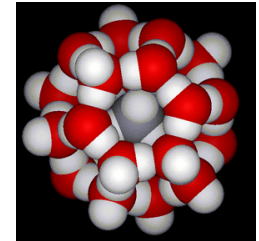
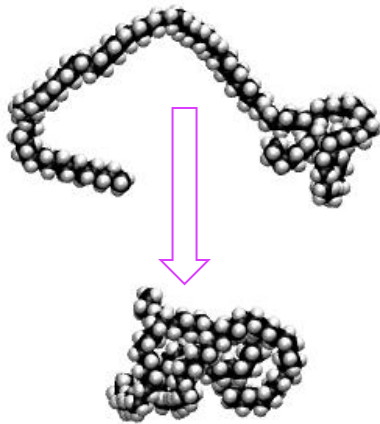


# Water Mediated Hydrophobic Interactions: The Emperor's New Hydrophobic Bathing Suit

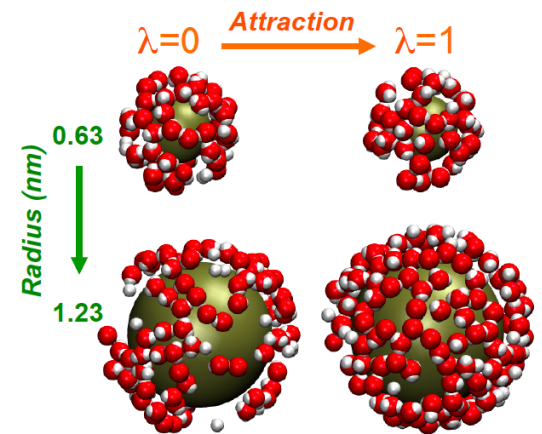
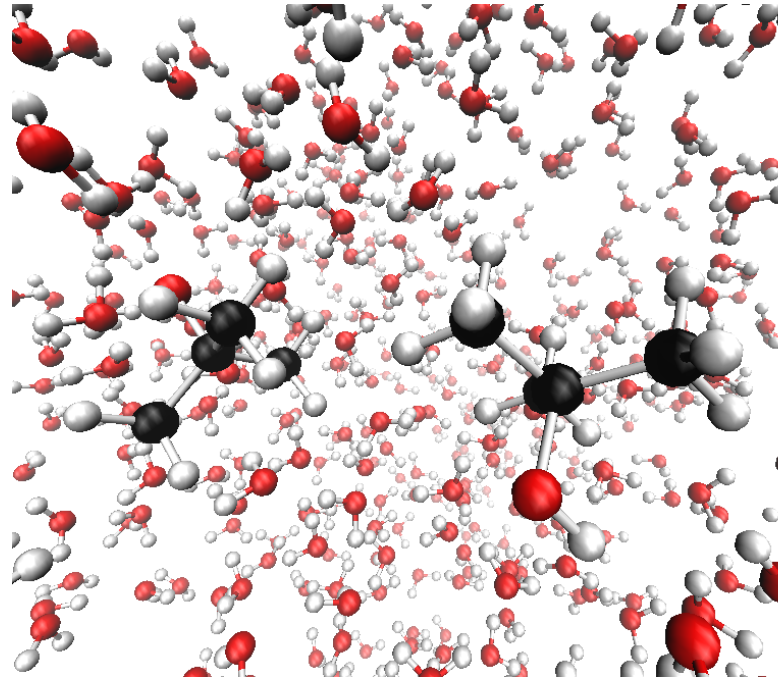
*Dor Ben-Amotz (Purdue University)*



Clathrate Hydrate



Hydrophobic collapse



Hydrophobic Crossover

## Outline

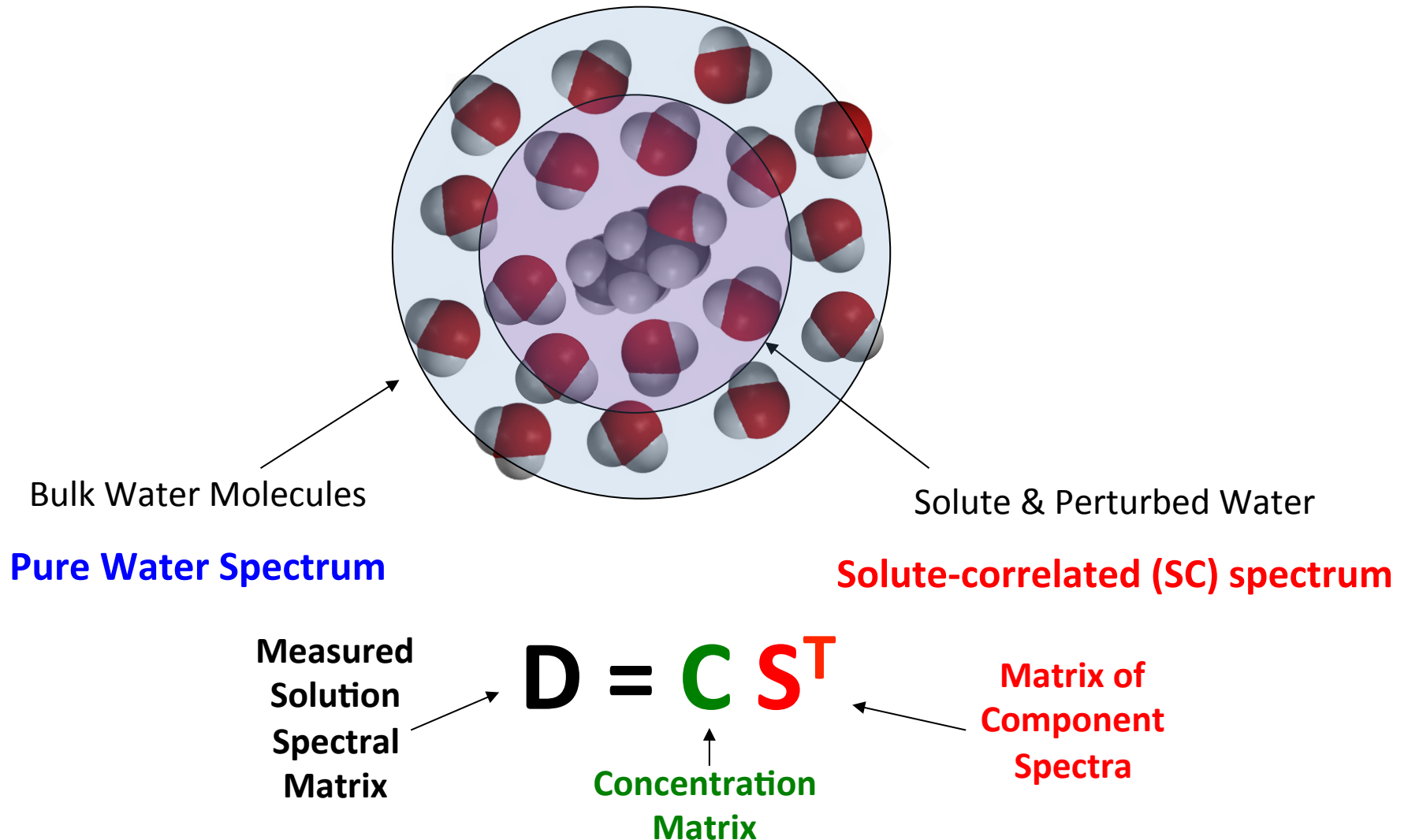
- *Hydration-shell spectroscopy*
- *Crossover Experiments*
- *Hydrophobic Interactions*



Ben-Amotz, D., *J. Phys. Chem. Lett. Perspective* 6, 1696 (2015)  
Ben-Amotz, D. *Ann. Rev. Phys. Chem.*, under review



# Raman Multivariate Curve Resolution (Raman-MCR) Hydration-Shell Spectroscopy

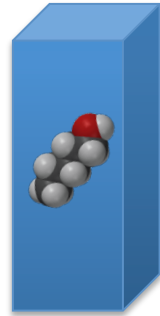


P. Perera, M. Wyche, Y. Loethen and D. Ben-Amotz, *J. Am. Chem. Soc.* 130, 4576 (2008)

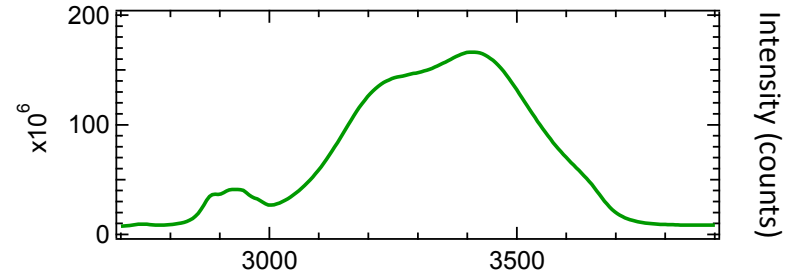
” Multivariate curve resolution (MCR) from 2000” de Juan & Tauler, *Crit. Rev. Anal. Chem.* 36, 163 (2006)

