



Quantum chemistry modeling of local solvation effects

Avogadro User Group Meeting
Pittsburgh, PA, August 25th, 2018

John A. Keith
Department of Chemical and Petroleum Engineering, University of Pittsburgh

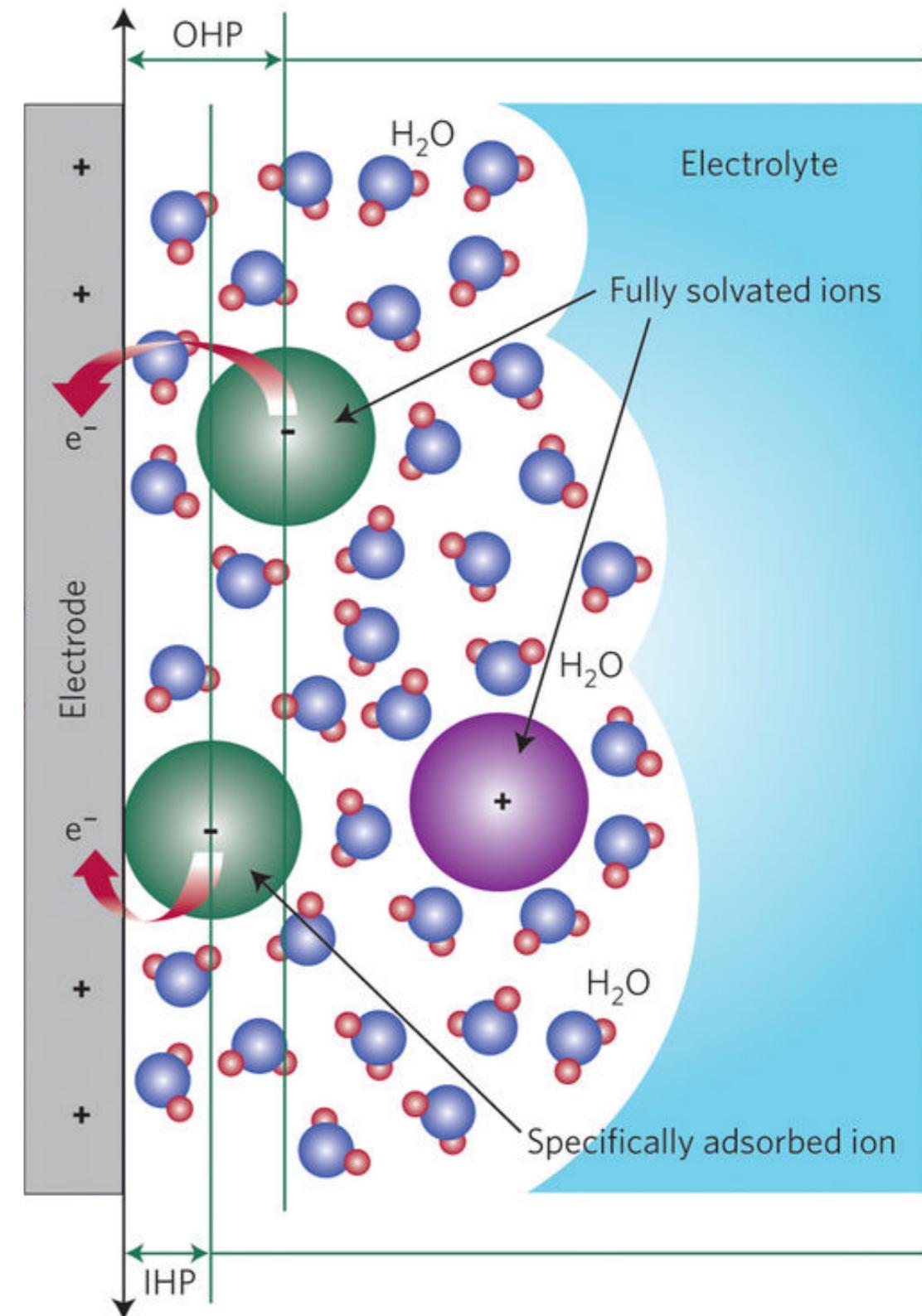


Nelson Mandela
1918-2013

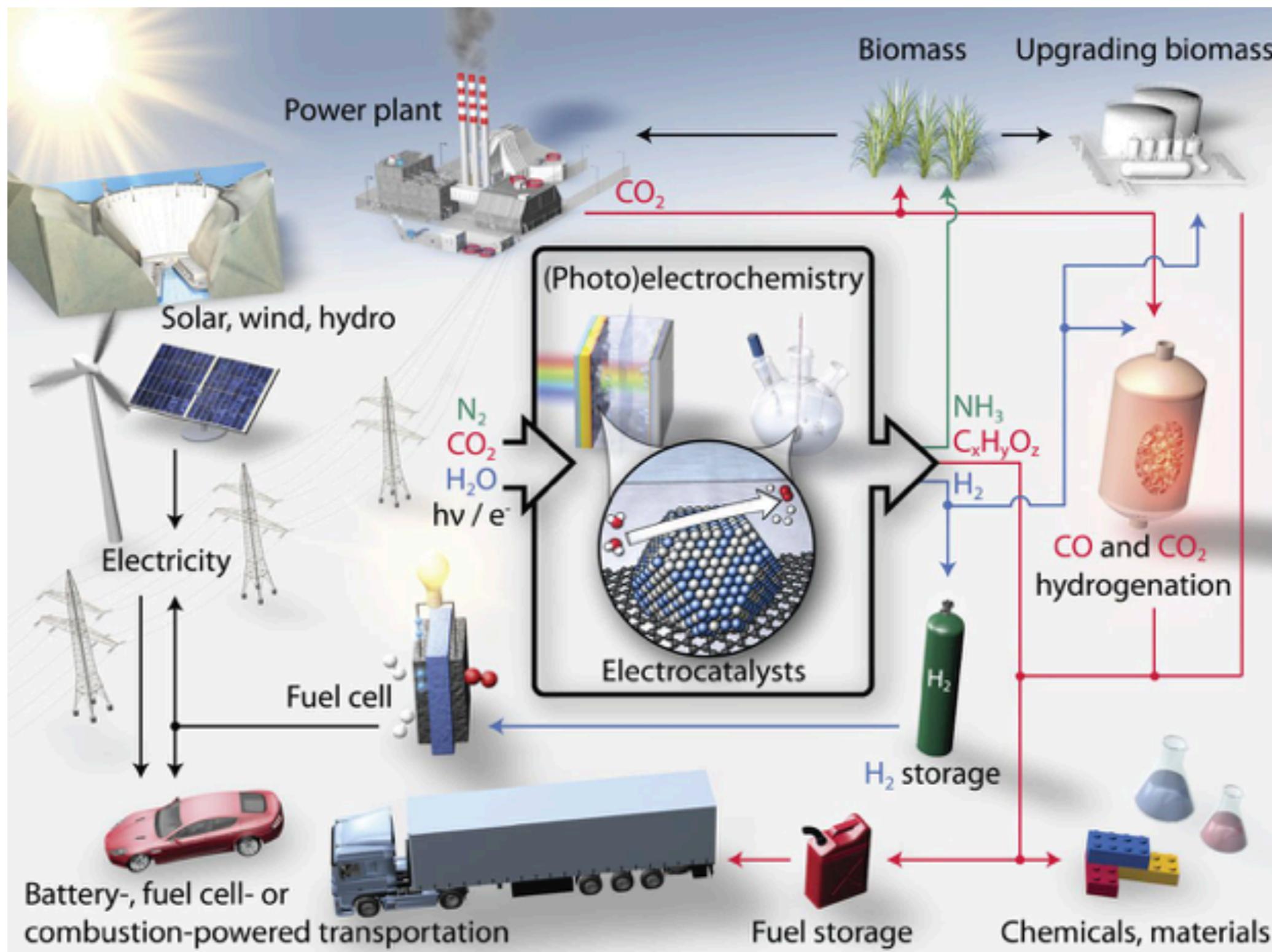
“No one is born hating another person because of the color of his skin or his background or his religion...”

