

SHG Studies of Liquid-Liquid Interfaces via Planar Liquid Sheets

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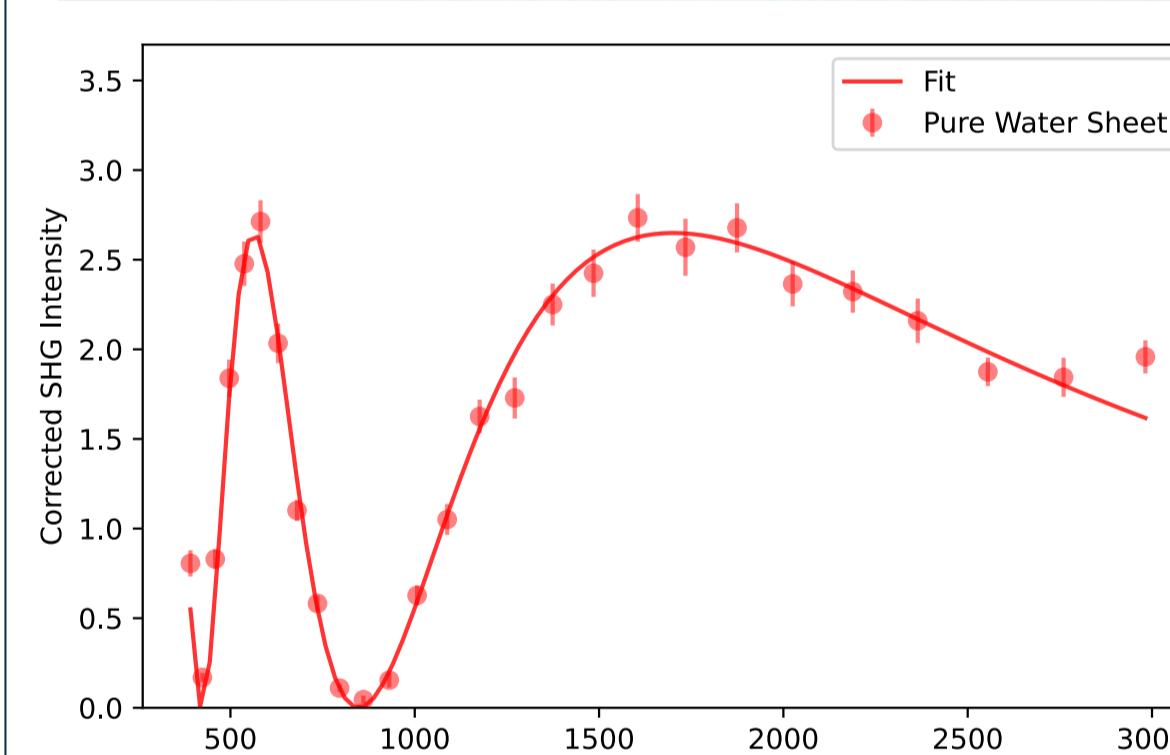
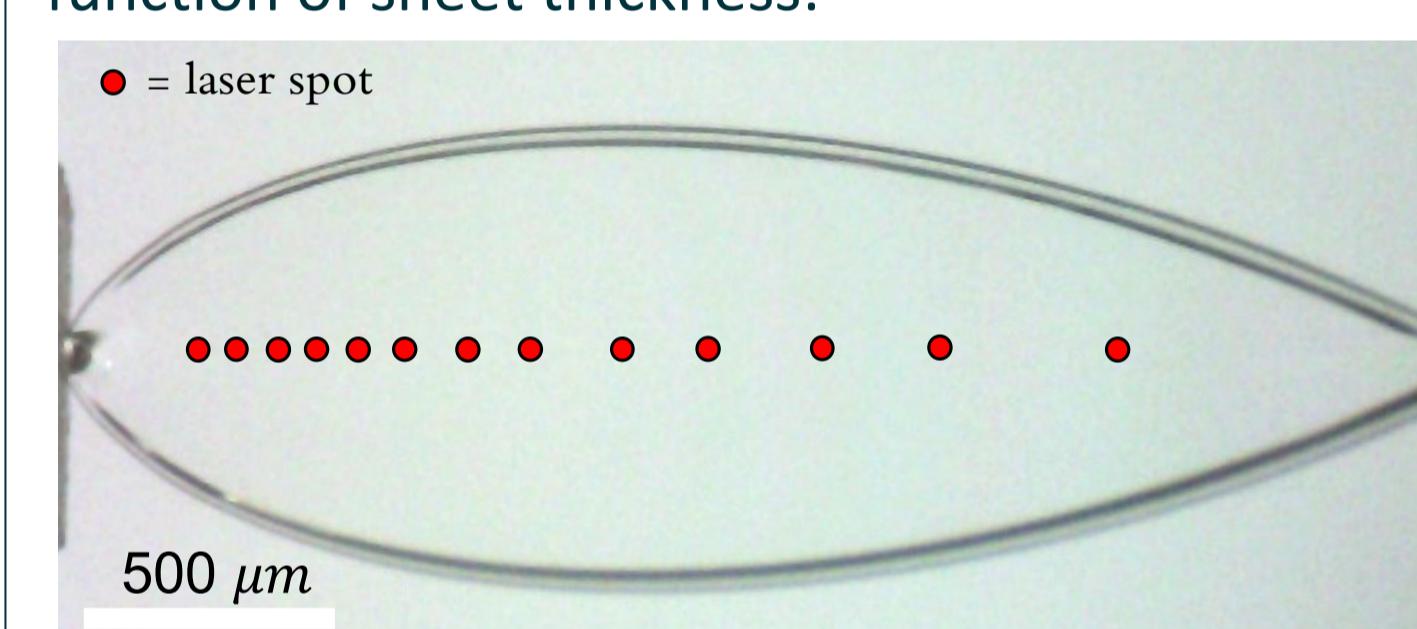
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Abstract