# Raman Multivariate Curve Resolution (Raman-MCR) Hydration-Shell Spectroscopy

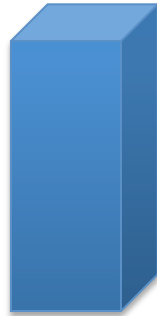
*solute  
in water*



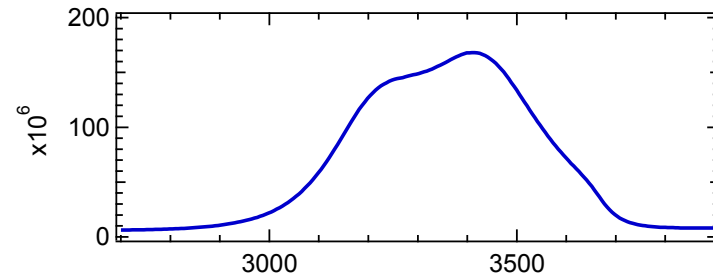
*Raman  
Spectrum*



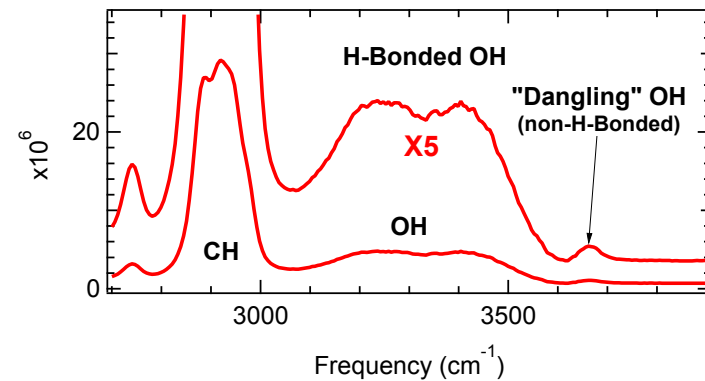
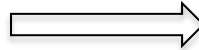
*Pure  
Water*



*Raman  
Spectrum*



*Solute-Correlated  
Spectrum*





Joel Davis

nature

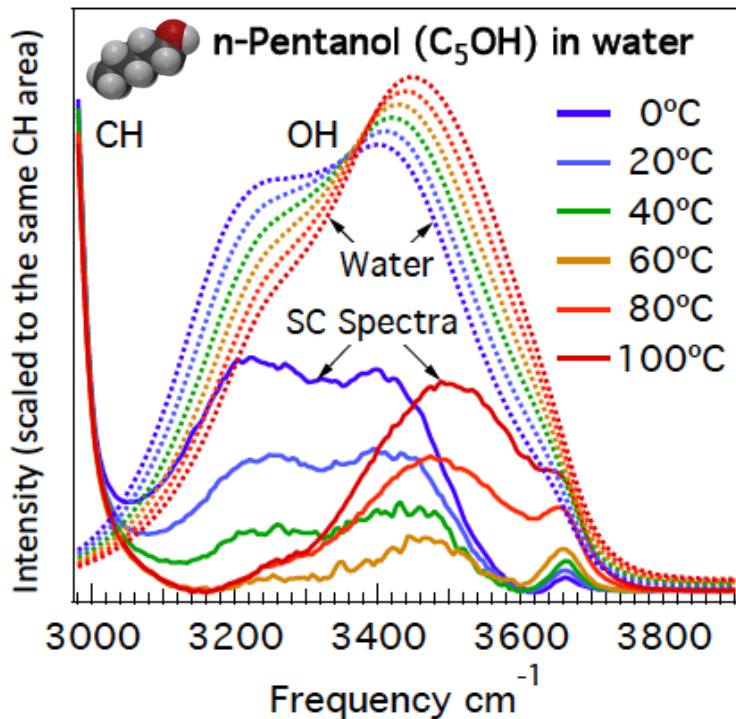
582 | NATURE | VOL 491 | 22 NOVEMBER 2012

# Water structural transformation at molecular hydrophobic interfaces

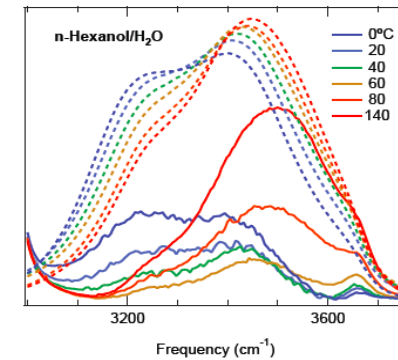
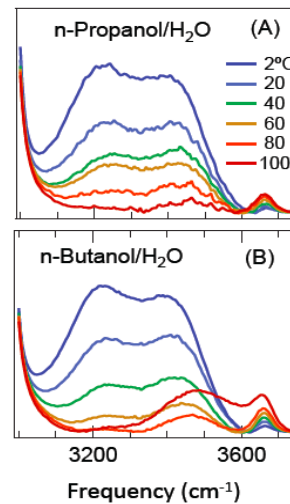
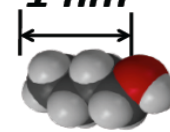
Joel G. Davis<sup>1</sup>, Kamil P. Gierszal<sup>1</sup>, Ping Wang<sup>1</sup> & Dor Ben-Amotz<sup>1</sup>



Kamil Gierszal



Crossover Length Scale ~1 nm



See also Huib Bakker *Research News & Views, Nature*, 491, 533 (2012)

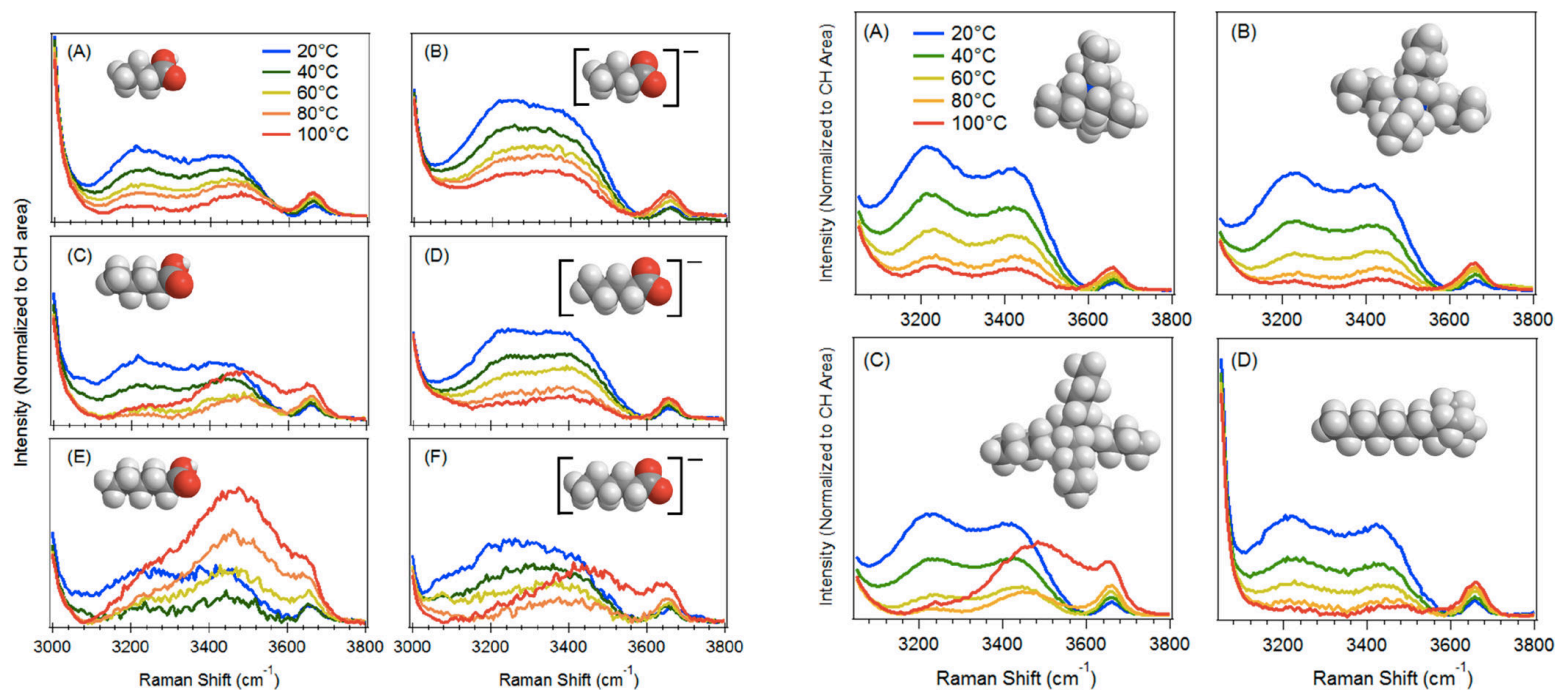




Sam Zukowski

# Influence of a Neighboring Charged Group on Hydrophobic Hydration Shell Structure

Joel G. Davis,<sup>†</sup> Samuel R. Zukowski, Blake M. Rankin, and Dor Ben-Amotz\*



Davis, J. G.; Zukowski, S. R.; Rankin, B. M.; Ben-Amotz, D.

*J. Phys. Chem. B* **2015**, *119*, 9417–9422.