→ we are *products of our environment*
...so are *chemical reactions*

From: Electrocatalysis:
Interfacing
electrochemistry,
Nenad M. Markovic
Nature Materials
12, 101–102 (2013)
doi:10.1038/nmat3554



Motivation: Sustainable living through chemistry...



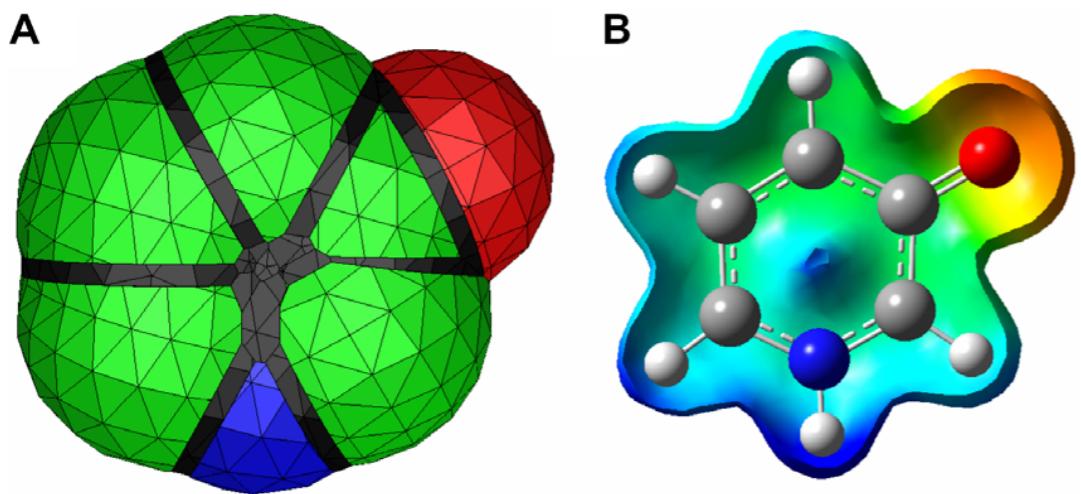
Seh, Z.W. et al, Science, 2017, 355, aad4998

Research challenge: how to optimize these reactions?

Our interests

- Accelerating studies of biomimetic reaction mechanisms for sustainable fuels and chemicals
- Unveiling and correcting local solvation effects on thermochemistry and reaction pathways
- Opening opportunities for high throughput screening for green chemical design, functional polymer hydrate materials, and heterogeneous catalysts

semi-empirical continuum solvation models



Solve the Poisson equation for electrostatics around a cavity and couple the potential energy term to the self-consistent calculation

$$-\nabla^2 V(\vec{r}) = 4\pi\rho_M(\vec{r}) \quad \text{inside cavity}$$

$$-\epsilon\nabla^2 V(\vec{r}) = 0 \quad \text{outside cavity}$$

The solute charge distribution is decomposed into both nuclear and electronic terms:

$$\rho(r) = \rho_M^e(r) + \rho_M^n(r)$$

Express energetic contribution with an effective (semi-empirical) Hamiltonian:

$$G_{\text{HF}}^{\text{PCM}} = \langle \Psi_{\text{HF}} | \hat{H}_M^0 + \frac{1}{2} \hat{V}^{\text{int}} | \Psi_{\text{HF}} \rangle$$

Solvent polarization is 1/2 the magnitude and
opposite in sign to the interaction energy within
linear dielectric theory



Chem. Rev. 94 (1994) 2027-2094

Chem. Rev. 105 (2005) 2999-3093

Computational electrochemistry: prediction of liquid-phase reduction potentials†

Cite this: *Phys. Chem. Chem. Phys.*,
2014, 16, 15068

Aleksandr V. Marenich,^{*a} Junming Ho,^{*b} Michelle L. Coote,^{*b} Christopher J. Cramer^{*a} and Donald G. Truhlar^{*a}

