Global Optimisation of Hydrated Sulfate Clusters

Lewis Smeeton

University of Birmingham
School of Chemistry

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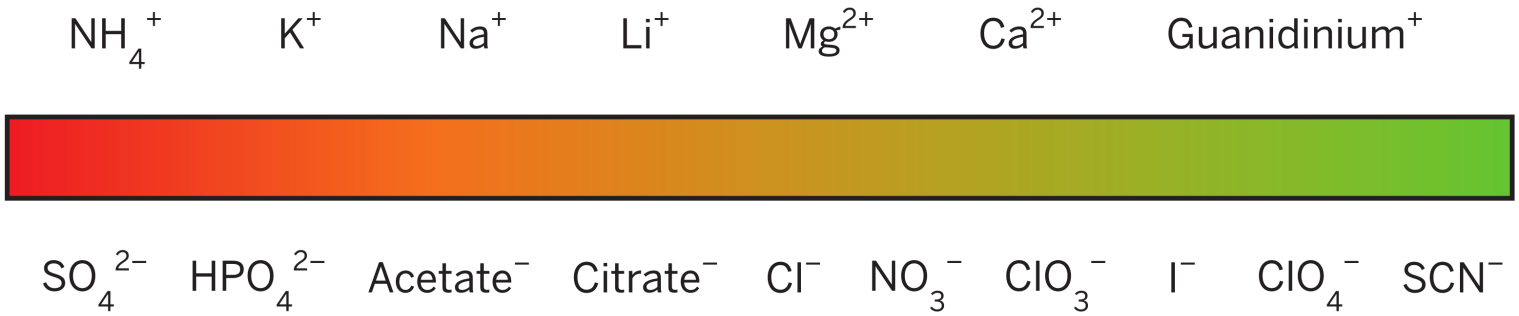
Introduction

The Hofmeister Series

Hofmeister series ranks the relative effectiveness of anions or cations on a wide range of phenomena.

Cations



Anions

Ions can be characterised as being either;

- kosmotropes (SO_4^{2-}, NH_4^+) $\longrightarrow$ Increased surface tension, decreased protein solubility, increased protein stability, ...
- chaotropes (SCN^-, Guanidinium$^+$) $\longrightarrow$ Decreased surface tension, increased protein solubility, decreased protein stability, ...

Hofmeister, *Arch. Exp. Pathol. Parmacol.*, **1887**, *24*, 247-260

The Hofmeister Series *continued*

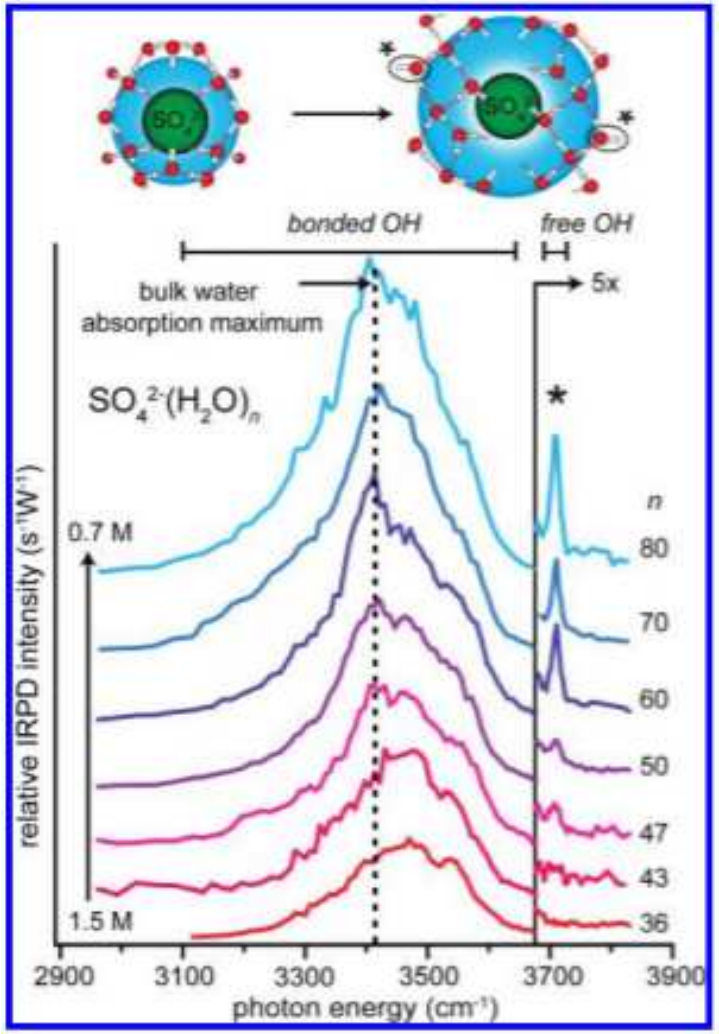
Chemical origins of the series are unclear. There is evidence supporting **both** direct ion-protein interaction **and** long-range effects of ion on solvent structure.

Hofmeister, *Arch. Exp. Pathol. Parmacol.*, **1887**, *24*, 247-260

Kunz *et al*, *Curr. Opin. Colloid. In.*, **2004**, *9*, 1-18

Why are we Interested in Hydrated Sulfate Clusters?

Long-range solvent effects in $SO_4^{2-}(H_2O)_n$ can be investigated experimentally using Infrared Photodissociation (IRPD) spectroscopy. IRPD spectra of size selected $SO_4^{2-}(H_2O)_n$ clusters suggest that dangling OH bonds appear around $n \geq 43$ water molecules.

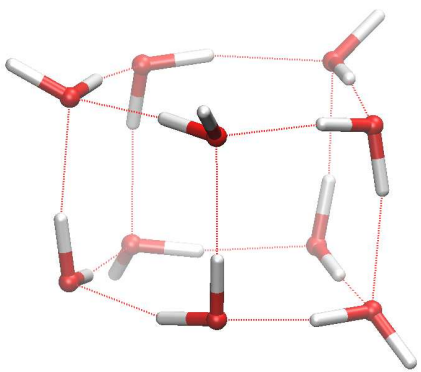


Ensemble average IRPD spectra of $SO_4^{2-}(H_2O)_n$ with $n \leq 80$ at 130K.

Williams *et al*, *JACS*, **2010**, *132*, 8248-8249

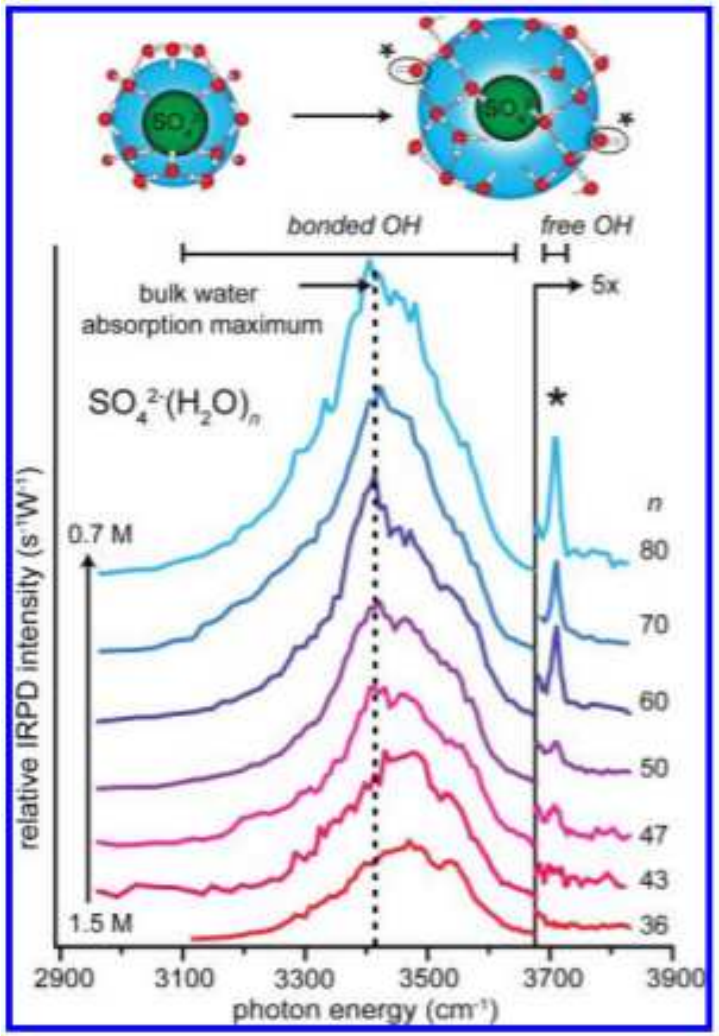
Why are we Interested in Hydrated Sulfate Clusters? *continued*