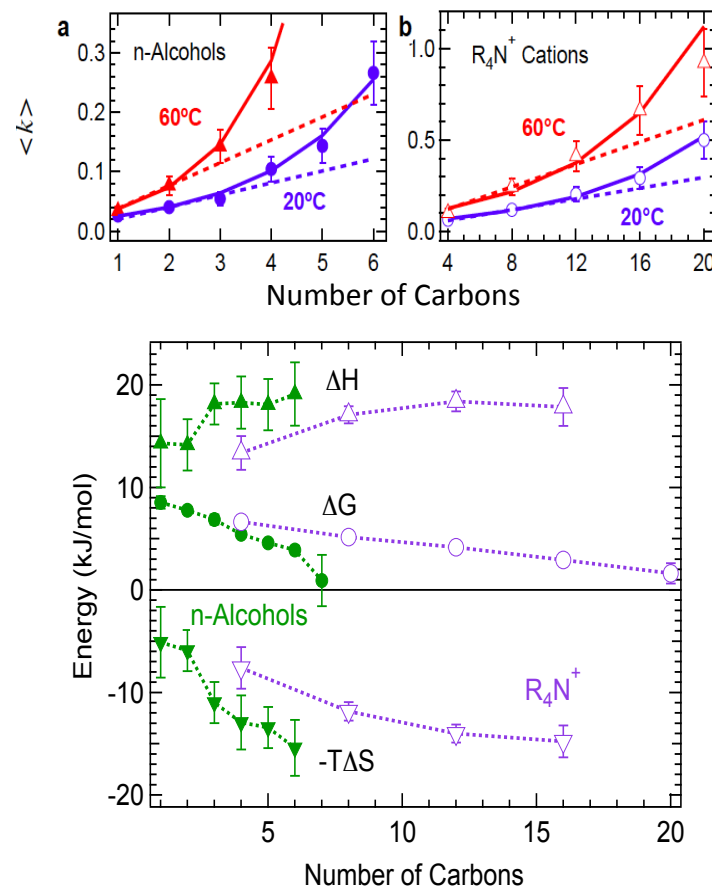
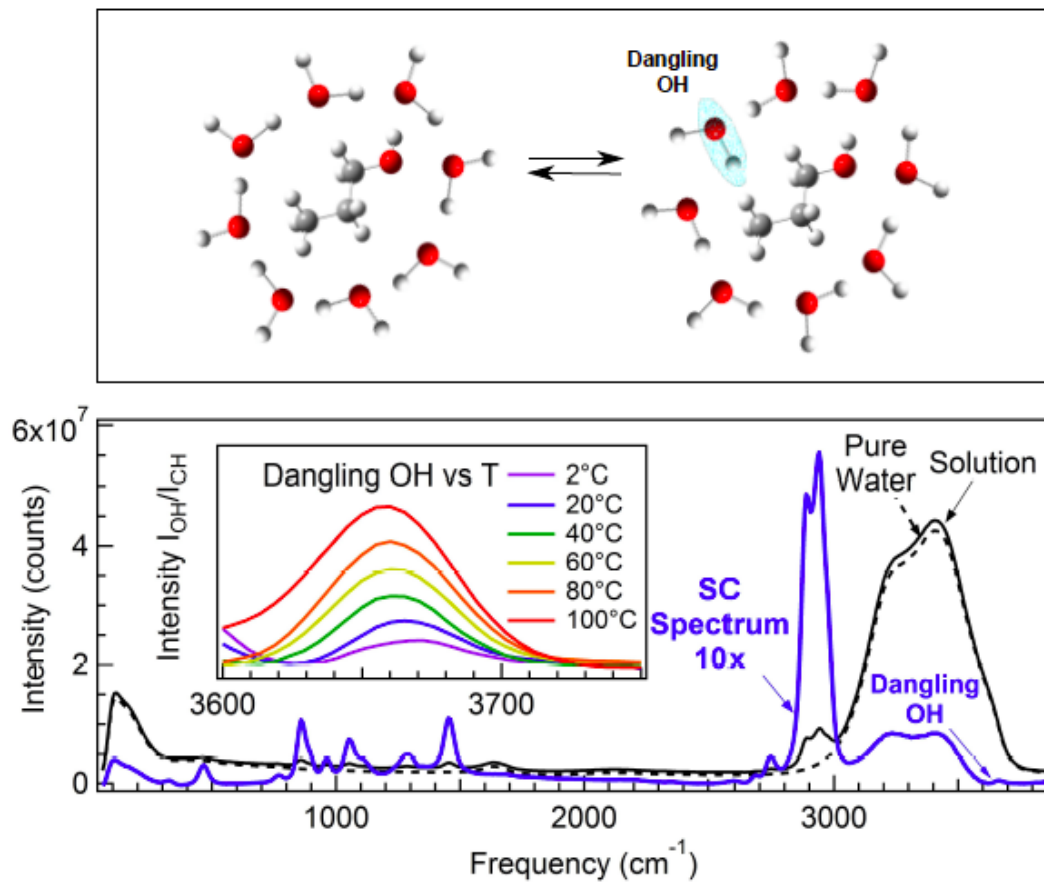
Joel Davis

# On the cooperative formation of non-hydrogen-bonded water at molecular hydrophobic interfaces

Joel G. Davis, Blake M. Rankin, Kamil P. Gierszal and Dor Ben-Amotz\*

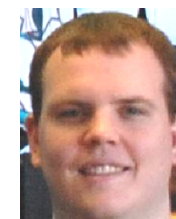


Blake Rankin



## Micelle Structure and Hydrophobic Hydration

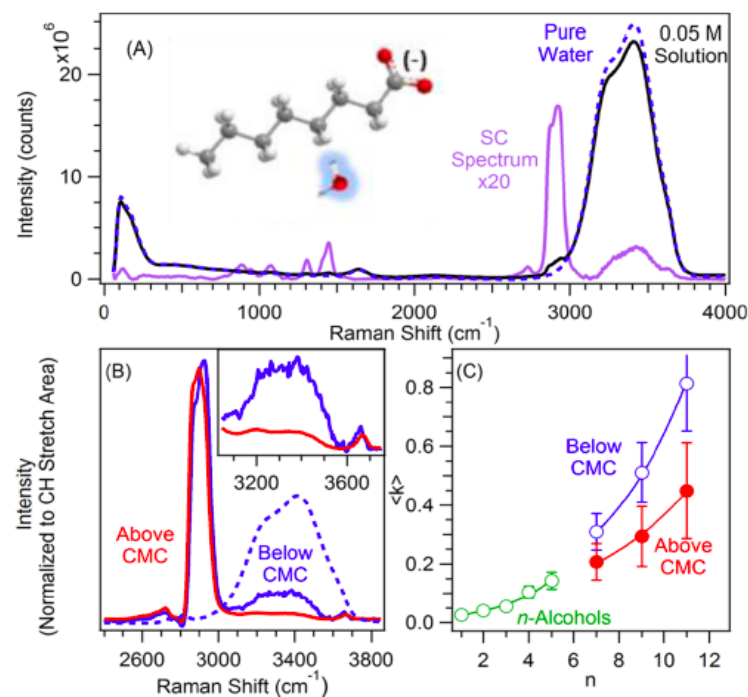
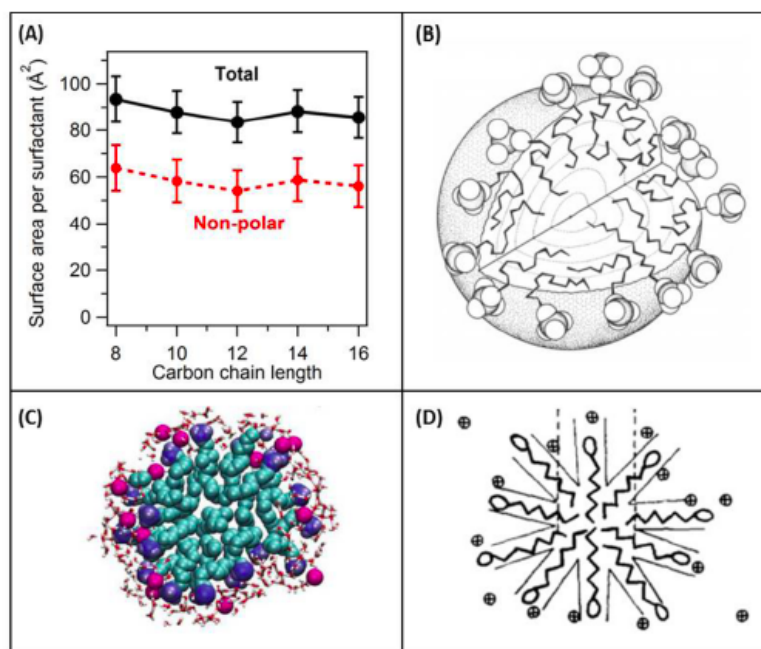
Joshua A. Long, Blake M. Rankin, and Dor Ben-Amotz\*



Josh Long

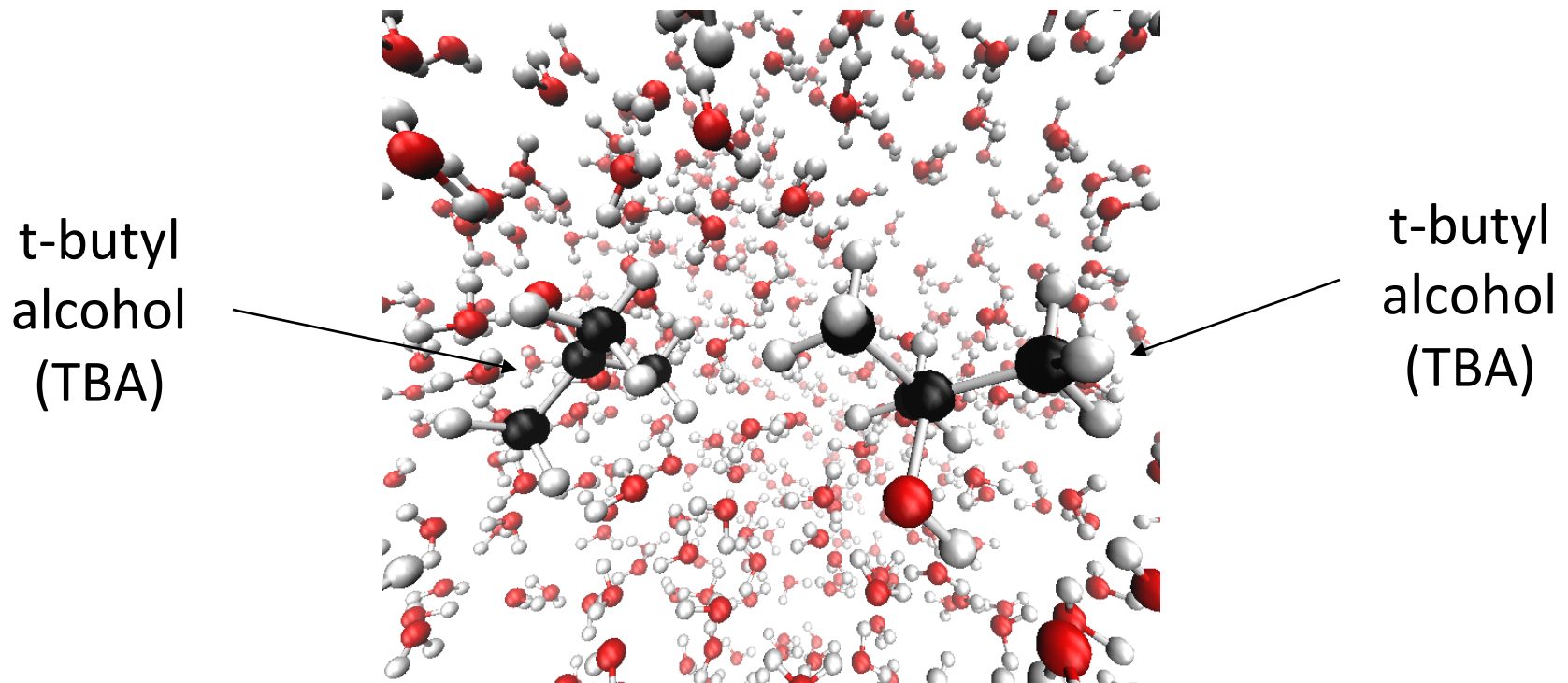


Blake Rankin



Long J. A, Rankin B. M, Ben-Amotz, D. *J. Am. Chem. Soc* **2015**, ASAP (on-line).