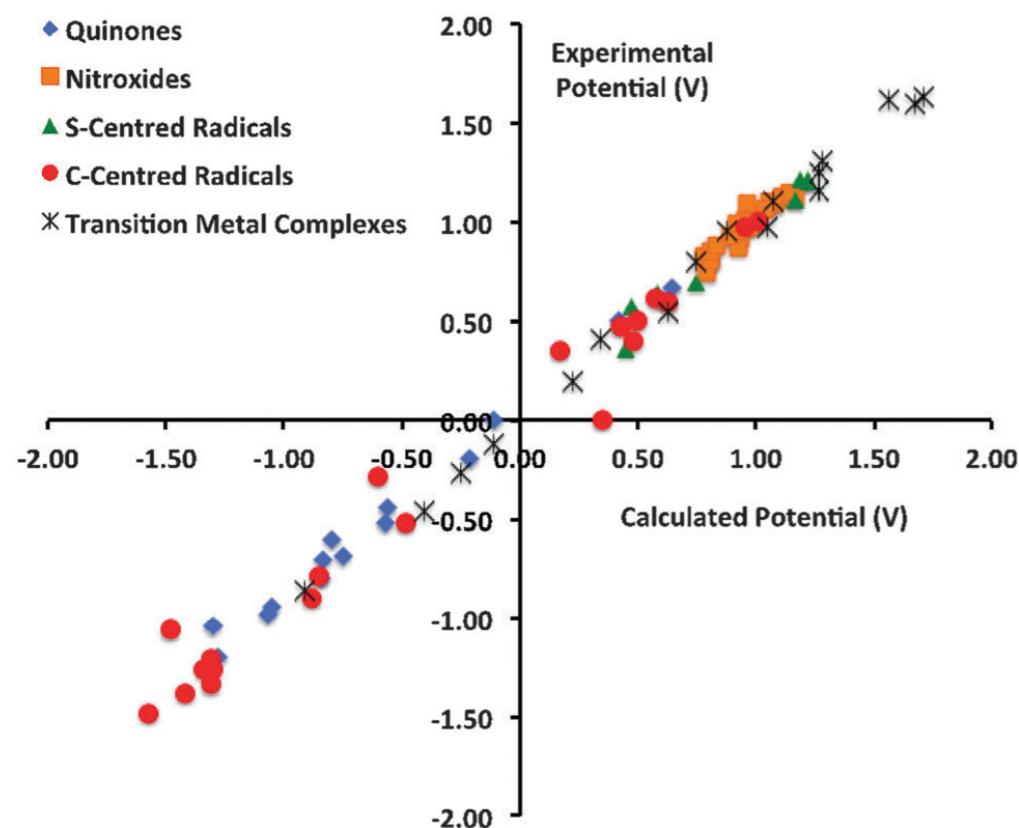


Fig. 1 Theoretical reduction potential versus experimental one for 84 chemical compounds of various classes.^{140,212,213,215,217,219–221}