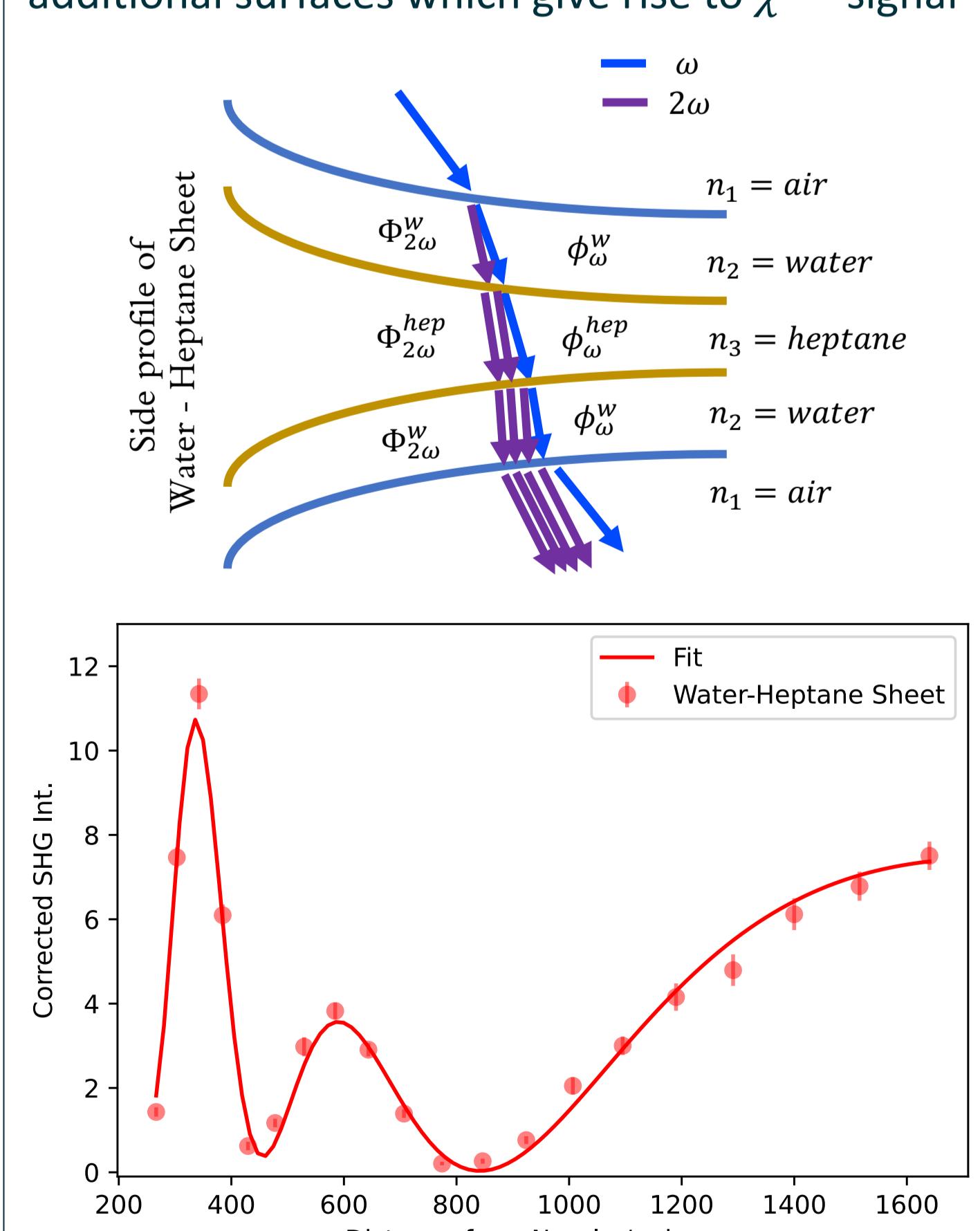
Characterization of liquid-vapor and liquid-liquid interfaces is vital for understanding broad areas of chemistry, physics, and biology. A quantitative understanding of these neat interfaces, as well as phenomena such as ion adsorption are therefore of much interest. Here, we report the use of thin planar liquid sheet technology, interrogated with deep-UV second harmonic generation spectroscopy for studies of buried liquid interfaces, which feature continually refreshed solution and freedom from contamination and sample damage. We present the mathematical framework used to model and interpret SHG experiments at both the air-water and buried water-heptane interface in a transmission geometry, for both absorbing and non-absorbing solutions. Specifically, we study the adsorption behavior of a prototypical anion, thiocyanate, to the water-heptane interface as a function of bulk anion concentration, which permits quantitative determination of the Gibbs free energy of adsorption. Temperature dependent SHG measurements allow decoupling the enthalpic and entropic contributions to the overall Gibbs free energy, providing key insights into the mechanism driving ion adsorption phenomena.

