



# Characterizing Anion Adsorption to Water-Hydrophobe Interfaces

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## Abstract

The study of liquid-liquid interfaces is crucial for understanding many important processes in broad areas of science. Developing both a quantitative understanding of ion adsorption to these interfaces, as well as a molecular level picture of the solvation environment are therefore of great interest. In this work, we continue our investigation of the behavior of simple ions at aqueous interfaces, employing the combination of two surface-sensitive nonlinear spectroscopy tools, broadband deep UV electronic sum-frequency generation and UV second harmonic generation, to characterize the adsorption of thiocyanate ( $\text{SCN}^-$ ) to the interface of water with prototypical liquid hydrophobes. We find that both the interfacial spectra and the Gibbs-free energies of adsorption closely match results obtained for the air-water interface. We observe no relative spectral shift in the higher-energy CTTs transition of thiocyanate, implying similar solvation environments for these seemingly very different interfaces. Furthermore, the Gibbs free energies of adsorption agree within error; however, we expect the respective enthalpic and entropic contributions to differ between the interfaces, as for our earlier findings for the air-water vs. graphene-water interfaces. Nevertheless, the similarities indicate a remarkably general behavior for ion adsorption to water-hydrophobe interfaces.

## DUV-SHG and the Langmuir Adsorption Model

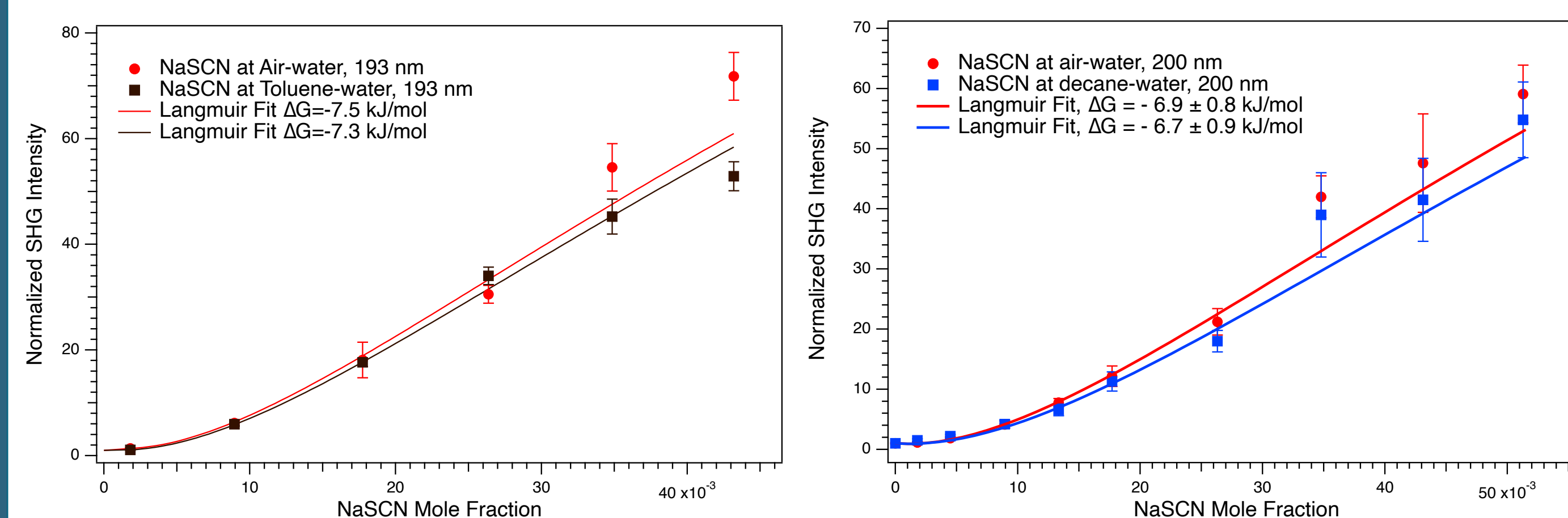
The use of a simplified Langmuir adsorption model for the determination of thermodynamic properties from SHG experiments is well established, and a brief description is given below:

$$\frac{I_{2\omega}}{(I_\omega)^2} \propto |\chi_{\text{eff}}^{(2)}|^2 \propto |\chi_{\text{water}}^{(2)} + \chi_{\text{hydrocarbon}}^{(2)} + \chi_{\text{anion}}^{(2)}|^2$$

$$\frac{I_{2\omega}}{(I_\omega)^2} \propto \left( A + B \frac{C_{\text{anion}}}{(1 - C_{\text{anion}})e^{\frac{\Delta G}{RT}} + C_{\text{anion}}} \right)^2 + \left( D \frac{C_{\text{anion}}}{(1 - C_{\text{anion}})e^{\frac{\Delta G}{RT}} + C_{\text{anion}}} \right)^2$$

- A, B, D = fitting parameters
- $I_{2\omega}$  and  $I_\omega$  = SH and fundamental intensities
- $C_{\text{anion}}$  = bulk anion concentration
- $\Delta G$  = Gibbs' free energy of adsorption

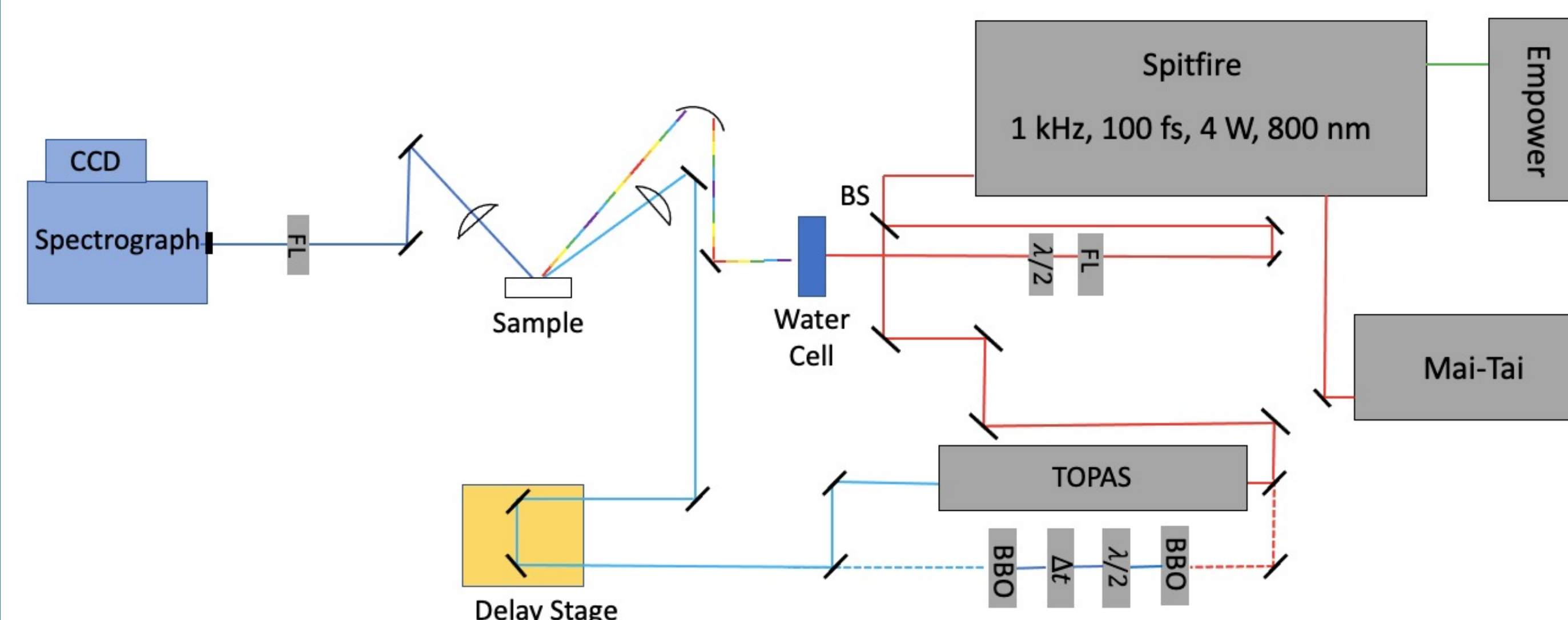
The above equation relates the observed SH intensity to the bulk anion concentration and allows for the determination of the Gibbs' free energy of adsorption.