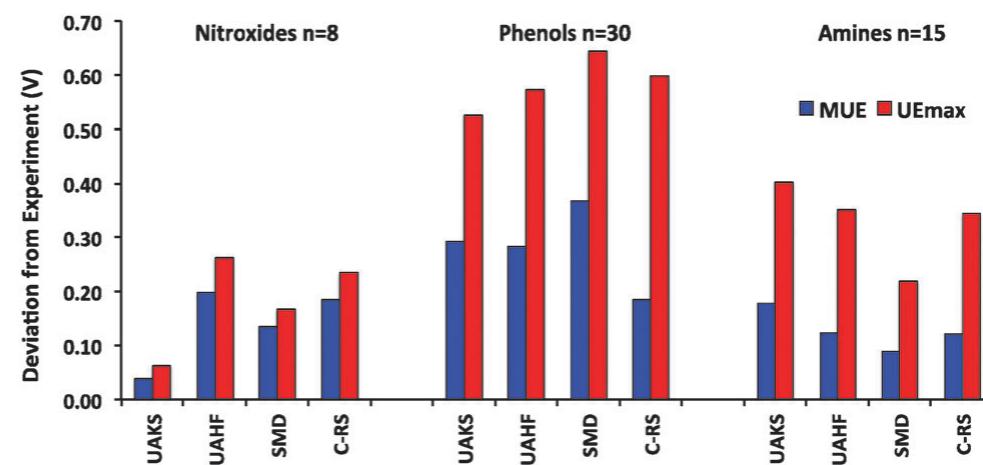
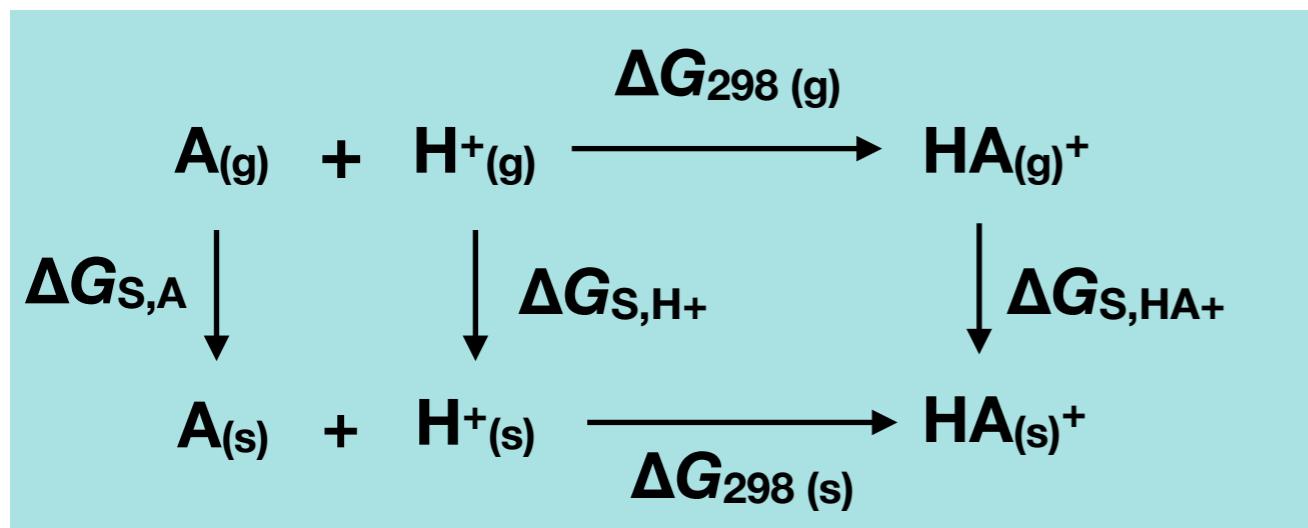


Fig. 3 Performance of various continuum solvent models in conjunction with the G3(MP2,CC)(+) method in calculating the aqueous reduction potentials of a range of compounds that have been broadly categorized as nitroxides, alcohols and amines (n = number of compounds in a dataset). C-RS means COSMO-RS.