# Quantifying Hydrophobic Interactions

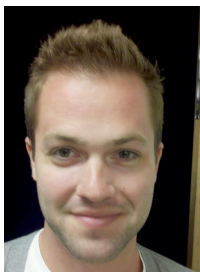


**Mean Force Potential**  $w(r) = u(r) + \Delta w(r)$

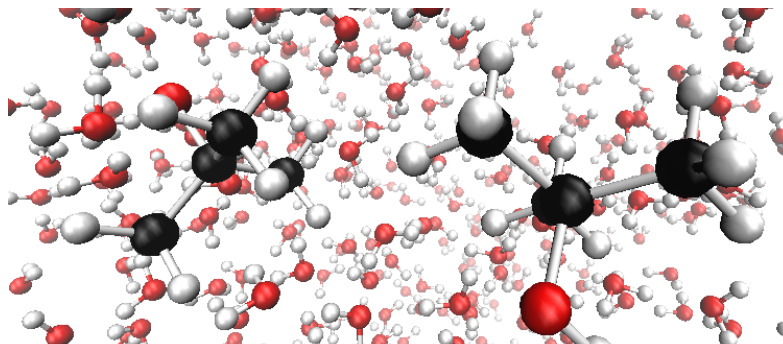
*Direct*  $\nearrow$  *Water-Mediated*  $\nwarrow$

Wilcox, D. S.; Rankin, B. M.; Ben-Amotz, D., *Faraday Discussion* **167**, 177 (2013)  
Rankin, B. M.; Ben-Amotz, D.; van der Post, S.; Bakker, H. *in review* (2015)

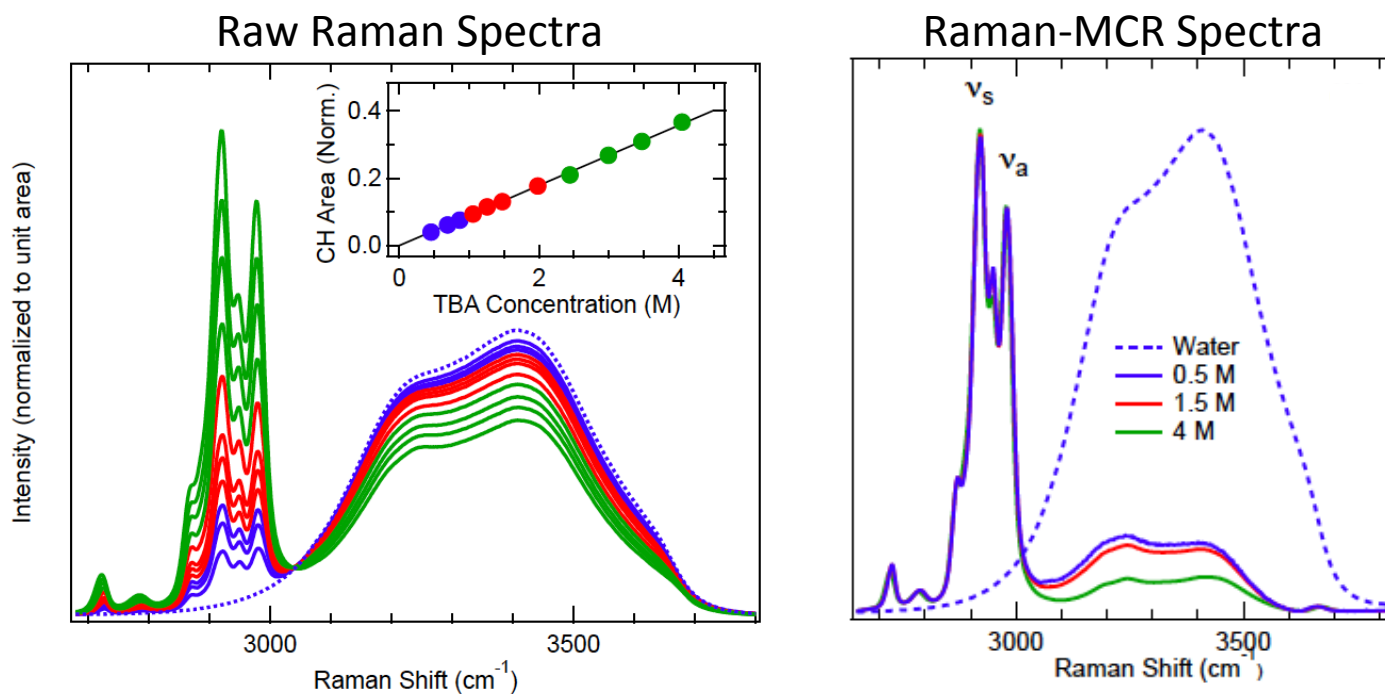
# Raman-MCR Spectroscopy of Aqueous TBA



David Wilcox



Blake Rankin



Wilcox, D. S.; Rankin, B. M.; Ben-Amotz, D., *Faraday Discussion* **167**, 177 (2013)





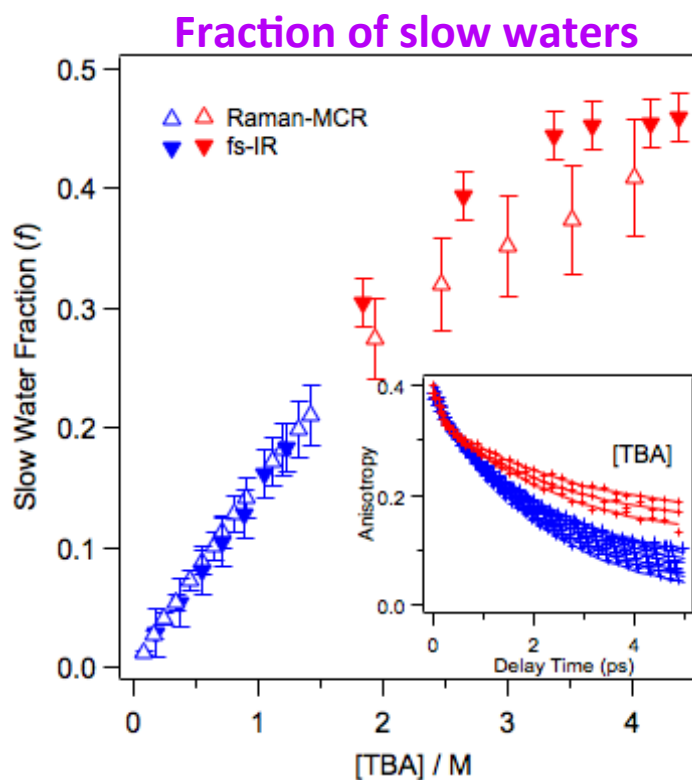
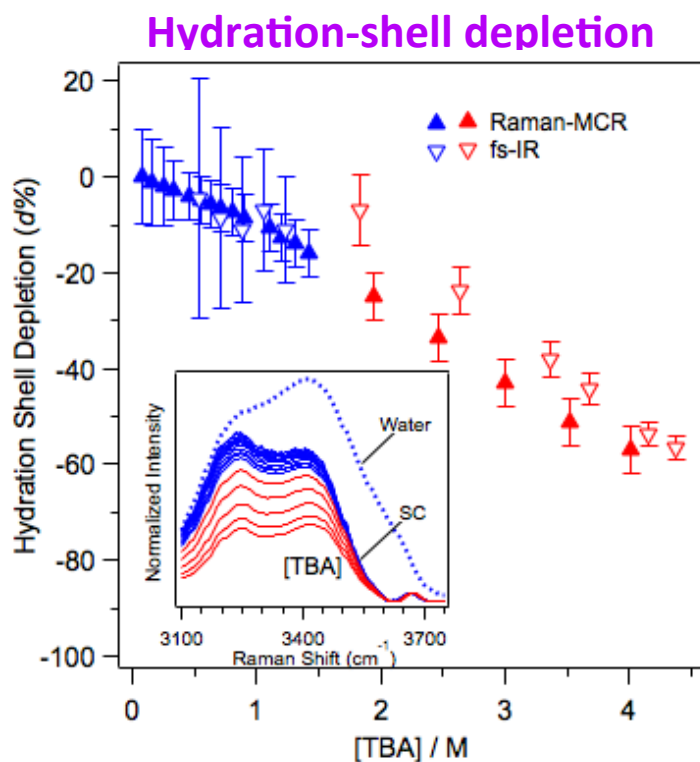
Blake Rankin