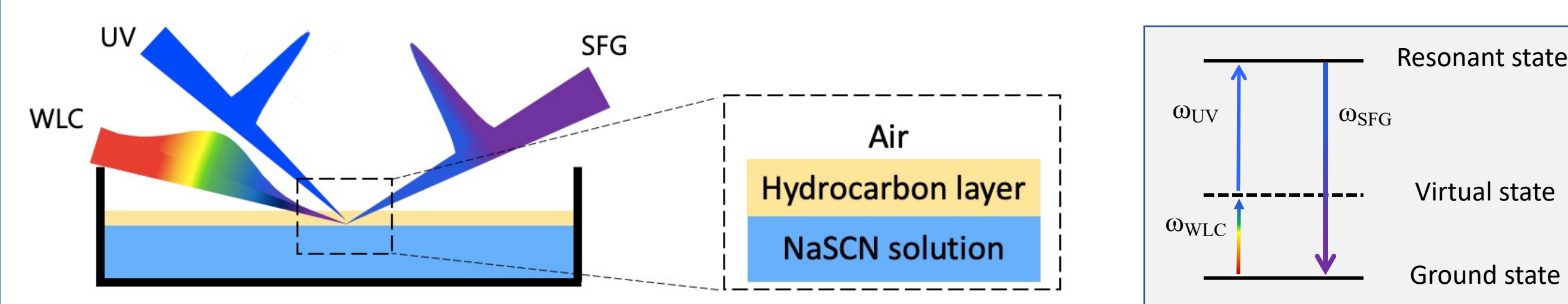
Normalized SH Intensities for NaSCN at the air-water (red circles), toluene-water (above left black squares), and decane-water (above right, blue squares). The determined Gibbs-free energies of adsorption all agree within error of one another.

## Interfacial CTTs Spectra of $\text{SCN}^-$

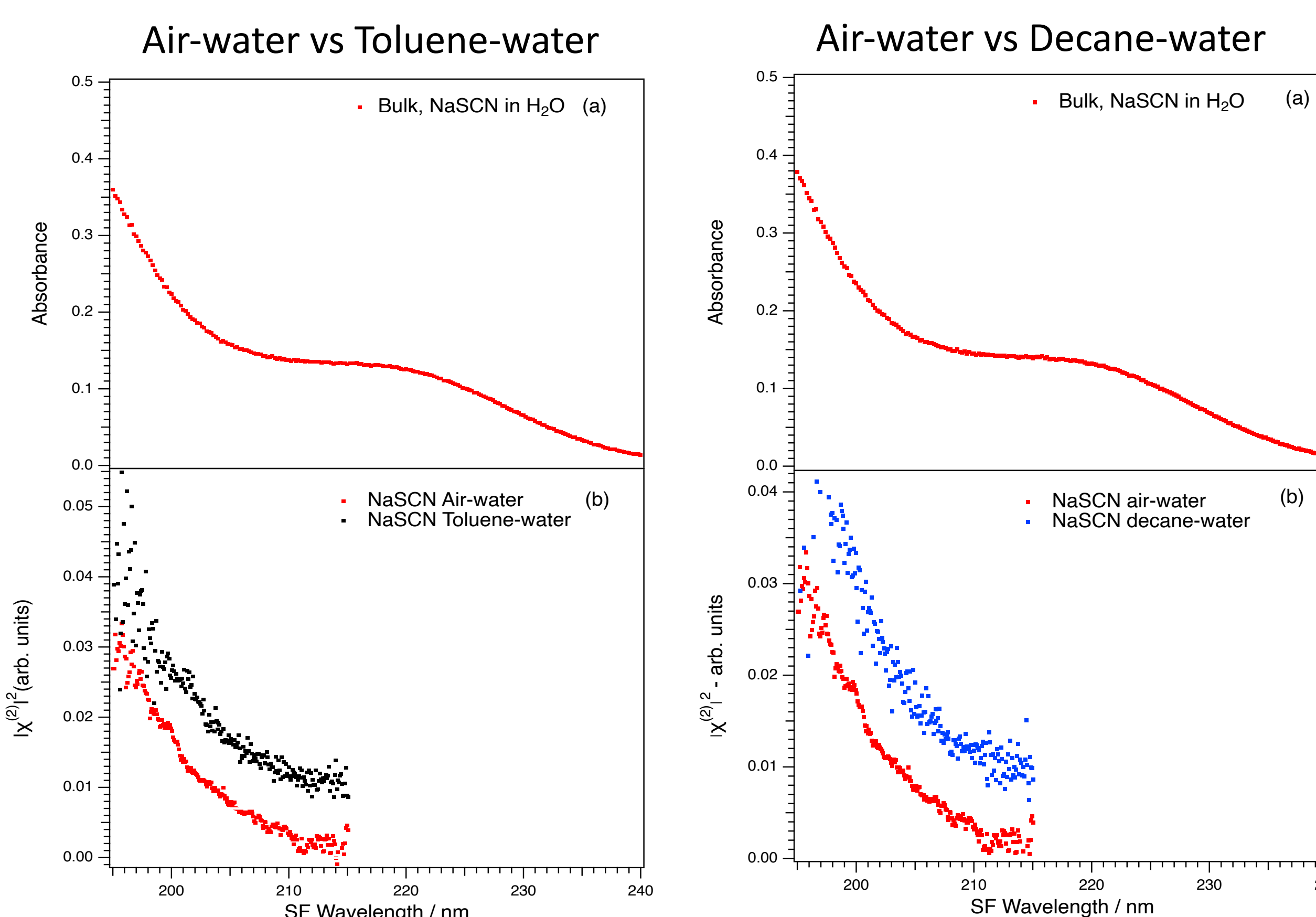
### Broadband Deep UV Electronic Sum-Frequency Generation Spectroscopy