In contrast: Some water molecules at the surface of bulk solutions and in pure water clusters are oriented so that a hydrogen atom is protruding $\longrightarrow$ is a dangling OH.



TIP4P $(H_2O)_{10}$ GM. Note$\longrightarrow$ Plenty of dangling OH bonds

Williams *et al*, *JACS*, **2010**, *132*, 8248-8249



Ensemble average IRPD spectra of $SO_4^{2-}(H_2O)_n$ with $n \leq 80$ at 130K.

Aims of Study

Can simulation detect the size-dependent appearance of dangling OH bonds in hydrated sulfate clusters?

Methodology

Computational Methodology

Methodology

Detect size-dependent appearance of dangling OH bonds by searching for low energy minima on the Potential Energy Surface (PES) of the $SO_4^{2-}(H_2O)_n$ cluster.

To do this we need;

1. A way to model the $SO_4^{2-}(H_2O)_n$ PES.
2. A method to explore the PES.

Modelling Hydrated Sulfate Clusters

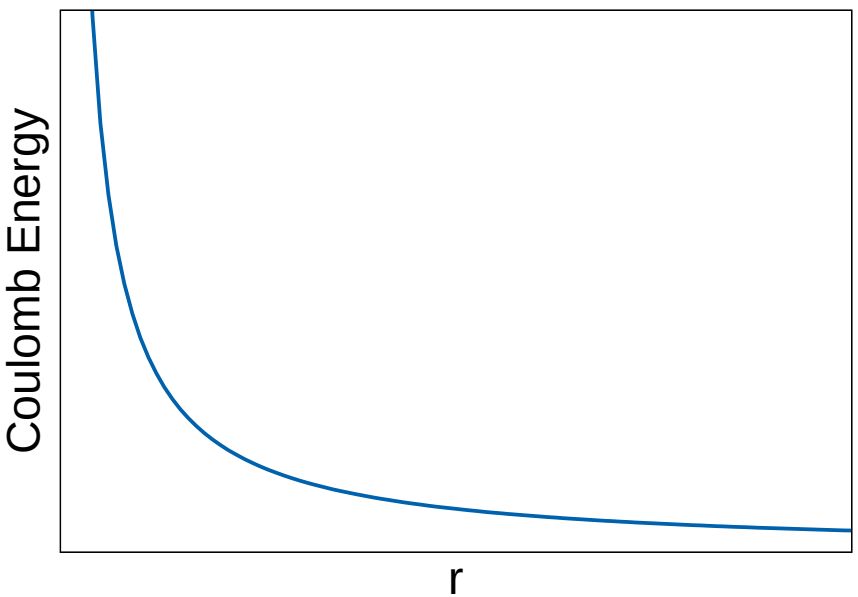
$$U = \sum_i \sum_j \left\{ \frac{q_i q_j}{r_{ij}} + 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \right\}$$

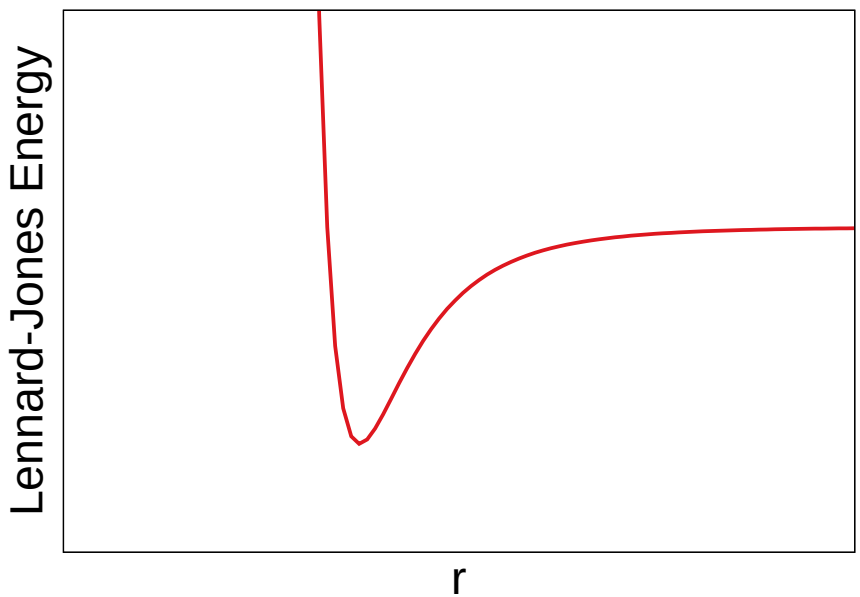
U = interaction energy

r_{ij} = distance between non-bonded atoms

q_i = partial charge on atom

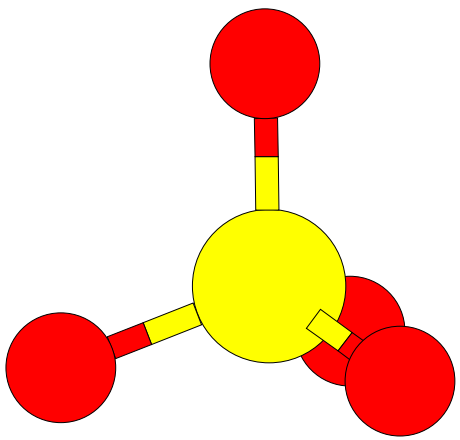
σ, ε = Lennard-Jones parameters





Modelling Hydrated Sulfate Clusters

Model Parameters: SO_4^{2-}



SO_4^{2-}

$$U = \sum_i \sum_j \left\{ \frac{q_i q_j}{r_{ij}} + 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \right\}$$

Sulfate Anion Parameters

S-O bond length = 1.49Å

O-S-O bond angle = 109.5°

Atom	q_i / e	σ / Å	ε / kcal mol^{-1}
Sulfur	+2.4	3.55	0.25
Oxygen	-1.1	3.15	0.25

Cannon *et al*, *J. Phys. Chem.*, **1994**, *98*, 6225-6230

Modelling Hydrated Sulfate Clusters

Model Parameters: Water

$$U = \sum_i \sum_j \left\{ \frac{q_i q_j}{r_{ij}} + 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right] \right\}$$

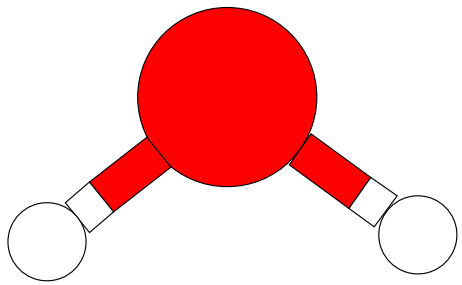
TIP4P parameters

O-H bond length = 0.9572 Å

H-O-H bond angle = 104.52°

Lone pair pseudo-atom lies 0.15 Å along H–O–H bond angle bisector.