Huib Bakker



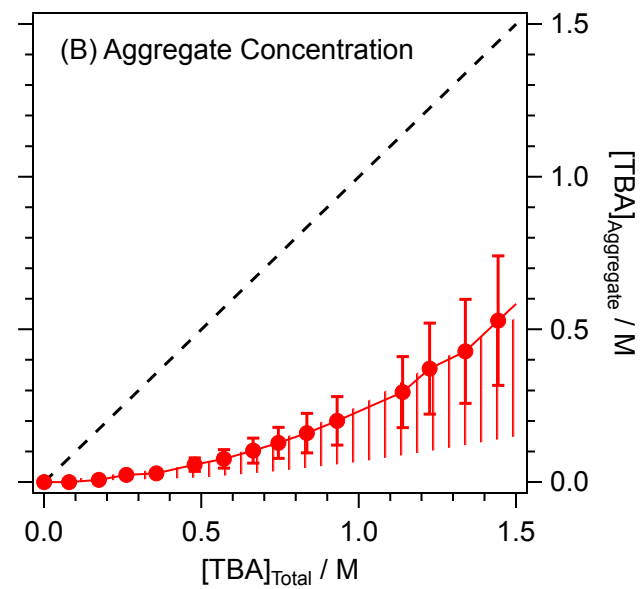
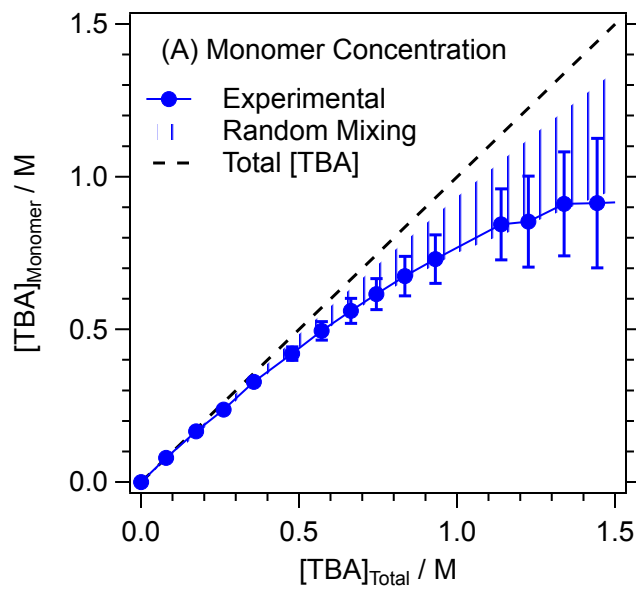
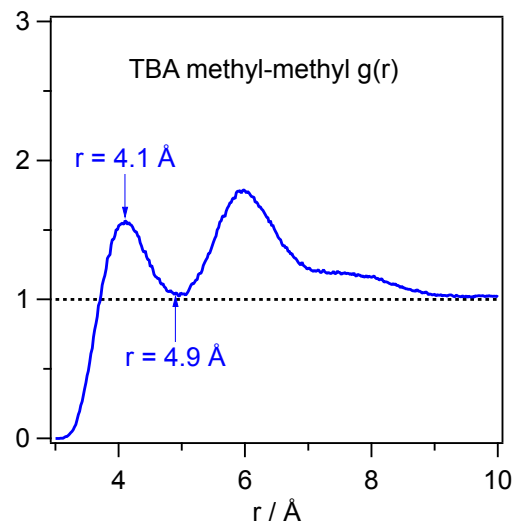
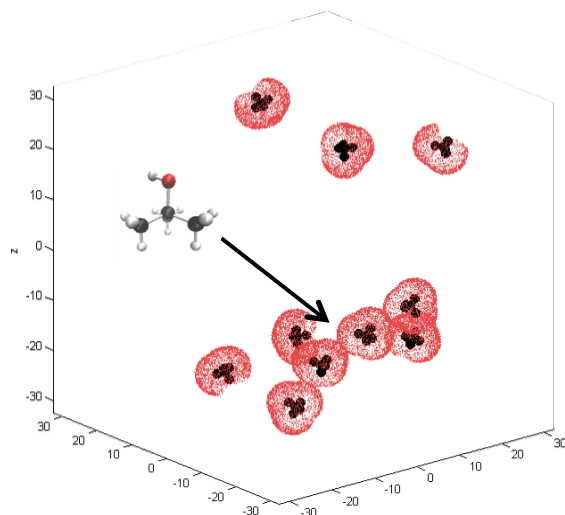
Sietse van der Post



~8 water molecules around TBA are more structured and slowly rotating than bulk water

Rankin, B. M.; Ben-Amotz, D.; van der Post, S. T.; Bakker, H. J. *J. Phys. Chem. Lett.* **2015**, *6*, 688.

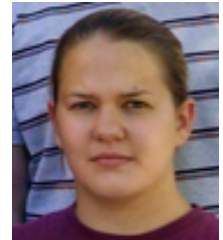
# Comparison with Random Mixing Predictions



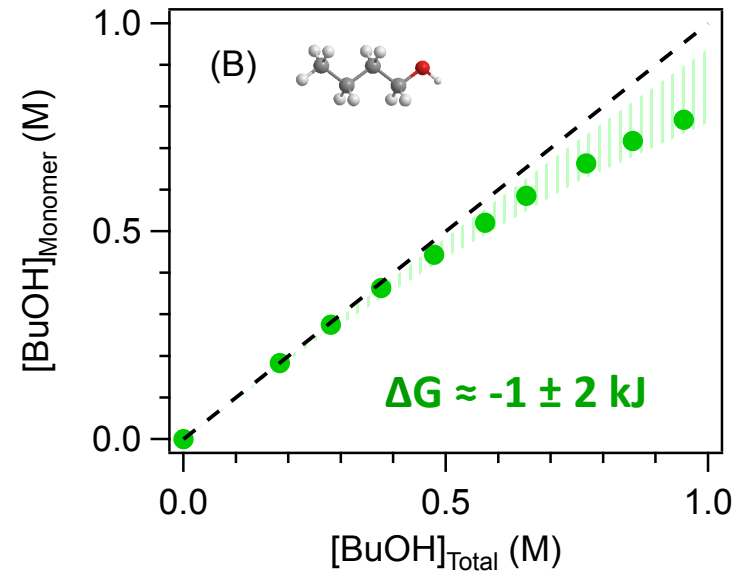
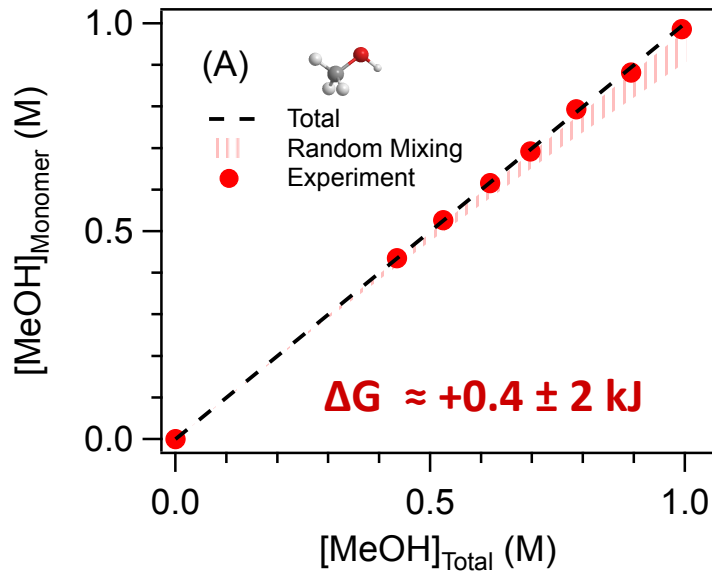


Blake Rankin

## What about other small alcohols?



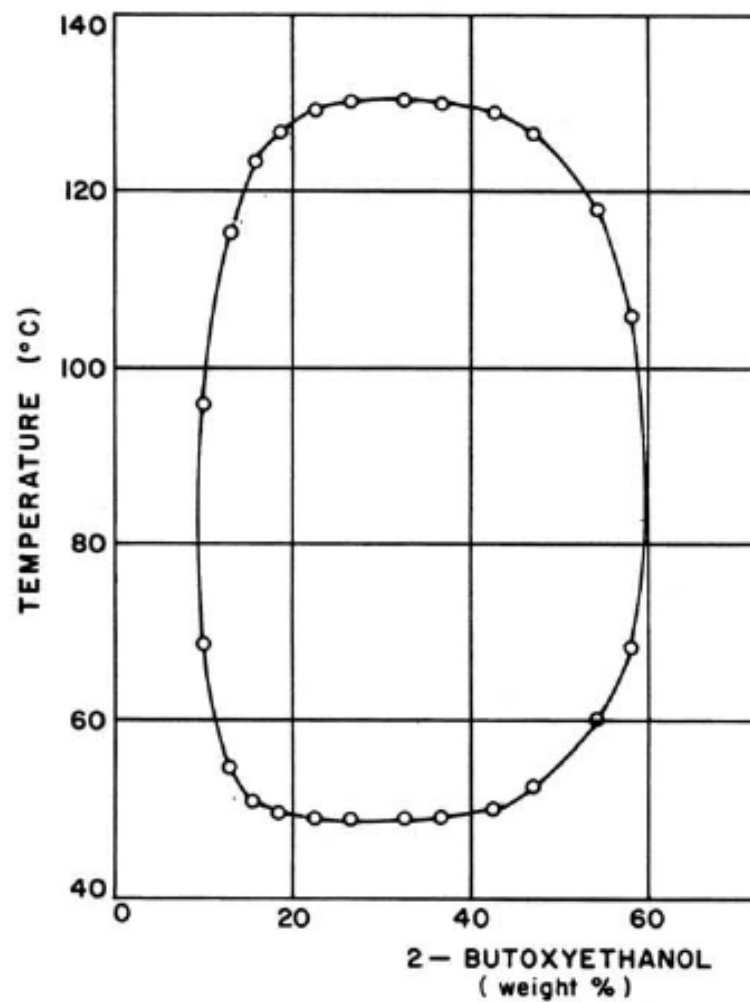
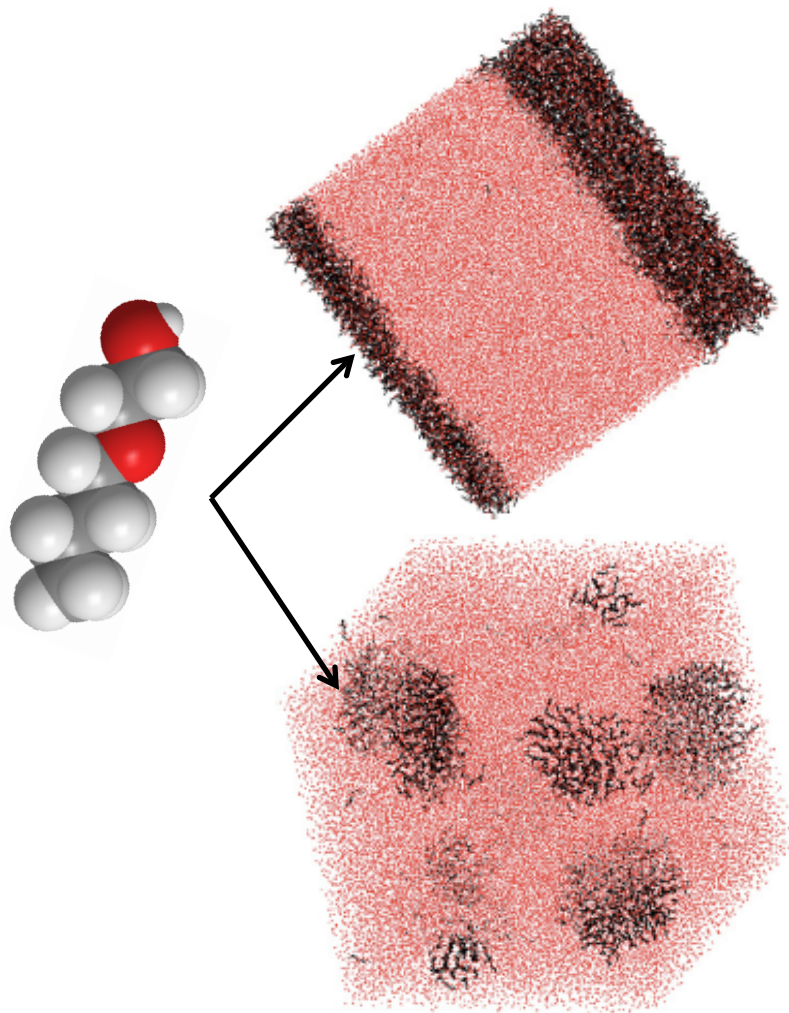
Shannon Pattenaude