SHG From Thin Sheets

For thin films, the signal from each surface can interfere, modulating the SHG intensity as a function of sheet thickness:

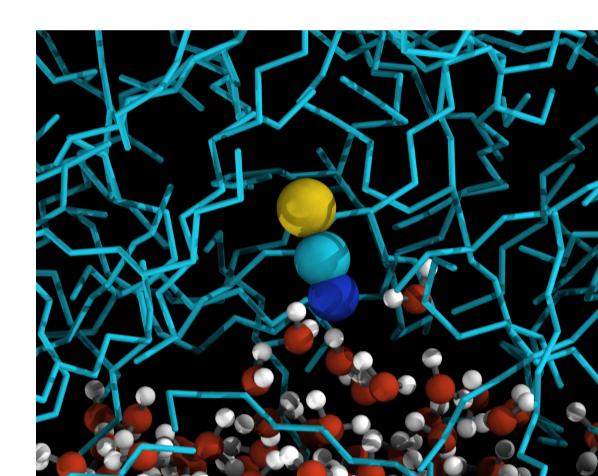


For single fluid sheets (**Above**), the oscillation pattern is simple. For multi-fluid sheets (**Below**), it becomes more complex, as there are two additional surfaces which give rise to $\chi^{(2)}$ signal

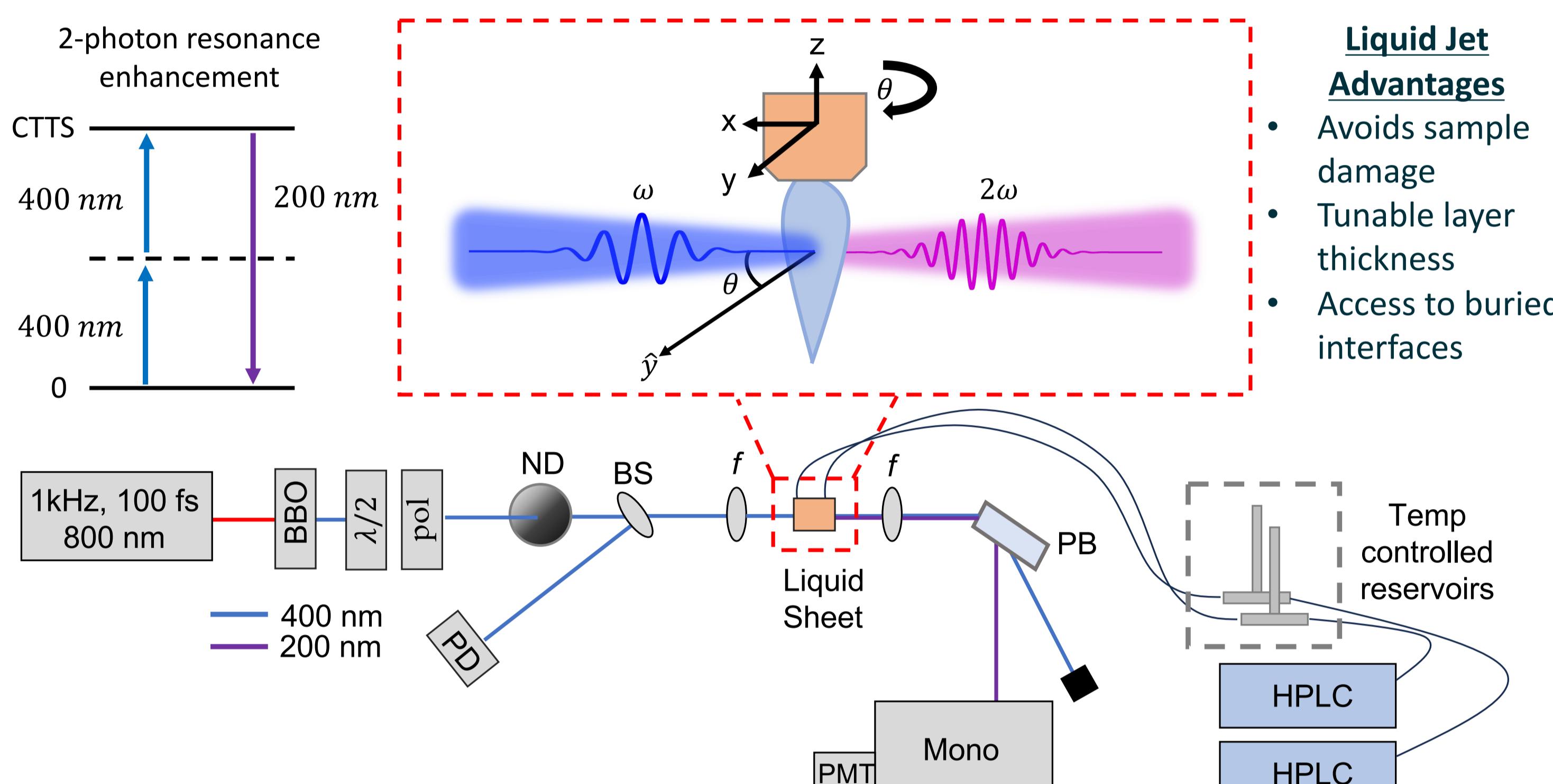


Coupling Planar Liquid Sheets with Deep UV SHG