Atom	q_i / e	σ / Å	ε / kcal mol^{-1}
Hydrogen	+0.52	0.0	0.0
Oxygen	0.0	3.15	0.155
Lone Pair	-1.04	0.0	0.0



A TIP4P water.

Jorgensen *et al*, *J. Chem. Phys.*, **1983**, *79*, 926-935

In order to search the PES for low-energy minima, we used a Basin-Hopping algorithm;

1. Start at an initial local minimum with position $\mathbf{x}_i$ and energy E_i
2. Take a random step in configuration space
3. Quench to a new local minimum with position $\mathbf{x}_j$ and energy E_j
4. Accept step according to Metropolis criterion

$$p(i \rightarrow j) = \begin{cases} 1 & E_j \leq E_i \\ e^{-(E_j - E_i)/T} & E_j > E_i \end{cases}$$

5. Repeat

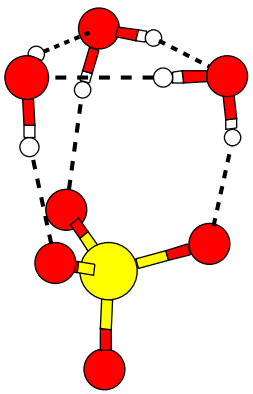
Chakrabarti *et al*, *Phys. Chem. Chem. Phys.*, **2009**, *11*,1970-1976
Wales DJ, *GMIN*, *A program for basin-hopping global optimisation*

Results

Putative Global Minima

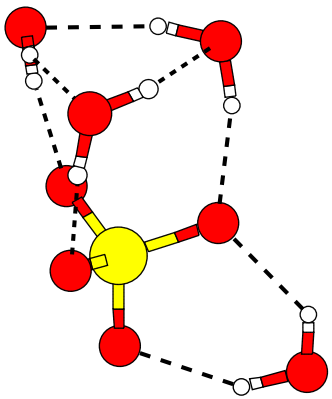
n: Number of water molecules

Experiment and theory suggests that for $n < 3$, $SO_4^{2-}(H_2O)_n$ is electronically unstable