**Aggregation Free Energy**  $\Delta G = -RT \ln \left( \frac{[A]_{Exp}}{[A]_{RM}} \right)$  (at 1 M)

- Hydrophobic interactions are too weak to compete with random thermal energy fluctuations ( $\Delta G < RT$ )

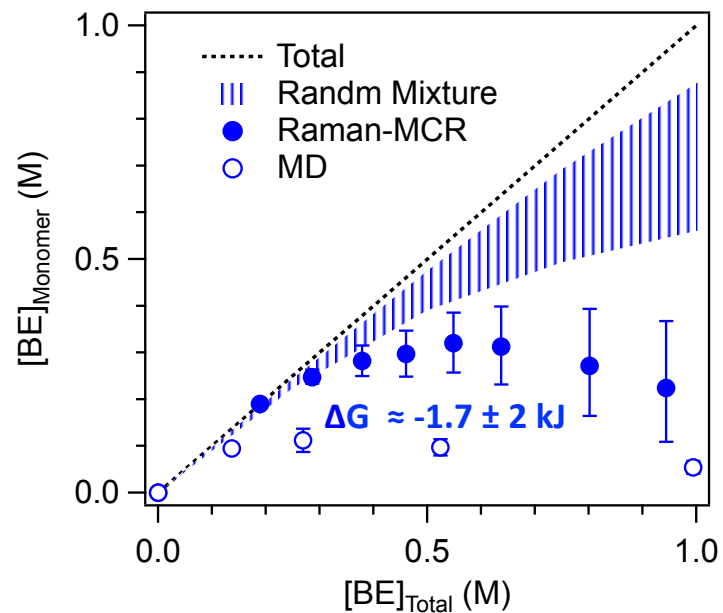
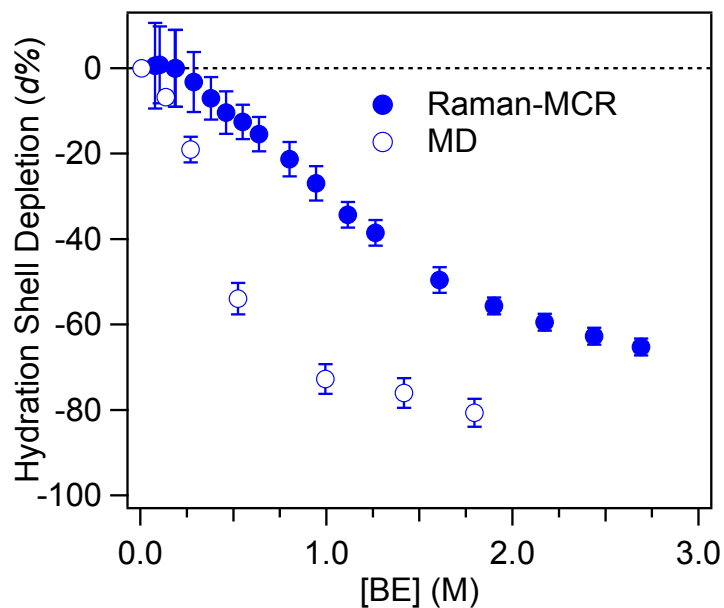
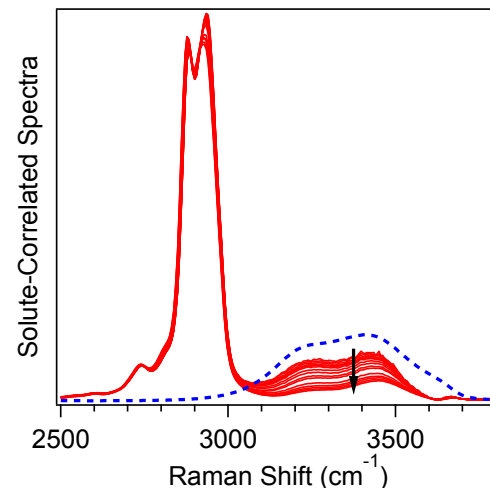
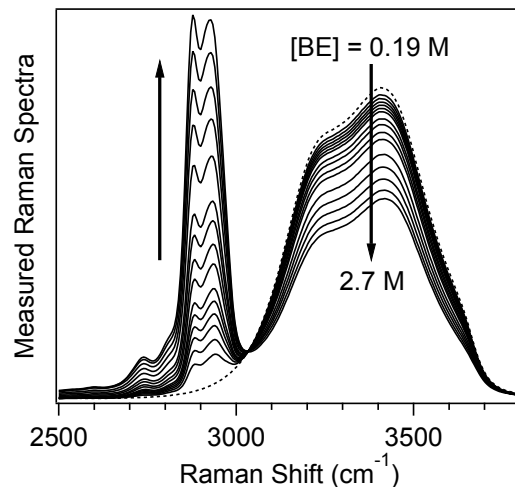
## Aggregation of Butoxyethanol (BE) in Water



# Aqueous BE Raman-MCR Results



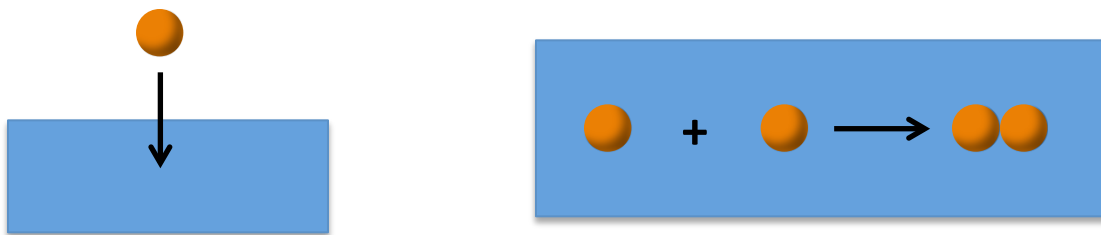
Shannon Pattenaude



- MD simulation predict more aggregation than observed experimentally



# Hydrophobic Hydration and Water-Mediated Interactions



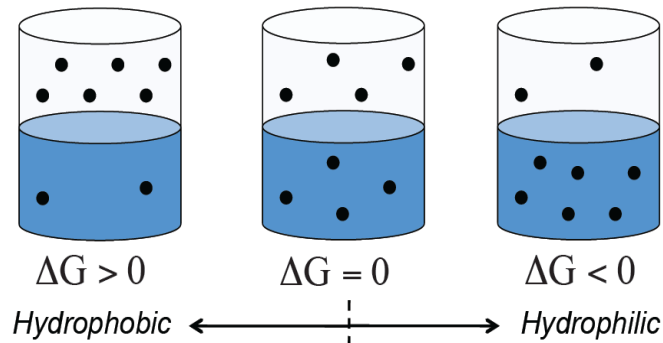
Ben-Amotz, D., *J. Phys. Chem. Lett. Perspective 6*, 1696 (2015)