Understanding Ion Solvation Thermodynamics at Aqueous Interfaces



Ions at interfaces influence reaction kinetics, atmospheric aerosol chemistry and much more. Our goal is to develop a mechanistic understanding of what drives ions to air-water and water-oil interfaces, to better understand their influence on important chemical processes.



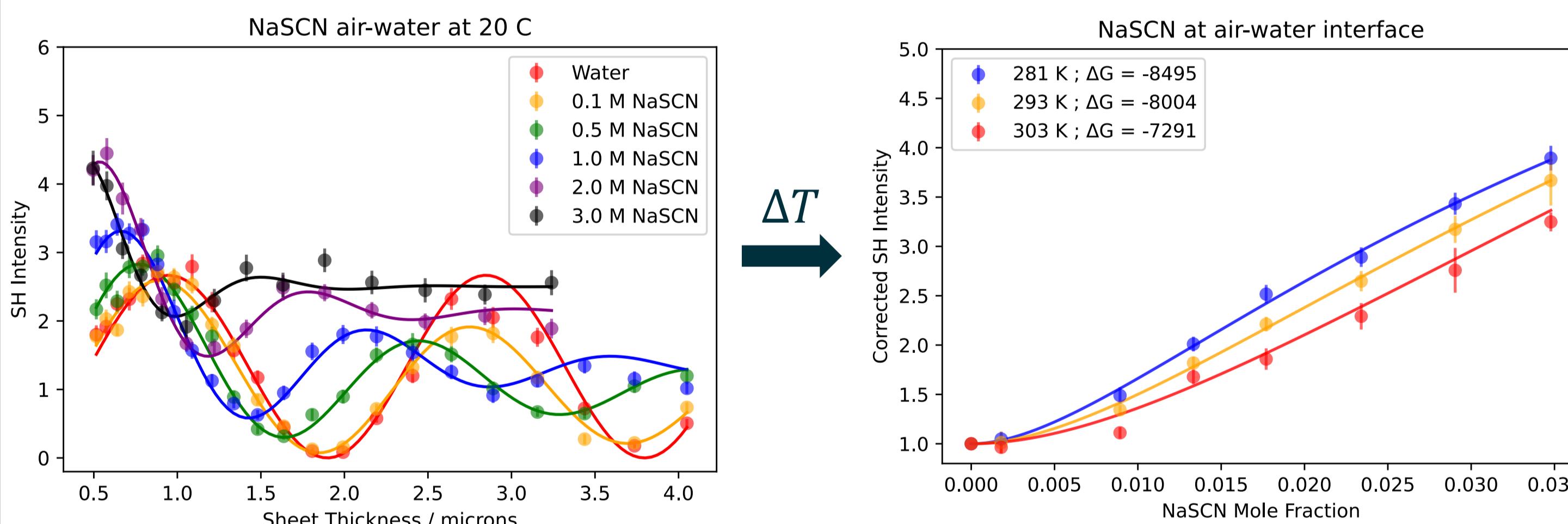
- Liquid Jet Advantages**
- Avoids sample damage
- Tunable layer thickness
- Access to buried interfaces