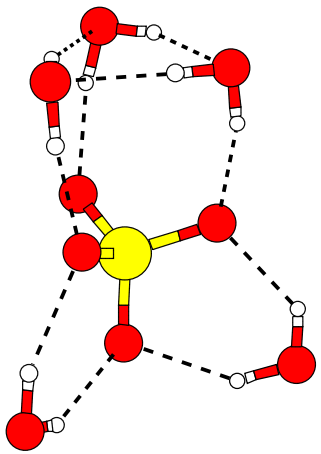
$n = 3$

-76.07 kcal mol^{-1}



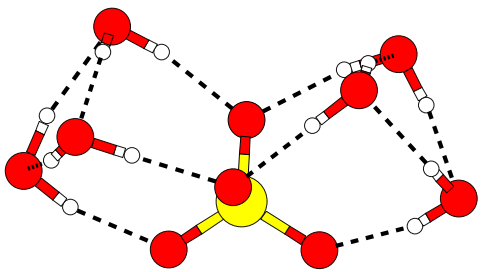
$n = 4$

-100.33 kcal mol^{-1}



$n = 5$

-123.45 kcal mol^{-1}



$n = 6$

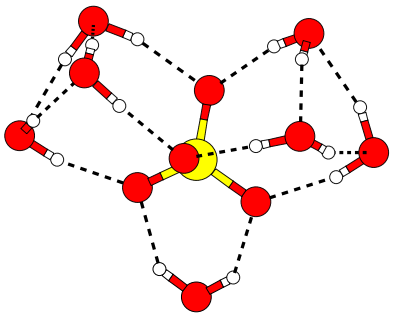
-146.00 kcal mol^{-1}

Wang *et al*, *J. Chem. Phys*, **2000**, *113*, 10837

Rudolph *et al*, *J. Phys. Chem. A*, **2001**, *105*, 905-912

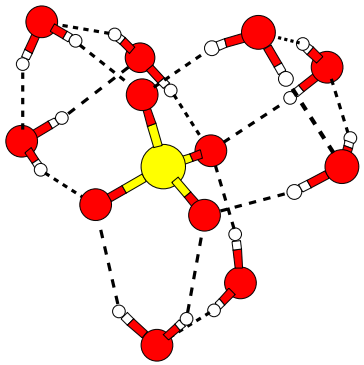
Putative Global Minima

n: Number of water molecules



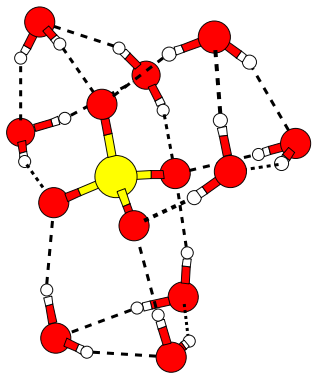
$n = 7$

-168.21 kcal mol^{-1}



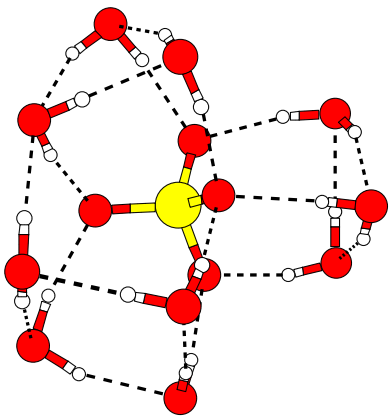
$n = 8$

-187.34 kcal mol^{-1}



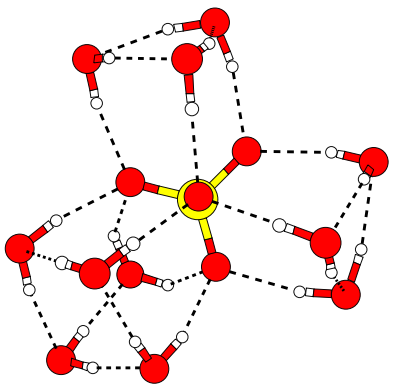
$n = 9$

-209.30 kcal mol^{-1}



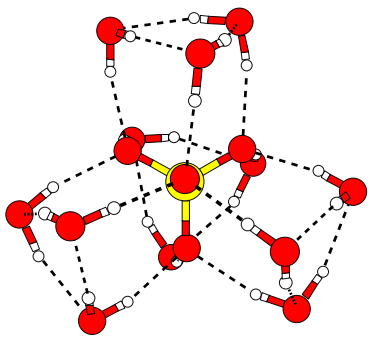
$n = 10$

-226.97 kcal mol^{-1}



$n = 11$

-245.73 kcal mol^{-1}



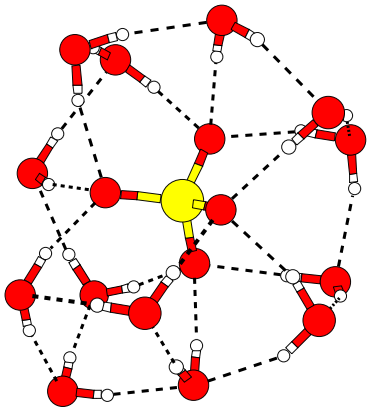
$n = 12$

-265.63 kcal mol^{-1}

Putative Global Minima

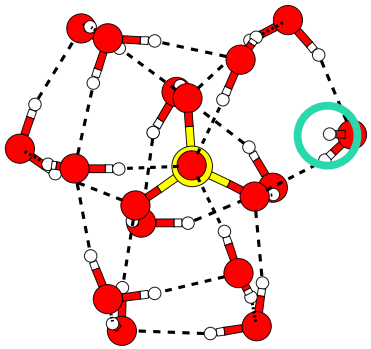
n: Number of water molecules

