRST EFRC.

Vibrational SFG signal arises only where symmetry is broken, thus making the technique surface selective. By tuning into the C-H stretching region, SFG can be used to track hydrocarbon orientation, adsorption and ordering on various carbon substrates. We have demonstrated that the use of femtosecond pulses overcomes the “strong optical absorber” problem inherent in nm-thick carbon substrates, which has curtailed efficient spectroscopic analyses of these materials in the past. The sum frequency response of mm-thick highly ordered pyrolytic graphite (HOPG) is dominated by a strong nonresonant response attributed to the delocalized electrons within HOPG, making spectroscopic analysis of

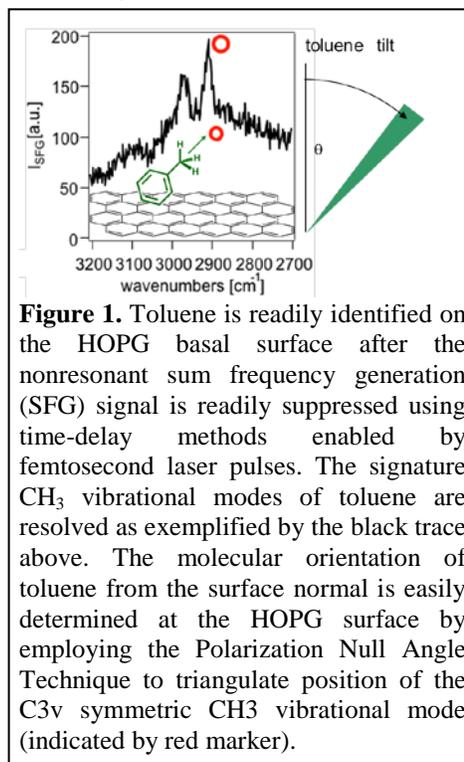


Figure 1. Toluene is readily identified on the HOPG basal surface after the nonresonant sum frequency generation (SFG) signal is readily suppressed using time-delay methods enabled by femtosecond laser pulses. The signature CH_3 vibrational modes of toluene are resolved as exemplified by the black trace above. The molecular orientation of toluene from the surface normal is easily determined at the HOPG surface by employing the Polarization Null Angle Technique to triangulate position of the C_{3v} symmetric CH_3 vibrational mode (indicated by red marker).

adsorbed hydrocarbons challenging. We combined a time-delay method and a null angle technique to suppress the nonresonant signal, resolve vibrational modes of the model hydrocarbon toluene, and triangulate the orientation of the C_{3v} axis of toluene from surface normal (**Figure 1**, Reference 3). The 37 to 42 degree tilt of the methyl group of toluene determined with SFG, was confirmed with DFT calculations, which suggested a high surface loading led to the observed tilt angle.

To investigate the aqueous/carbon interface, the non-resonant SHG $\chi^{(3)}$ method was utilized as this technique is highly sensitive to changes in interfacial potential which can provide important structural and thermodynamic information of interfacial interactions. In the FIRST center, we were able to obtain highly uniform, continuous, and pristine single layer graphene films to use for our SHG studies. We made use of various surface characterization methods to confirm the integrity of the graphene films. Comparing the aqueous/graphene/fused silica interface to the aqueous/bare fused silica interface we determined that the presence of a single layer graphene film in between the fluid and solid phases effectively screened the charges below it by 60%, or likewise reduces the interfacial charge density fused silica by 60% (**Figure 2A**). This corresponds to a factor of 7 reduction of the interfacial free energy density of the aqueous/fused silica interface (**Figure 2B**, Reference 2). In a second analysis we applied the $\chi^{(3)}$ method to probe Mg^{2+} adsorption in the same fluid/solid system with and without pristine and defected single layer graphene films (Reference 1). The SHG analyses revealed that the free energy of adsorption calculated for all system tested was the same. This indicates that the presence of a single layer of graphene with and without defects has a minimal to no influence on the adsorption mechanism of Mg^{2+} ions, allowing for the outer-sphere hydrogen bonding adsorption mechanism to be unimpeded by the presence of graphene. These results clearly indicate that a single layer of pristine or defected graphene over an oxide surface has minimal influence on the electrical double layer for all conditions surveyed.