Determining Mechanism of Anion Adsorption

Single Liquid Sheets

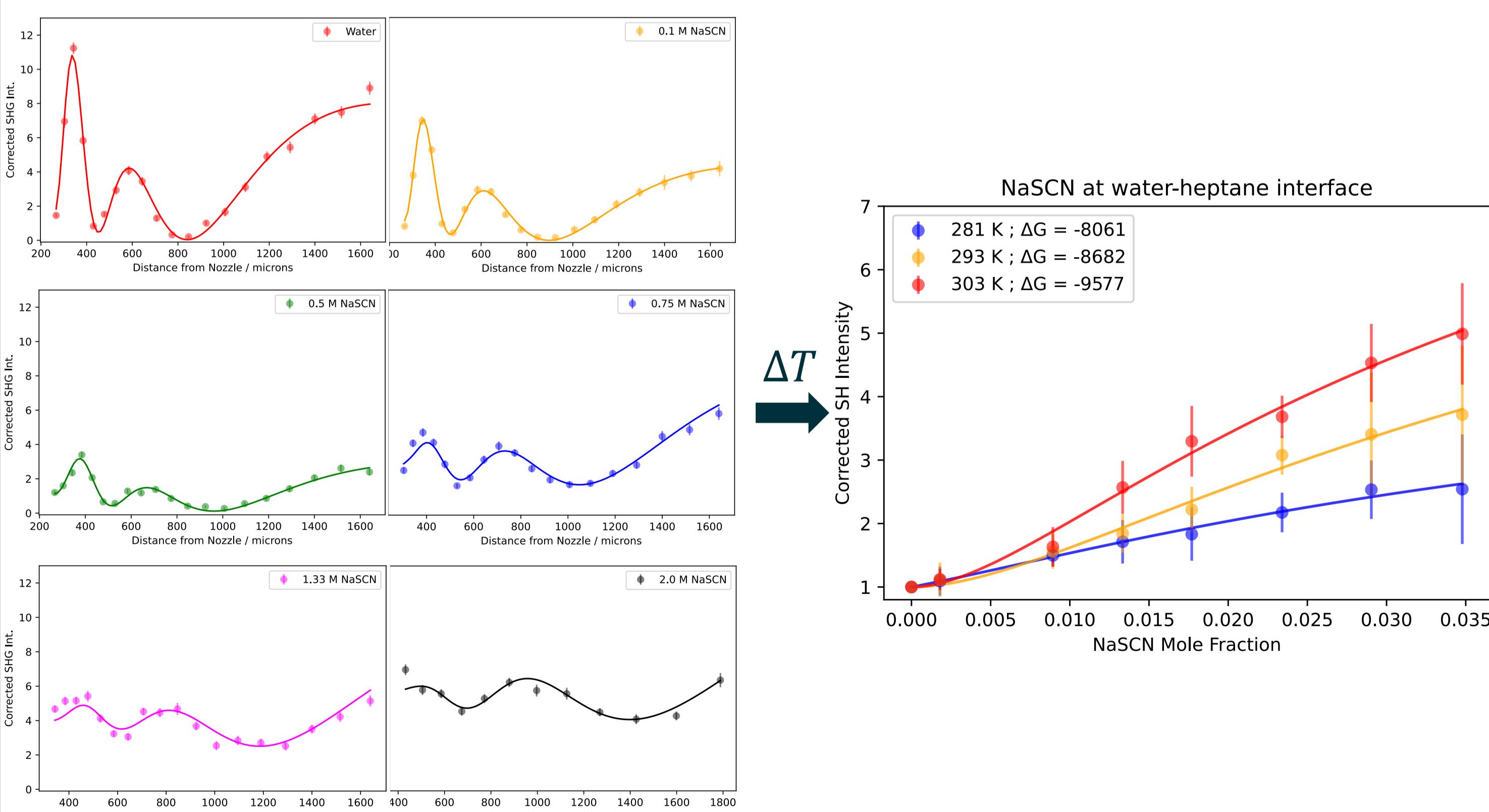
The Langmuir adsorption model relates the SH intensity and bulk anion concentration (X_{anion}) to the Gibbs free energy of adsorption (ΔG):