Highlighted: Dangling OH bond



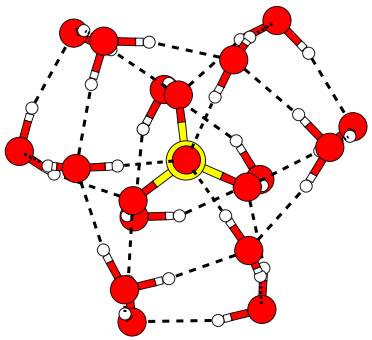
$n = 13$

-282.36 kcal mol^{-1}



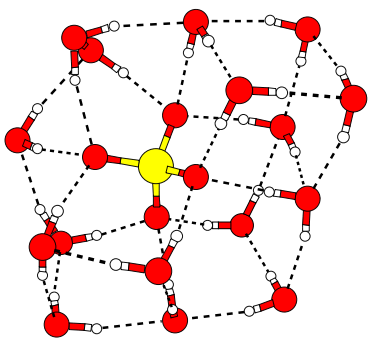
$n = 14$

-299.90 kcal mol^{-1}



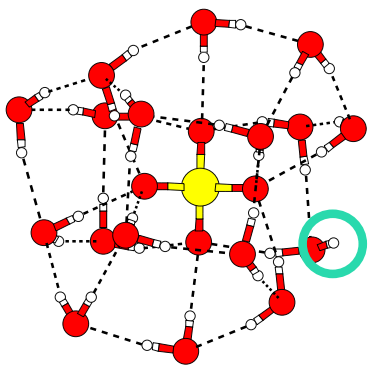
$n = 15$

-317.94 kcal mol^{-1}



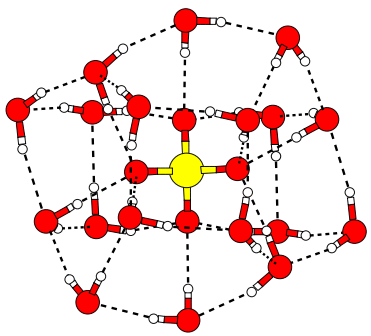
$n = 16$

-333.20 kcal mol^{-1}



$n = 17$

-349.07 kcal mol^{-1}



$n = 18$

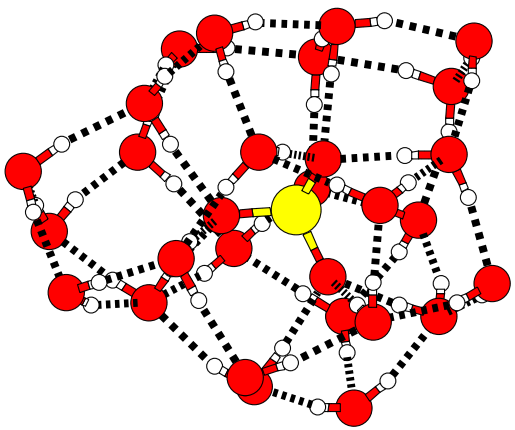
-367.01 kcal mol^{-1}

Putative Global Minima

n: Number of water molecules

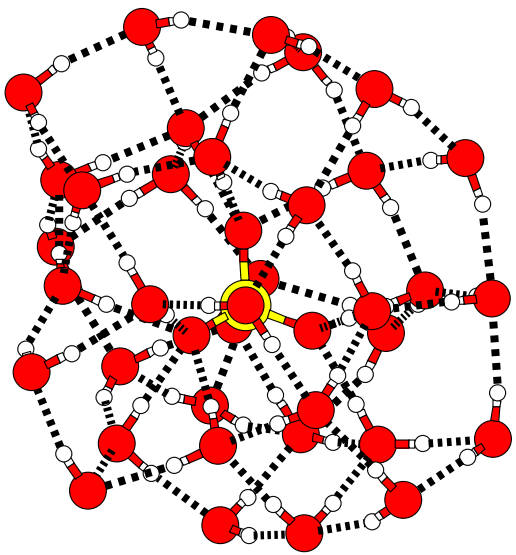
Highlighted: Dangling OH bond

Dangling OH bonds detected at $n = 43$, 45 and 47



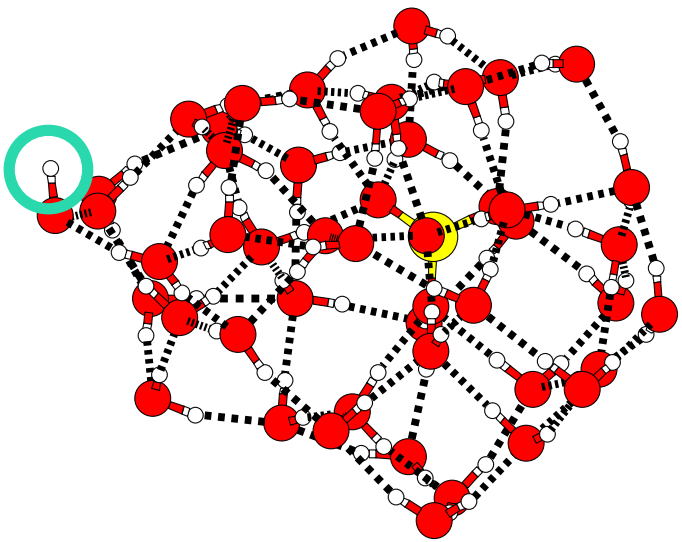
$n = 25$

-469.43 kcal mol^{-1}



$n = 35$

-597.62 kcal mol^{-1}

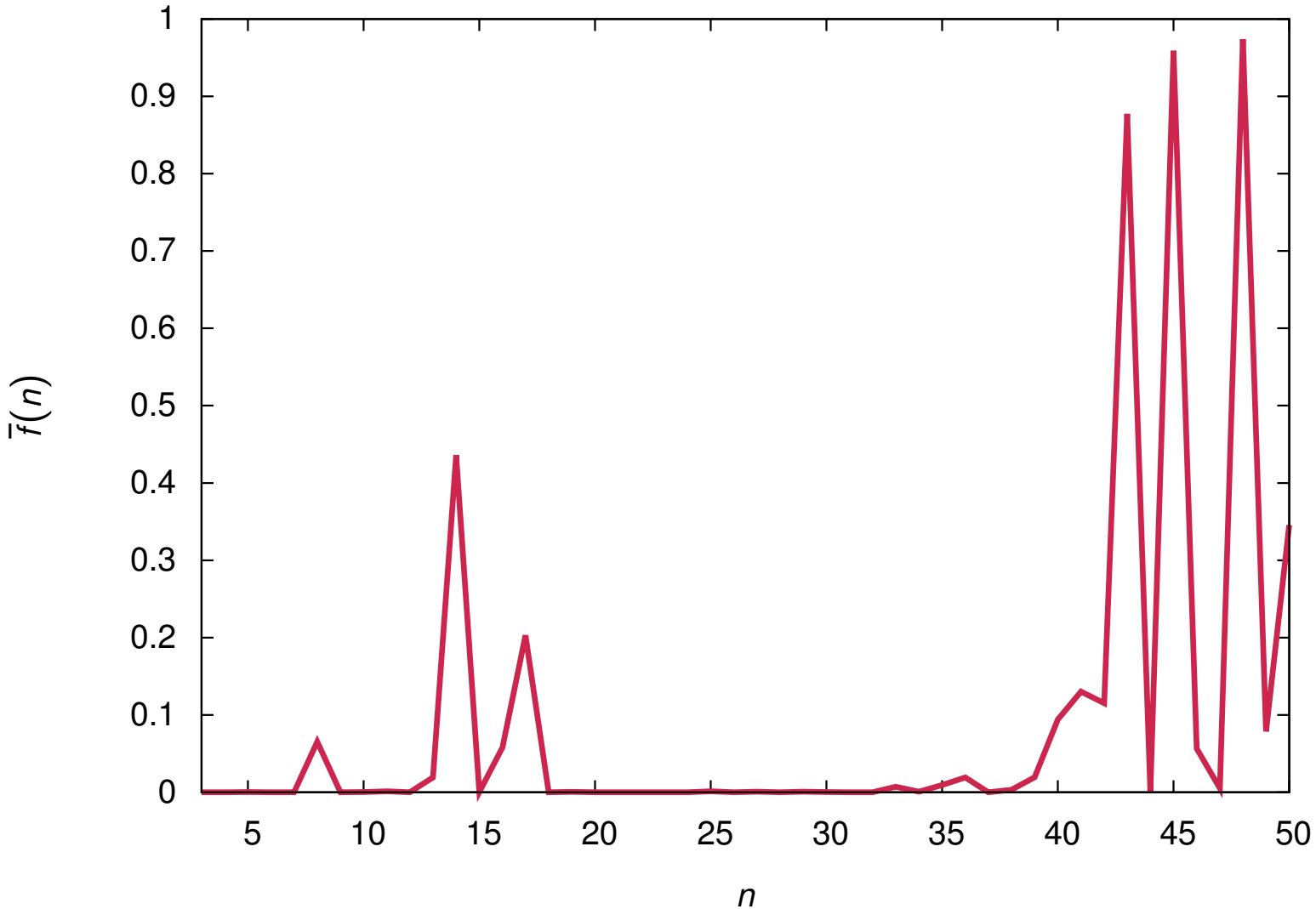


$n = 45$

-722.51 kcal mol^{-1}

Counting Dangling OH bonds

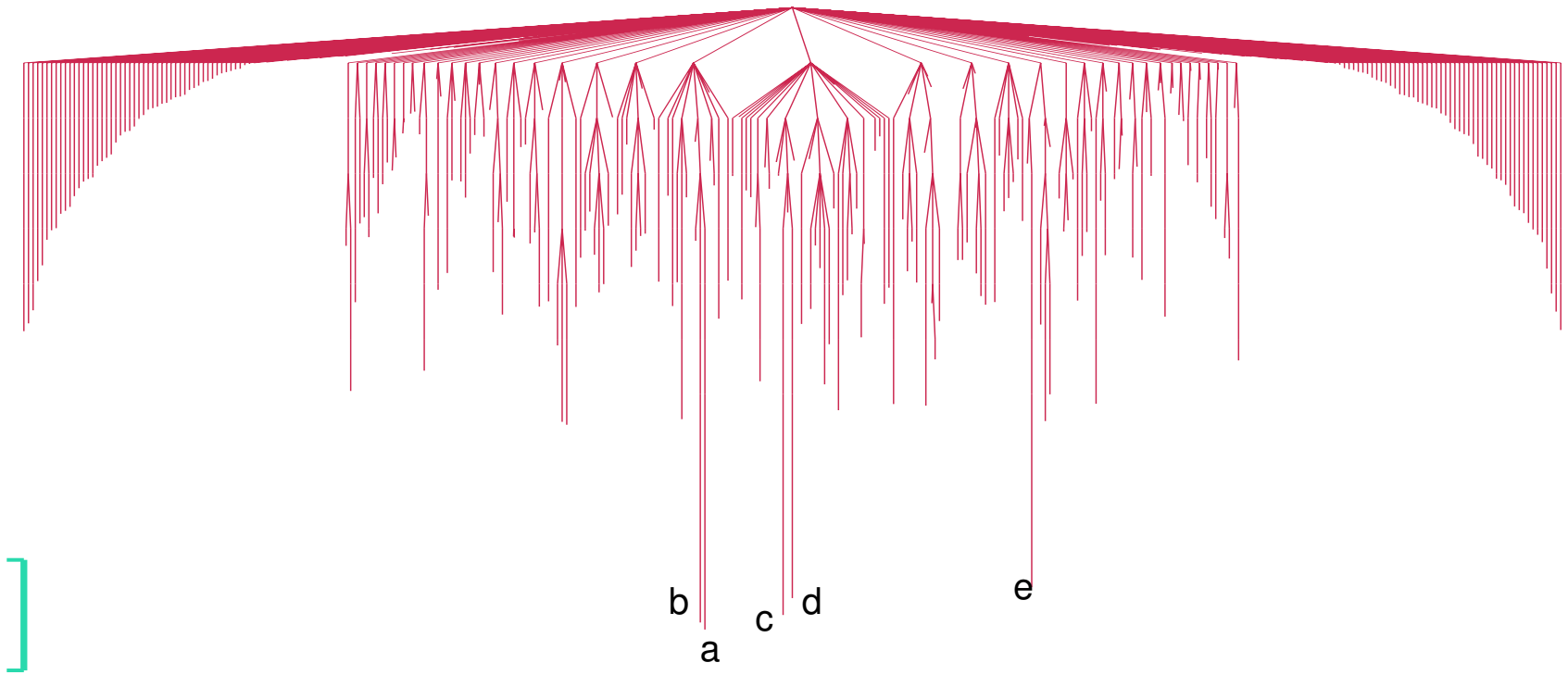
Boltzmann-weighted mean number of dangling OH bonds per cluster, $\bar{f}$.