Ben-Amotz, D. *Ann. Rev. Phys. Chem.*, under review

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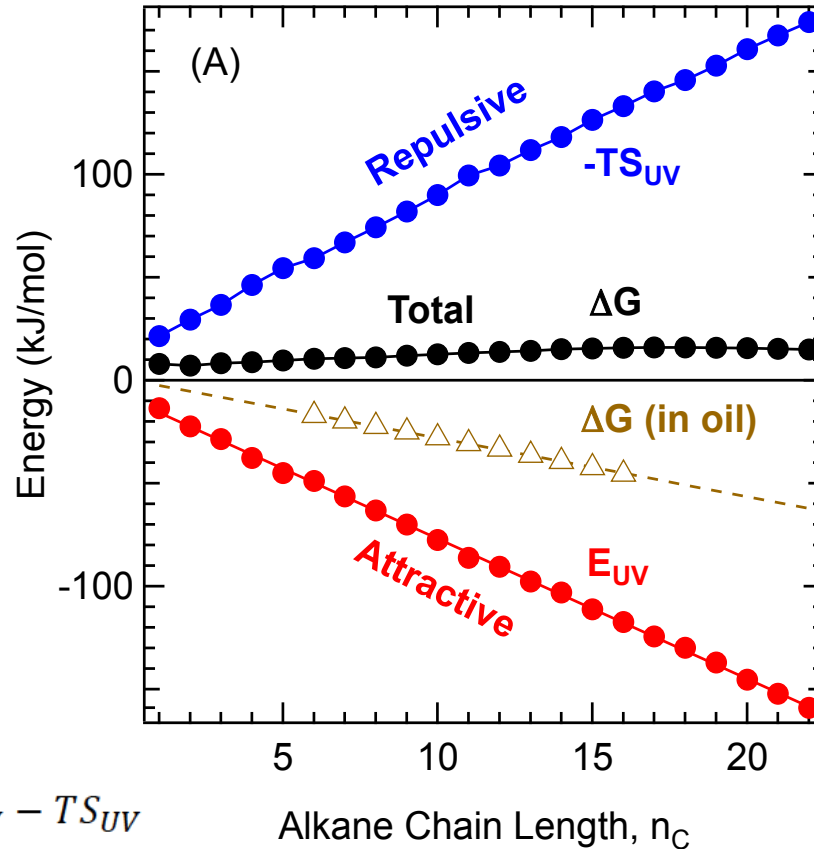
# Hydration Thermodynamics on *n*-Alkanes



$$\Delta G = G(L) - G(V) = -RT \ln \left( \frac{\rho_L}{\rho_V} \right)$$

## Potential Distribution Theorem:

$$\Delta G = RT \ln \langle e^{\Psi/RT} \rangle = \langle \Psi \rangle + RT \ln \langle e^{\delta\Psi/RT} \rangle \equiv E_{UV} - TS_{UV}$$



- Oil-water attraction and entropic cavity formation nearly perfectly cancel

Underwood R, Tomlinson-Phillips J, Ben-Amotz D. 2010. *J. Phys. Chem. B* 114:8646-51

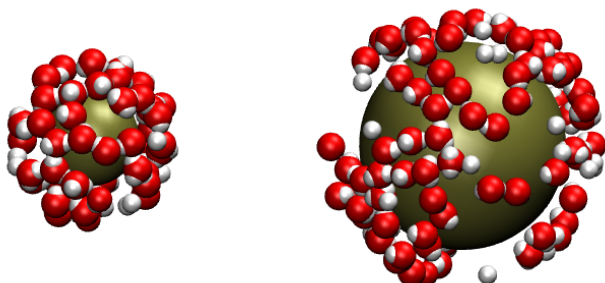
Ben-Amotz D, Underwood R. 2008. *Acc. Chem. Res.* 41:957-67

Widom B. 1982. *J. Phys. Chem.* 86:869-72, and references therein

# Hydration of Model Oil Drops vs. Size and Attraction

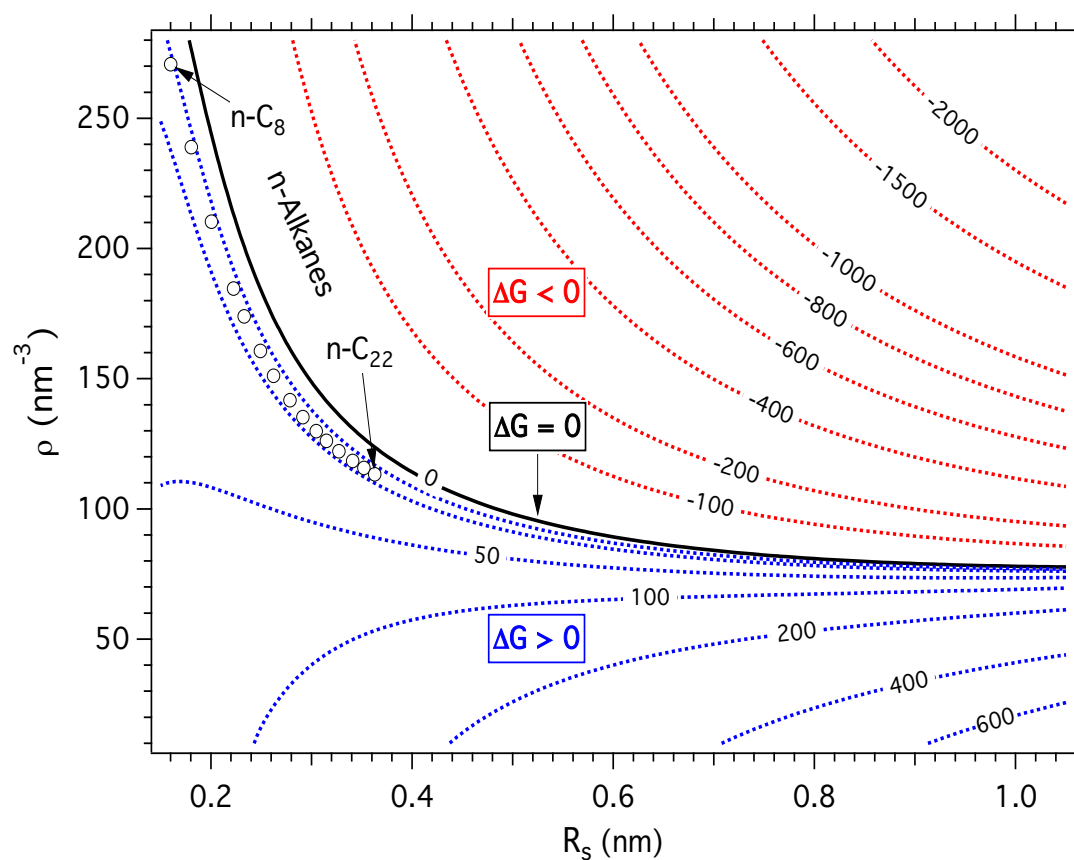
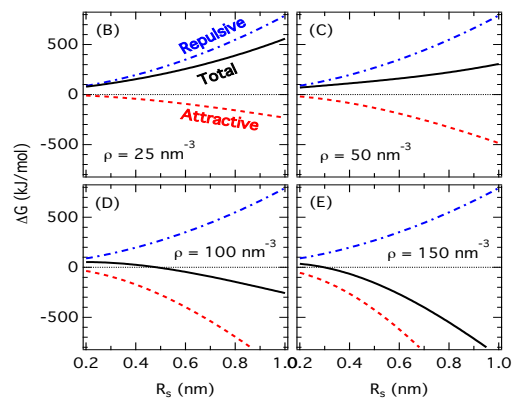
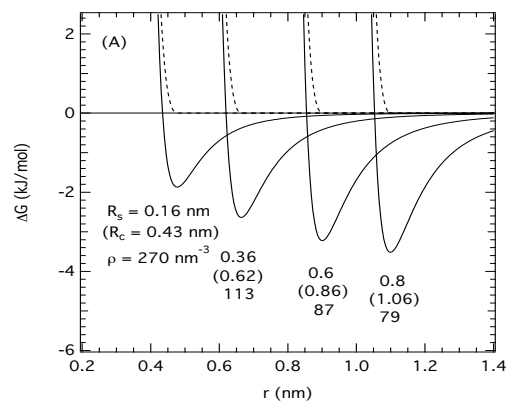


Robin Underwood



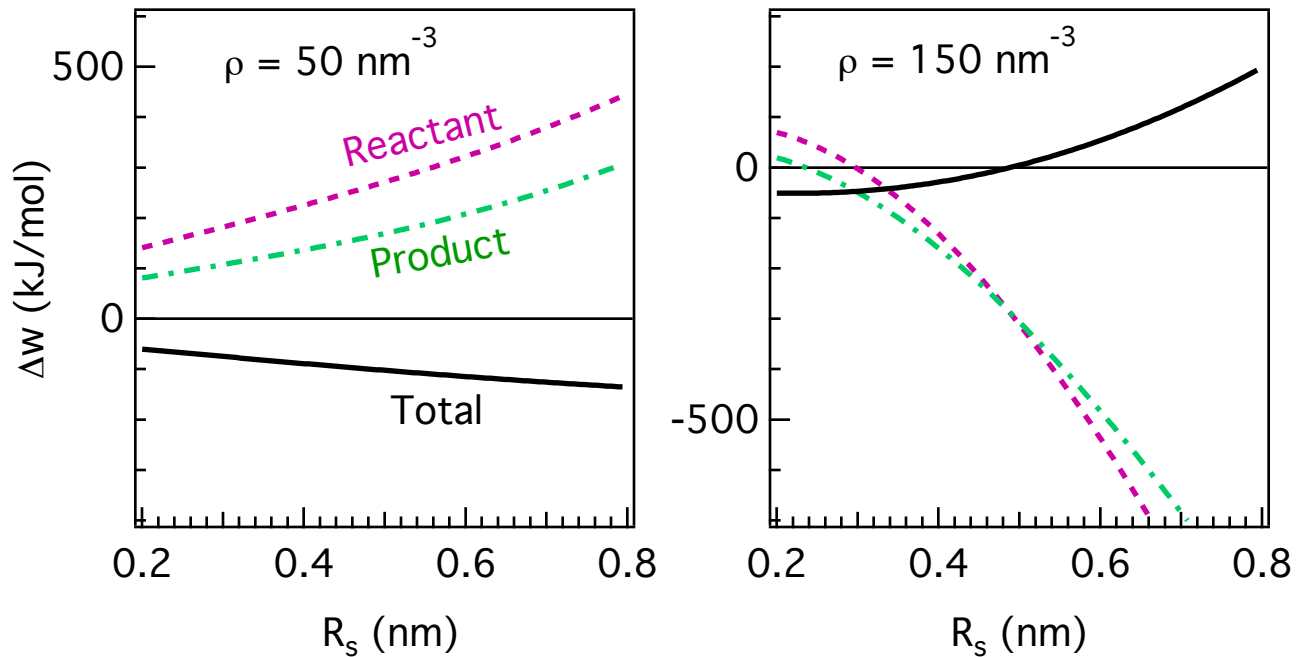
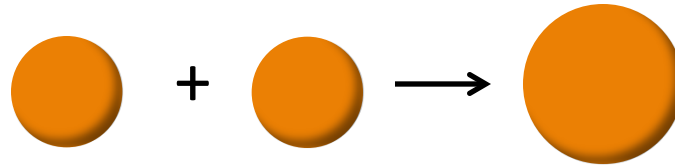
$\rho$  = Methyl density