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



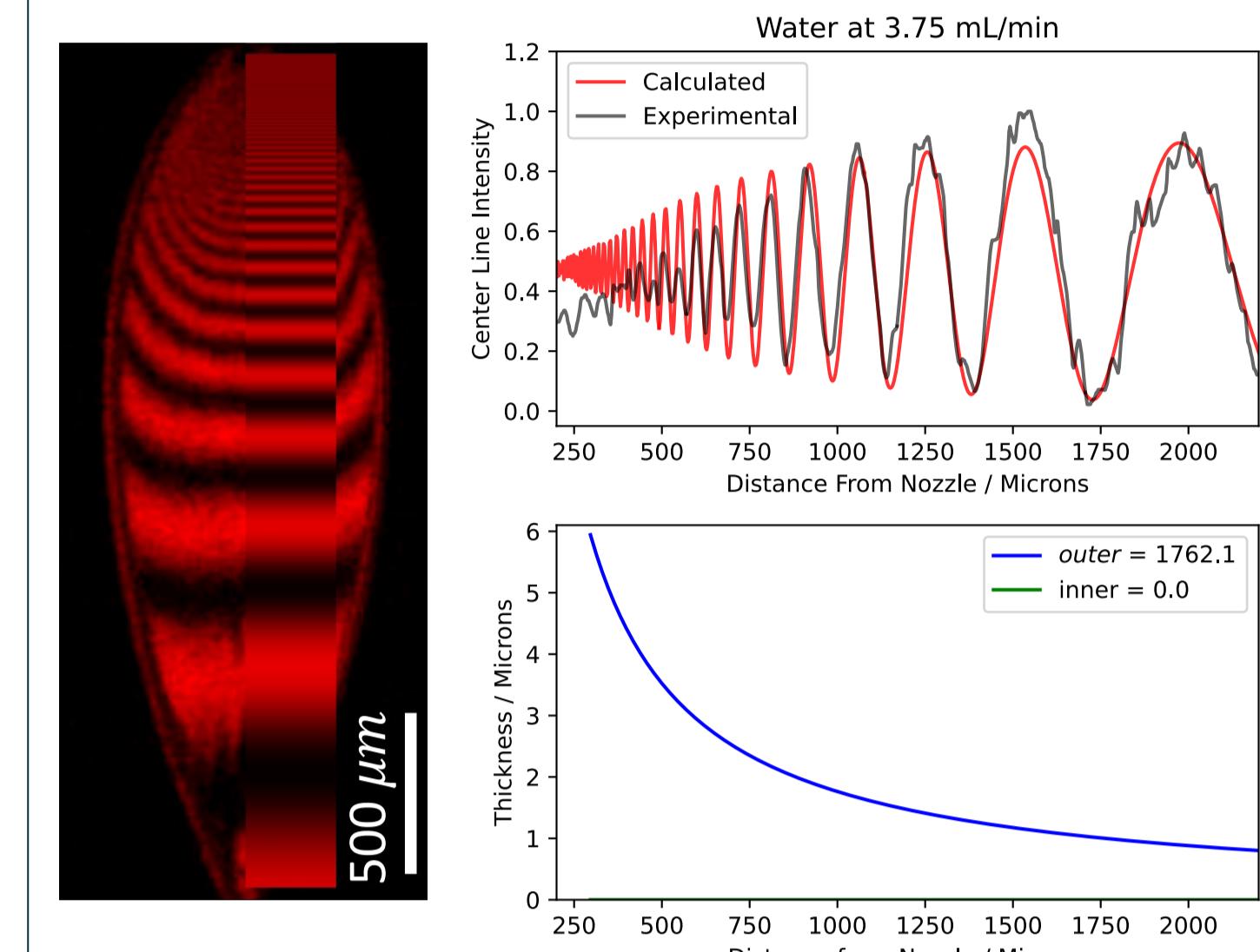
Above: Left: SH Intensity as a function of sheet thickness for 0 – 3.0 M NaSCN concentration series.
Right: Langmuir adsorption isotherms for NaSCN as a function of temperature