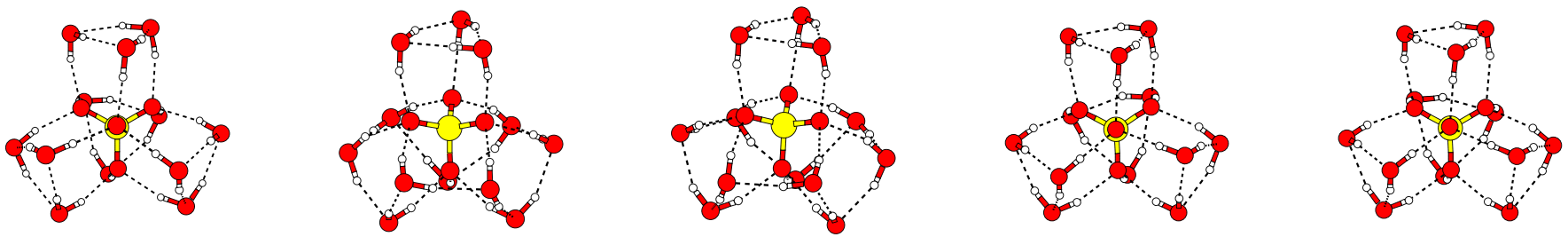


Disconnectivity Graph of $SO_4^{2-}(H_2O)_{12}$

335 Minima. 390 Transition States.

Energy Scale: 1 kcal mol^{-1}





Smeeton *et al*, *J. Comput. Chem*, **2014**, *35*, 1481-90

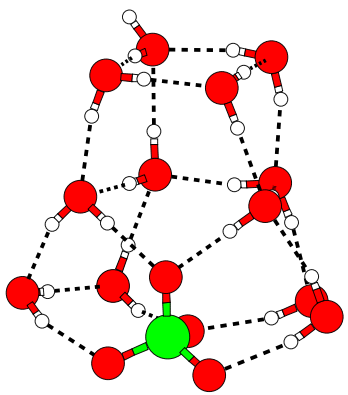
Summary

Summary

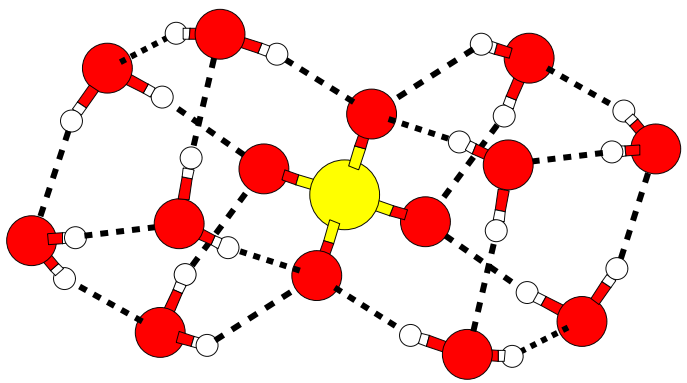
- The Hofmeister series is a well characterised phenomenon, but with an (as yet) undetermined chemical origin.
- The long-range effect of an ion on water structure is a possible explanation for the Hofmeister series.
- IRPD spectroscopy of hydrated sulfate ions suggests that the dangling OH bonds observed in bulk water are inhibited by the patterning of the H-bond network by the sulfate ion, and only appear above a critical size of $\approx$ 43 water molecules.
- Rigid-body potential results agree with DFT calculations.
- Simulation results suggest that protruding H atoms appear at $n \geq 43$ water atoms.

Future Work

- Begin searching at the DFT level using the GA.
- Investigate ClO_4^- $\longrightarrow$ similar structure, opposite end of Hofmeister series (John Hey, UoB).
- Calculate IR spectra of low energy structures



$ClO_4^-(H_2O)_{12}$



$SO_4^{2-}\left(H_2O\right)_{10} \longrightarrow$ DFT

Acknowledgements

- Prof. Roy Johnston
- Dr. Mark Oakley
- Dr. Sridhar Neelamraju
- Dr. Dwaipayan Chakrabarti
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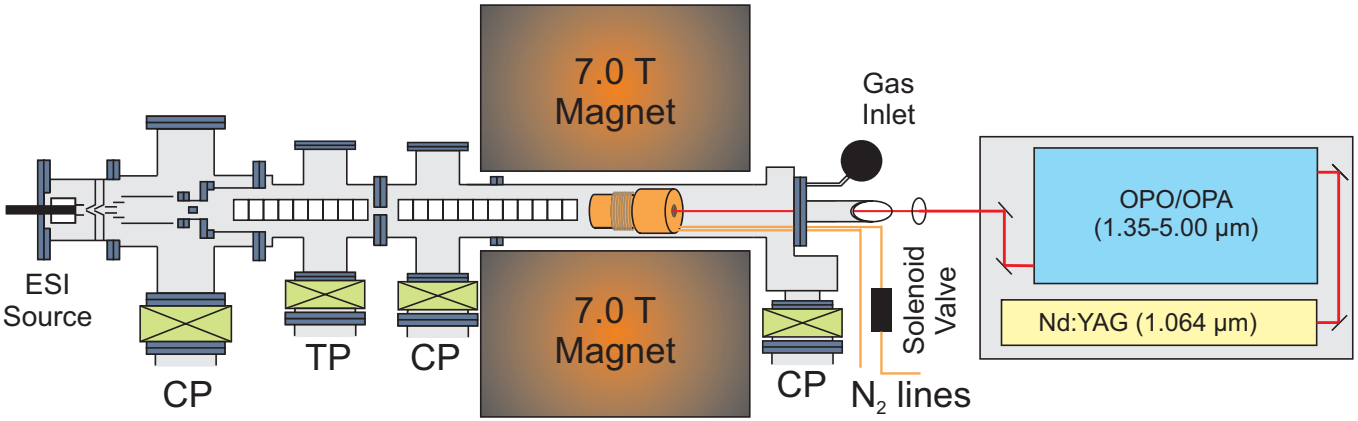
- Prof. Evan Williams and Dr. Sven Heiles (U.C. Berkeley)
- The Johnston Group
- BlueBear, Apocrita and ARCHER
- EPSRC Programme Grant EP/I001352/1: Simulation of Self Assembly

Thank you for your attention!

Johnston Group circa 2012

Experiment: Methodology



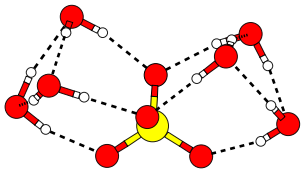
Schematic of a Fourier-transform ion cyclotron resonance mass spectrometer

- Ions are generated at the electrospray ionization (ESI) source and transferred into a Penning cell.
- Clusters are size selected using SWIFT isolation.
- Blackbody infrared radiative dissociation (BIRD) rate constant is measured
- Same size selected clusters are radiated with IR light of a given wavelength and an IR dissociaton rate constant is measured.

Williams *et al. JACS*, **2010**, *132*, 8248-8249

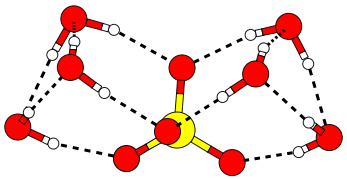
Comparison with Experiment for $SO_4^{2-}(H_2O)_6$