$R_S$  = Radius



- Oil has a delicately balanced love-hate relationship with water

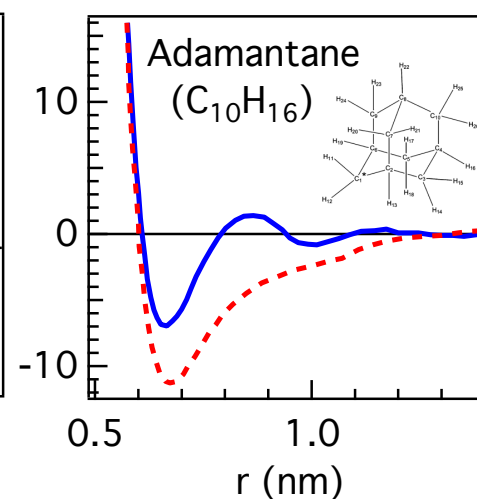
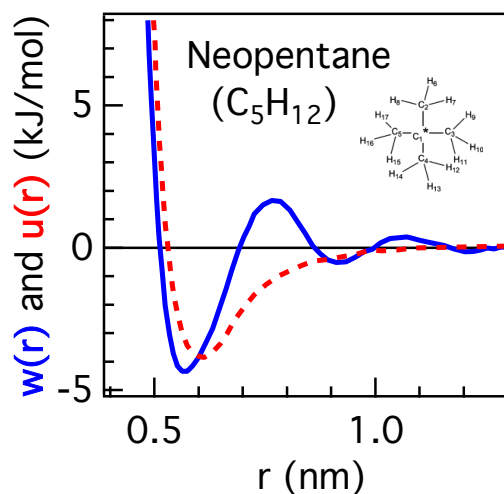
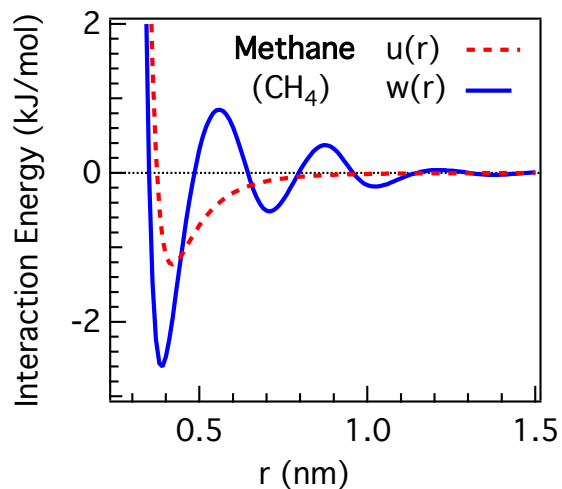
# Water Mediated Hydrophobic Interaction Oil-Drop Coalescence Model



- Water-Mediated Dual Crossover vs. Oil Drop Size and Attraction

# Water Mediated Hydrophobic Interactions

## MD Simulation Predictions

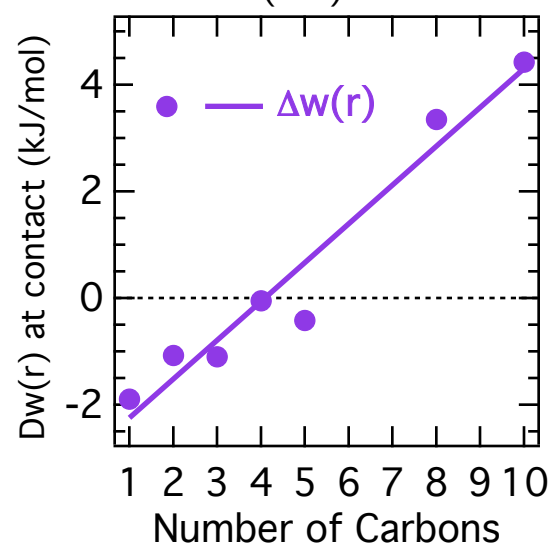
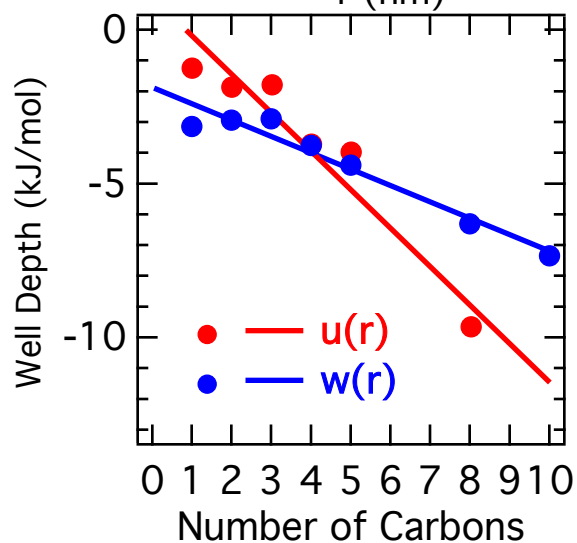


Mean Force Potential

$$w(r) = u(r) + \Delta w(r)$$

Direct

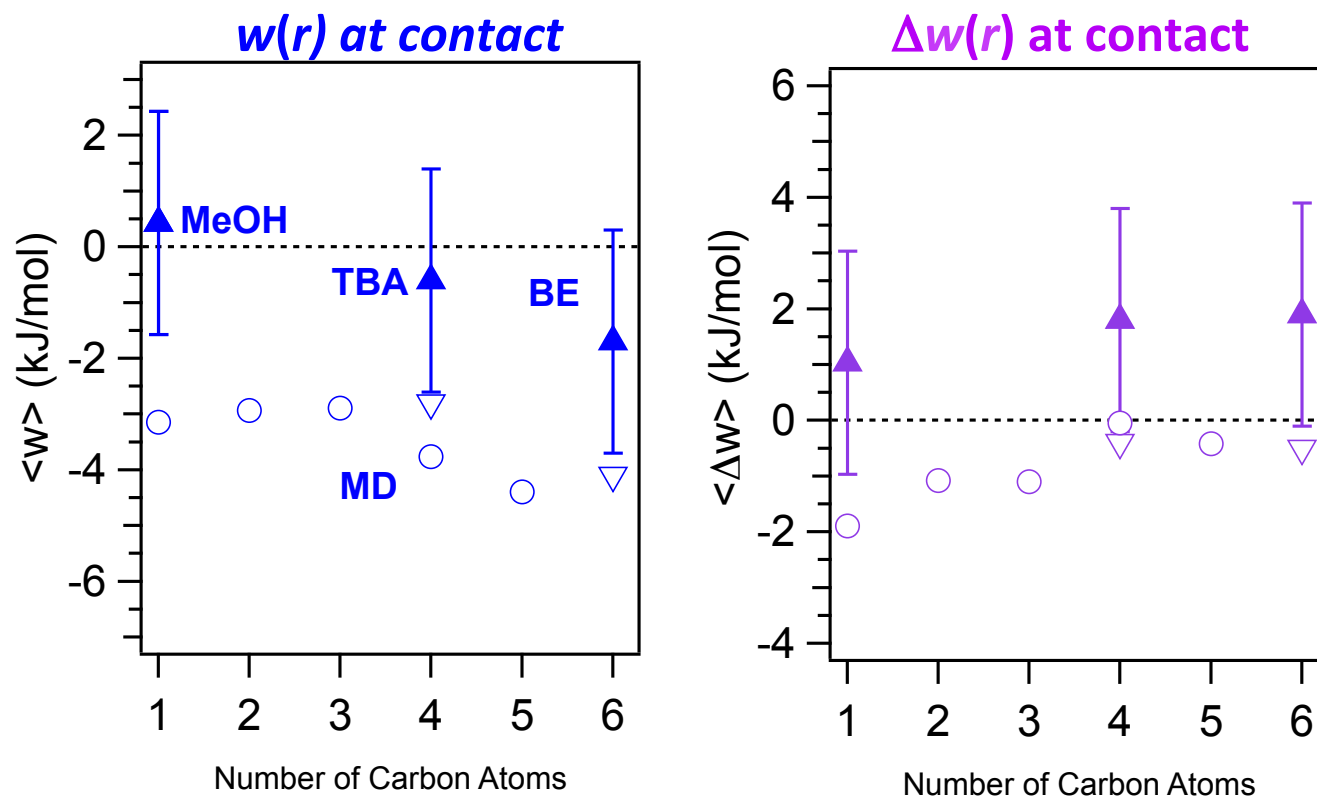
Water-Mediated





# Water-Mediated Hydrophobic Interactions

## Comparison of Raman-MCR Experiments and MD



- Hydrophobic interactions are weaker than classical MD predictions
- Water-mediated interactions are invariably slightly repulsive
- Direct interactions drive the aggregation of oily molecules

# What Kind of Solvent is Water?



*As far as oil is concerned, swimming in water is almost like swimming in nothing at all!*