Liquid-Liquid Sheets

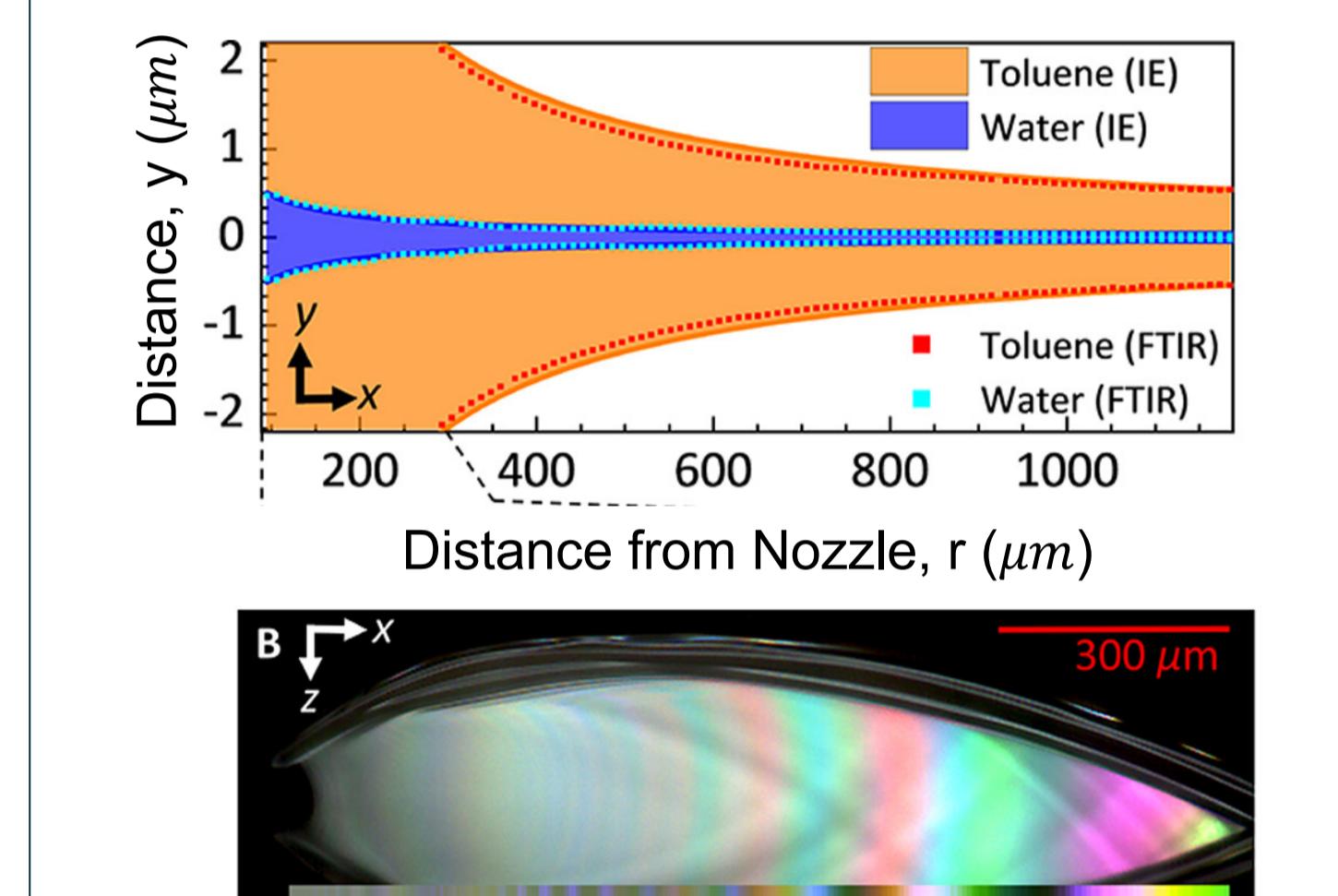


Characterizing Sheet Thickness

Thin film interference patterns allow accurate determination of the sheet thickness:

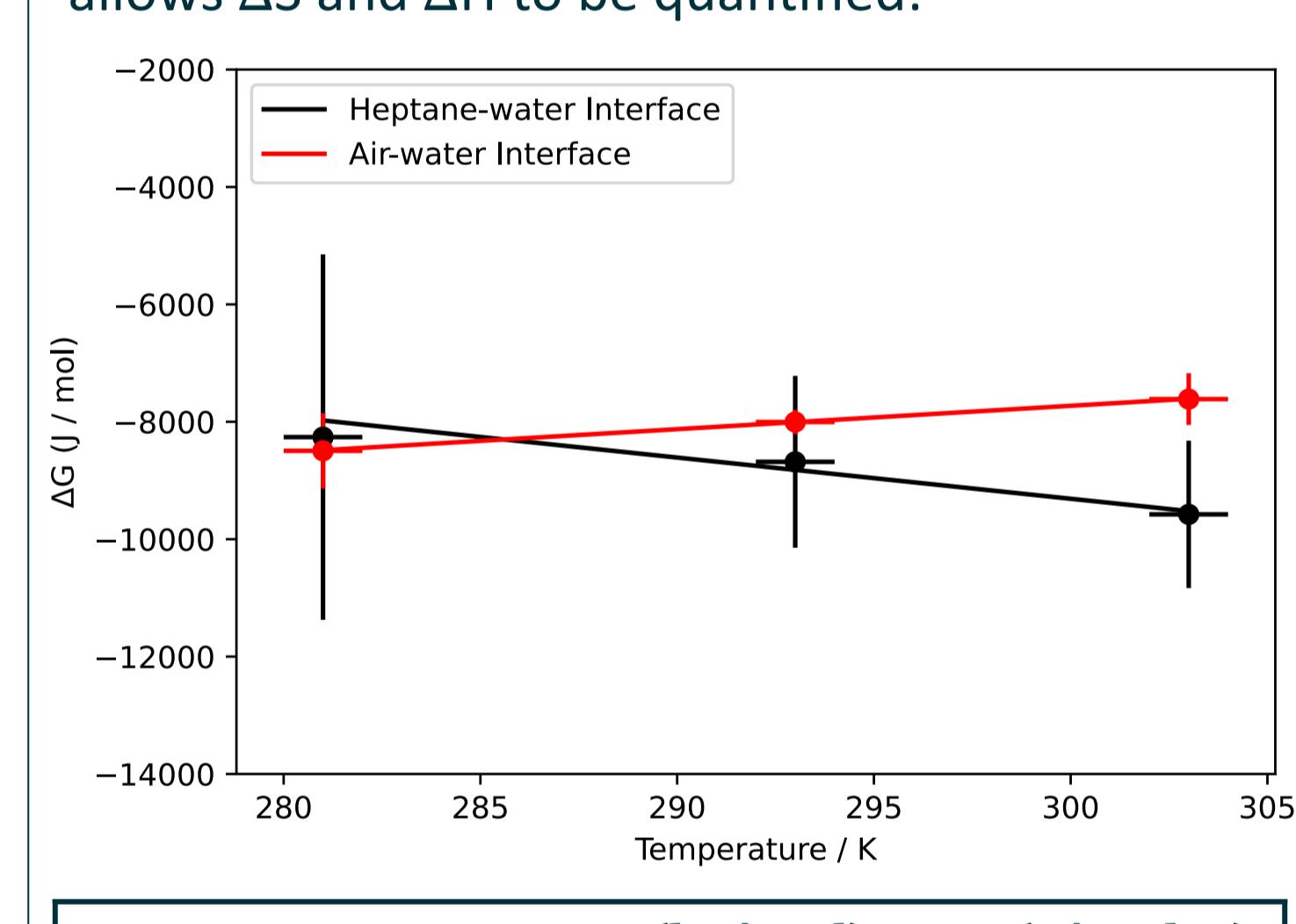


The thickness scales as $\sim 1/r$, with r being the distance away from the nozzle¹



Conclusions

Measuring ΔG as a function of temperature allows ΔS and ΔH to be quantified:



	ΔH (kJ/mol)	ΔS (J/mol K)
Heptane-water	11 ± 5	70 ± 20
Air-water	-19 ± 3	-39 ± 5

We have developed a new method for studying air-water and buried, liquid-liquid interfaces. Using this methodology, we have shown that the mechanism of anion adsorption to the water-heptane interface is driven by an increase in entropy, and hindered by enthalpy, in agreement with theoretical predictions² and in contrast with the mechanism for the air-water interface.³

Acknowledgements/References

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References:

- Hoffman, D.J. et al. *Langmuir*, 2022, 38, 12822 – 12832.
- Devlin, S. W. *PNAS*, 2022, 119(42) e2210857119.
- Otten, D. E. *PNAS*, 2012, 109 (3), 701-705.