n: Number of water molecules, m: Energetic Ordering of Minima



$n = 6, m = 1$

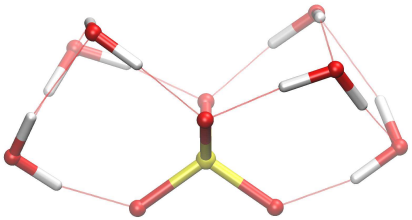
-165.77 kcal mol^{-1}



$n = 6, m = 2$

$\Delta E =$

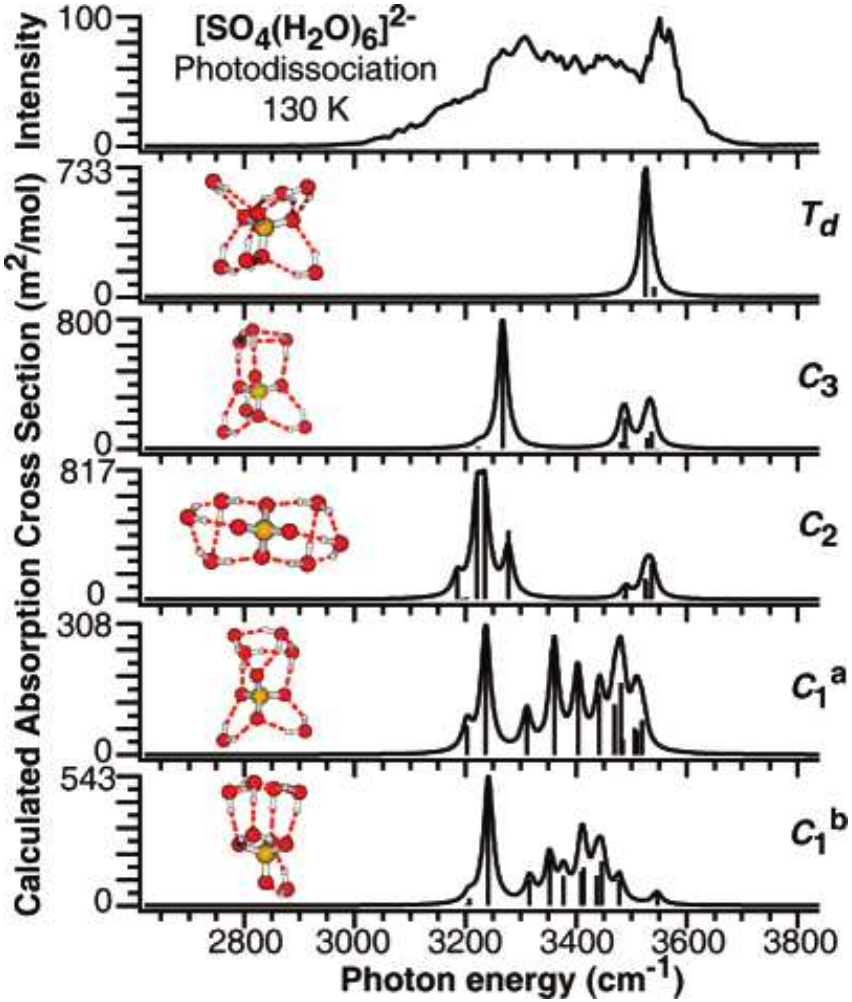
1.10 kcal mol^{-1}



$n = 6, m = 6$

$\Delta E =$

3.12 kcal mol^{-1}



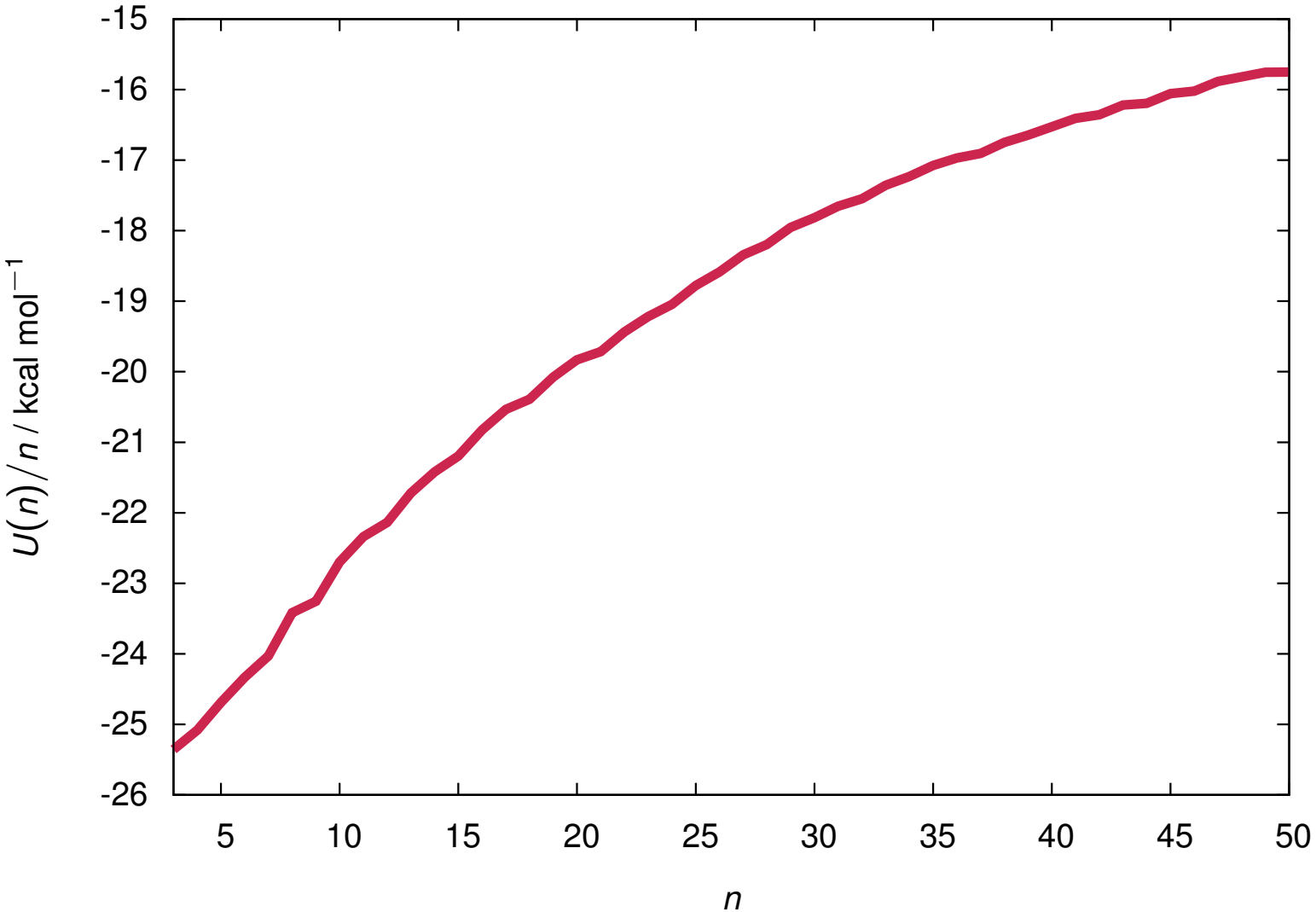
IRPD spectra from experiment and theory.