**Above:** Experimental set up for broadband DUV-ESFG spectroscopy, employing an 800 nm, 100 fs amplified laser system. The use of a white light continuum (WLC) photon allows for approximately 40 nm of spectral width to be captured in the deep UV with a single laser shot, offering improved signal to noise and reliability over time-consuming SHG spectra.



**Above Left:** Depiction of liquid-liquid interface formed by depositing a thin layer of hydrocarbon on top of the electrolyte solution. **Above Right:** Energy level diagram for SFG, showing two-photon resonant enhancement as employed in the described experiments



**Top Row:** Bulk absorption spectra of NaSCN in water, showing two CTTs transitions in the UV. **Bottom Row:** Interfacial DUV-ESFG spectra of NaSCN at the air-water (red dots) and NaSCN at the toluene-water (left, black dots) and decane-water (right, blue dots).

CTTS spectra are highly sensitive to the local solvation environment – the lack of a spectral shift implies there is little difference in the solvation environment around the anion at these interfaces

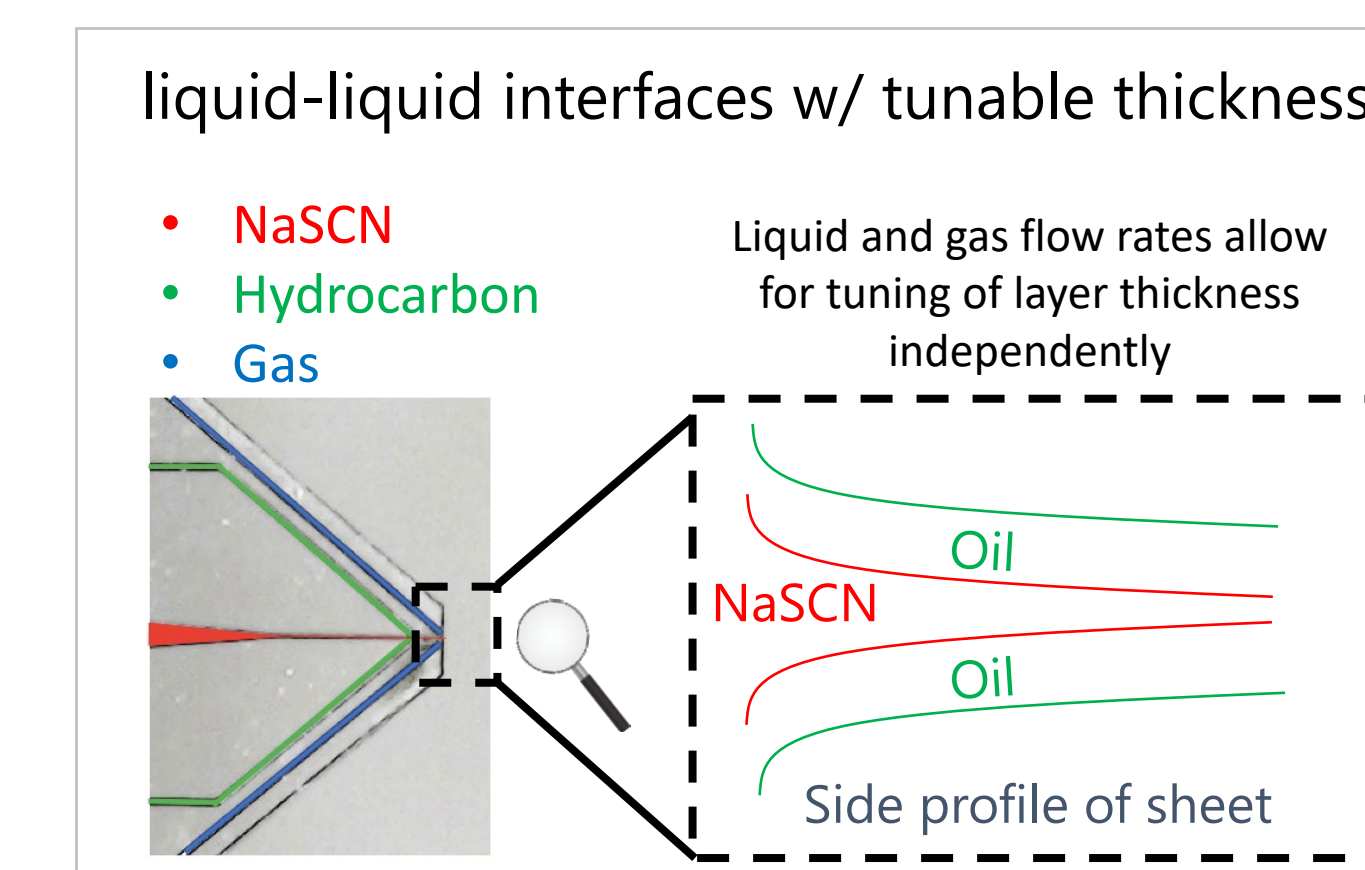
## Conclusions and Future Work

### Anion Affinities for Water-hydrophobe Interfaces as Determined by DUV-SHG Spectroscopy

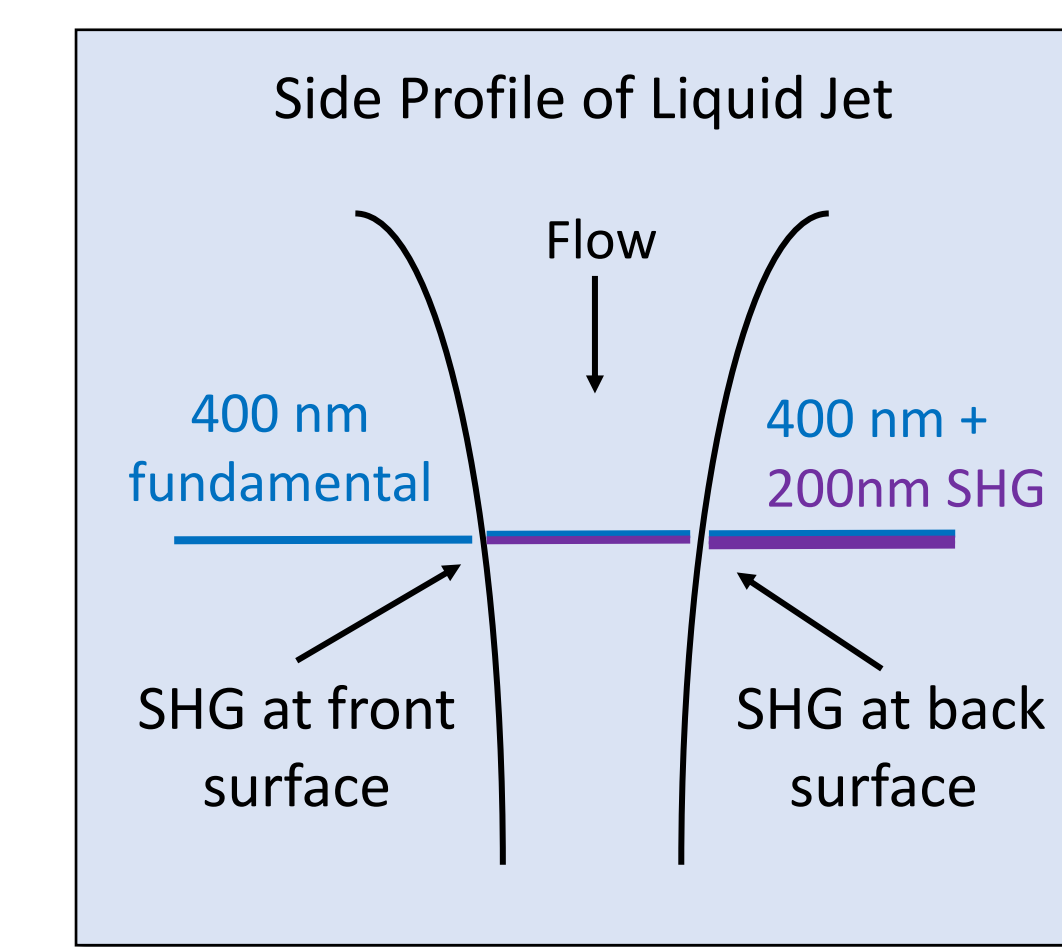
Ion / Interface	$\Delta G_{\text{ads}}$ (kJ/mol)
$\text{Br}^-$ / air-water	$\sim -1.4$
$\text{Br}^-$ / dodecanol-water	$\sim -2$
$\text{SCN}^-$ / air-water	$-7.5 \pm 0.1$
$\text{SCN}^-$ / dodecanol-water	$-6.7 \pm 1.1$
$\text{SCN}^-$ / graphene-water	$-8.5 \pm 1.1$
$\text{SCN}^-$ / toluene-water	$-7.3 \pm 0.7$
$\text{SCN}^-$ / decane-water	$-6.7 \pm 0.9$

Our results indicate that there is remarkably general behavior for anion adsorption to water-hydrophobe interfaces. Whether the molecular level details of adsorption remain the same for the air-water and oil-water interfaces is currently under investigation.