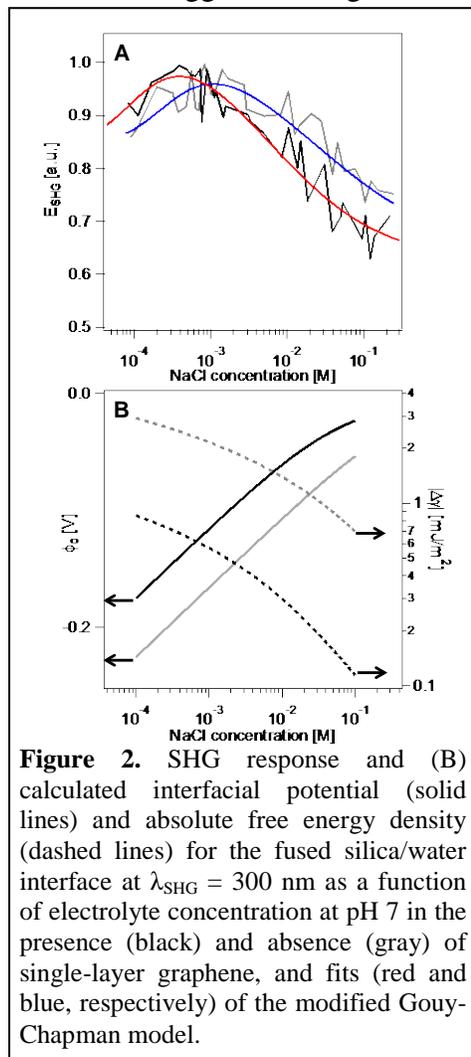


Figure 2. SHG response and (B) calculated interfacial potential (solid lines) and absolute free energy density (dashed lines) for the fused silica/water interface at $\lambda_{SHG} = 300$ nm as a function of electrolyte concentration at pH 7 in the presence (black) and absence (gray) of single-layer graphene, and fits (red and blue, respectively) of the modified Gouy-Chapman model.

Finally, through the use of vibrational SFG we were able to then investigate the interfacial interactions of an organic solvent over a graphene interface. In a model system, we used SFG to track the adsorption and ordering of 1-hexanol solvated in deuterated cyclohexane over an α -alumina substrate. The intensities of the methyl and methylene symmetric stretches resolved in the SFG spectra for various concentrations of 1-hexanol in cyclohexane were used to compare the interactions of this binary organic mixture on the hydrophilic bare α -alumina interface to that of the hydrophobic interface created by a single layer graphene supported on α -alumina. Surprisingly we find, that again the single layer of graphene, whether defected or pristine, did not

alter the free energy of adsorption of 1-hexanol or the general structure of 1-hexanol at the interface. Again we observe that the electrostatics induced by the oxides surfaces determine the interfacial interactions.

Significant Impacts on Science and Technology: With our original SFG studies, not only have we overcome the strong absorber problem intrinsic to thick carbon samples, but we have also shown how to overcome the chemical contrast (“carbon on carbon”) problem and determined the orientation of a hydrocarbon on a carbon substrate. This study benchmarks future research, which will use orientation analyses to understand how chemical reactions and physical processes at fluid-solid interfaces progress.

We have also reported the first SHG analyses quantifying changes in the free energy of the electrical double layer and ion adsorption at the aqueous graphene interface. Combined with the SFG studies of 1-hexanol adsorption to that interface, we have determined that the electrostatics of the interface are determined mainly by the underlying substrate. Specifically, our findings show that a single layer of graphene has little to no influence on changing the electrostatic potentials and free energy densities when it is placed between a liquid/oxide interface. This conclusion holds for the liquids water and cyclohexane but likely applies to more solvents as well, including ionic liquids. This finding will be important for the design of single layer graphene applications and provides important insight and benchmarks for computational studies of fluid/single layer graphene interfaces. Our results from defected graphene films mirror our results, and show that defects added into the graphene films do not alter the electrostatics when over oxide surfaces. This latter finding may be important for understanding the aging and decomposition of single layer graphene films or of graphene oxides.

Publications and Manuscripts:

1. Achtyl, J.; Vlassiouk, I.; Surwade, S.; Fulvio, P.; Dai, S.; Geiger, F. Interaction of Magnesium Ions with Pristine Single Layer and Defected Graphene/Water Interfaces Studied by Second Harmonic Generation, *J. Phys. Chem. B* **2013**, **Accepted**.
2. Achtyl, J.; Vlassiouk, I.; Fulvio, P. F.; Mahurin, S. M.; Dai, S.; Geiger, F. Free Energy Relationships in The Electrical Double Layer Over Single Layer Graphene, *J. Am. Chem. Soc.* **2013**, *135*, 979-981, [[10.1021/ja3120899](https://doi.org/10.1021/ja3120899)].
3. Achtyl, J.; Buchbinder, A. M.; Geiger, F. Hydrocarbon on Carbon Coherent Vibrational Spectroscopy of Toluene on Graphite (HOPG), *J. Phys. Chem. Lett.* **2012**, *3*, 280-282, [[10.1021/jz2016796](https://doi.org/10.1021/jz2016796)].