Bush *et al*, *JACS*, **2007**, *129*, 2220-2221

Head-Gordon *et al*, *J. Phys. Chem. A*, **2011**, *115*, 11438-11454

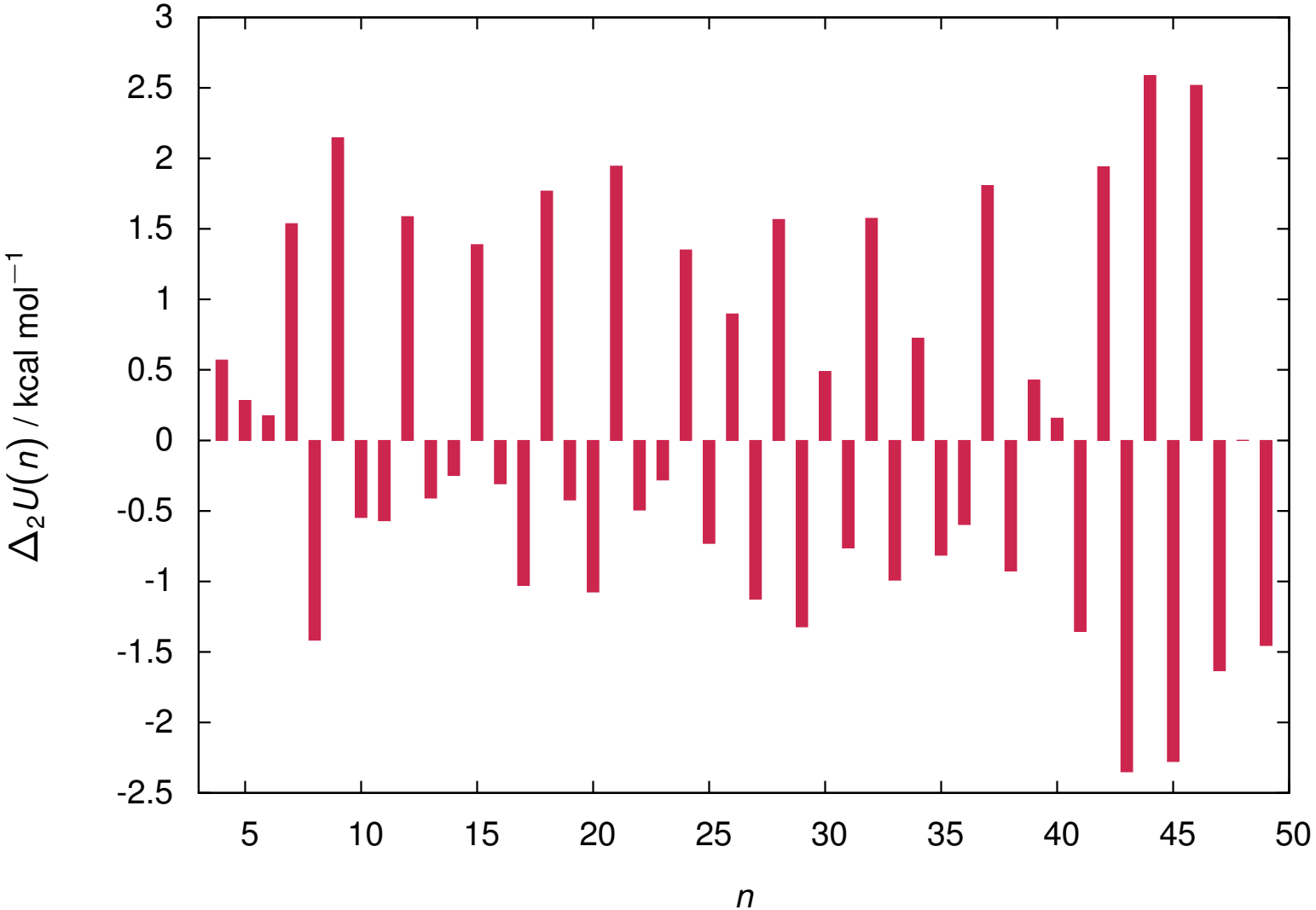
Energy per Water Molecule

Bulk TIP4P: $U(n)/n$ = -12.9 kcal mol^{-1}



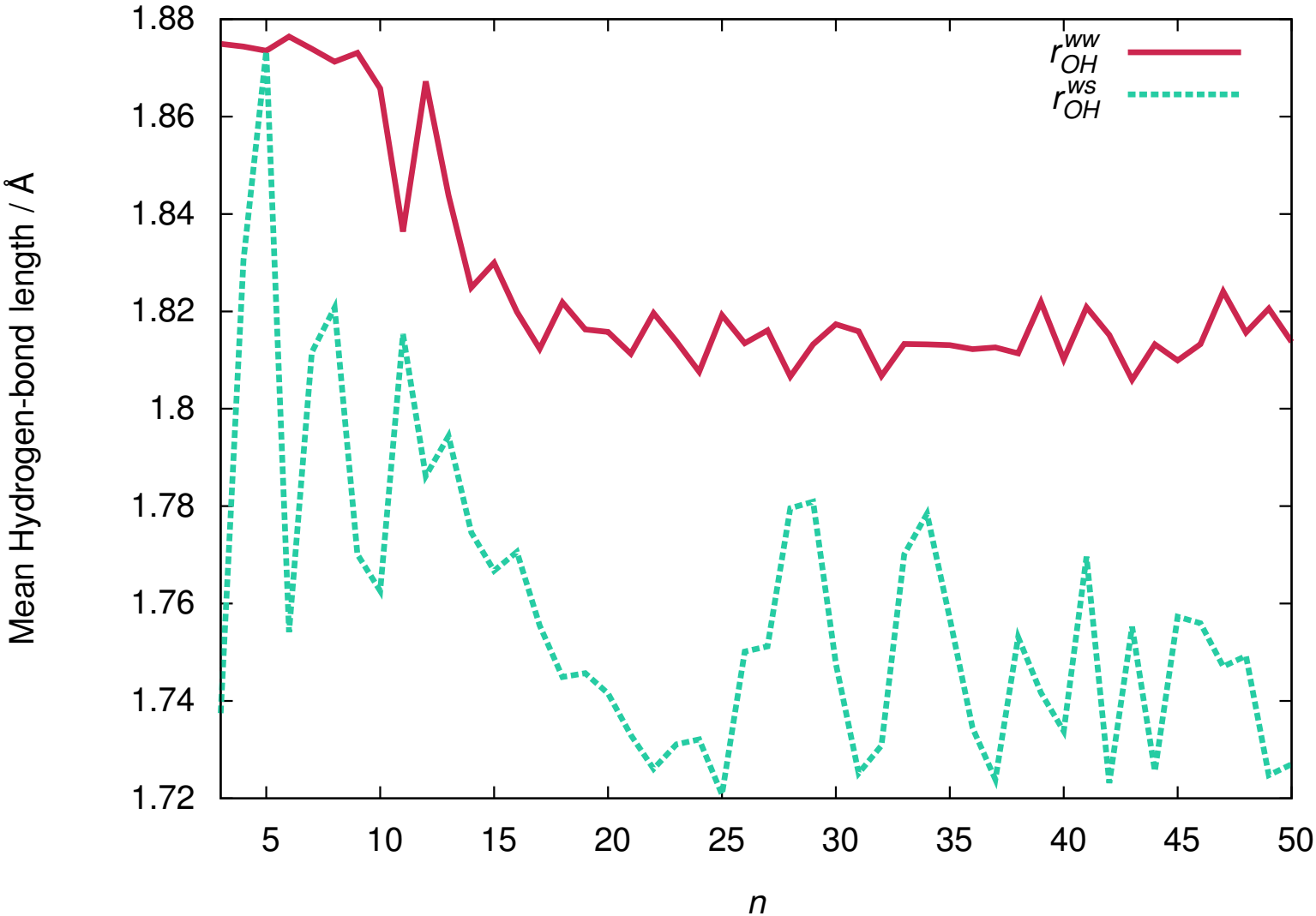
Central Difference Approximation

$\Delta_2 U = \frac{1}{2}\left(U(n+1) + U(n-1)\right) - U(n)$



Mean Hydrogen Bond Length

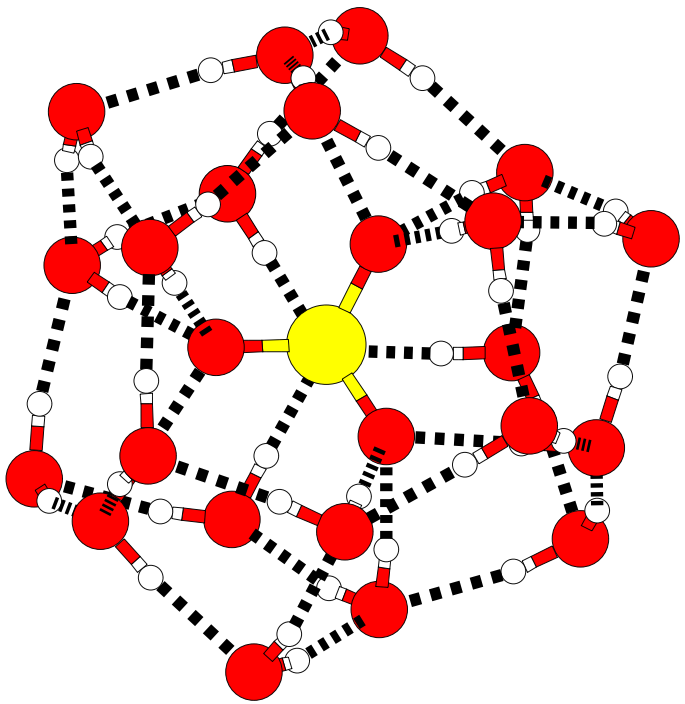
r_{OH}^{ww} = OH—H Mean Distance, r_{OH}^{ws} = SO—H Mean Distance,



Putative Global Minima

Starting point for low energy structures for $n \geq 20$?

- Particularly stable structure for $n = 21$
- ΔE =2.32 kcal mol^{-1} lower than next isomer
- Typically $\Delta E \approx$0.1 kcal mol^{-1}



$n = 25$

-414.04 kcal mol^{-1}