### Future Work: Studying hydrophobe-water interfaces with planar, ultra-thin flatjet technology



**Above Left:** Tip of hydrodynamic gas nozzle and cartoon depiction of a layered oil-water interface. **Above Right:** Depiction of side profile of jet, indicating multiple surfaces generating SHG signal



Hydrodynamic gas nozzle for flat jet generation was developed by Jake Koralek at SLAC and further work is being conducted in collaboration with him

## Acknowledgements and Ref.

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- 1) McCaffrey, D. L.; Nguyen, S. C.; Cox, S. J.; Weller, H.; Alivisatos, A. P.; Geissler, P. L.; Saykally, R. J. Mechanism of Ion Adsorption to Aqueous Interfaces: Graphene/Water vs. Air/Water. *Proc. Natl. Acad. Sci. U. S. A.* 2017, 114 (51), 13369–13373.
- 2) Devlin, S. W.; McCaffrey, D. L.; Saykally, R. J.; Characterizing Anion Adsorption to Aqueous Interfaces: Toluene-water vs Air-water. *J. Phys. Chem. Lett.* 2022, 13, 222–228.
- 3) Koralek, J. D.; et al. Generation and Characterization of Ultrathin Free Flowing Liquid Sheets. *Nat. Commun.* 2018, 9, 1358.