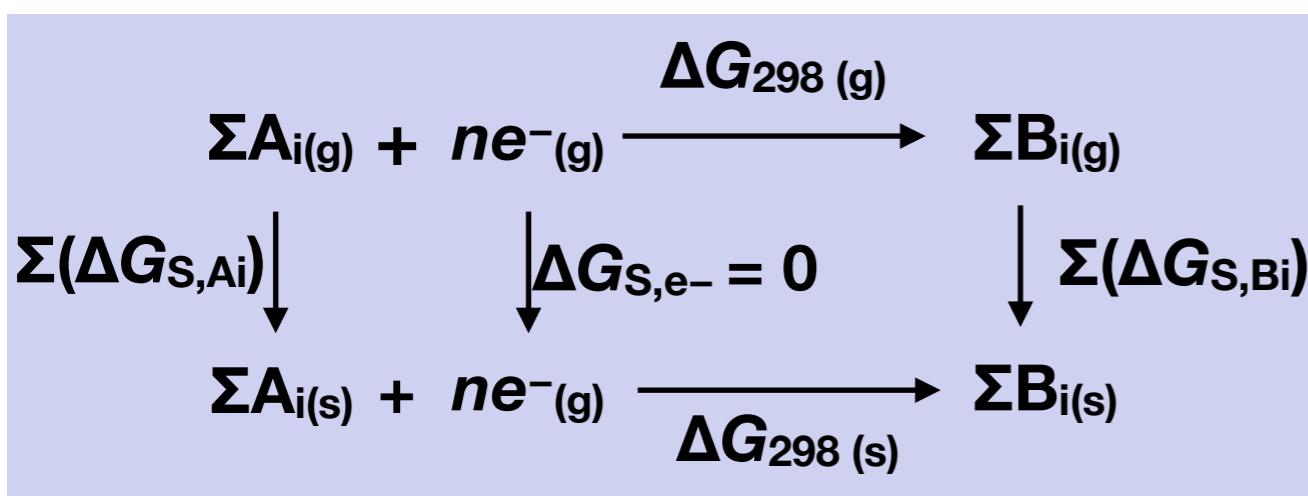
Calculations schemes are pretty good,
...except when they aren't...

Thermodynamic cycles involving solvation energies



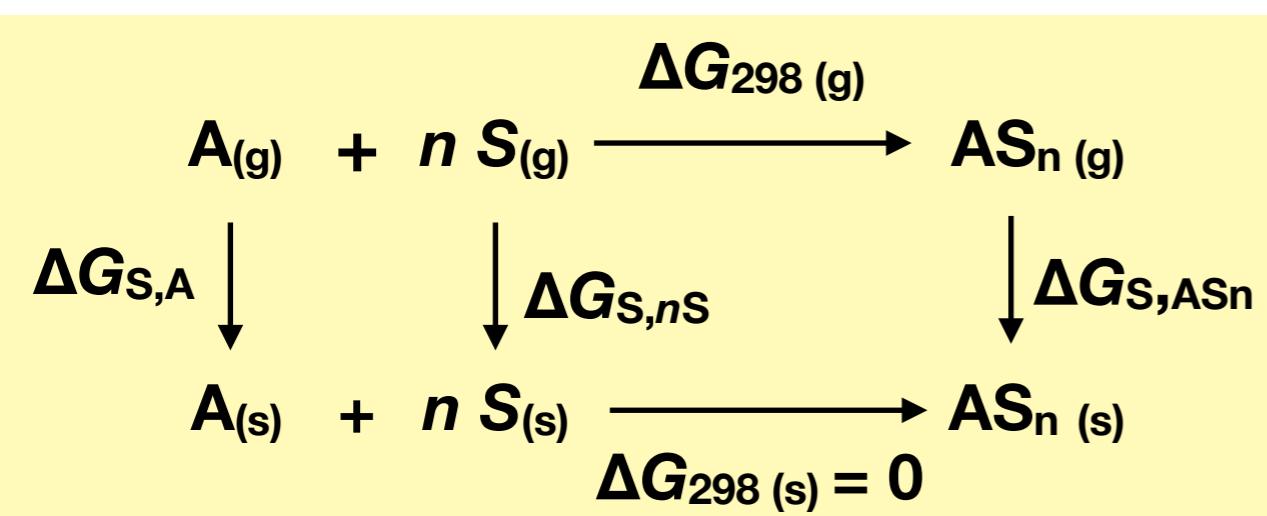
$$pK_a = -\Delta G_{298} \text{ (s)} / 2.303RT$$

absolute predictions
usually accurate to $\sim 1-2$ pK_a units
(relative data < 1 pK_a unit)



$$E^\circ = -\Delta G_{298} \text{ (s)} / nF$$

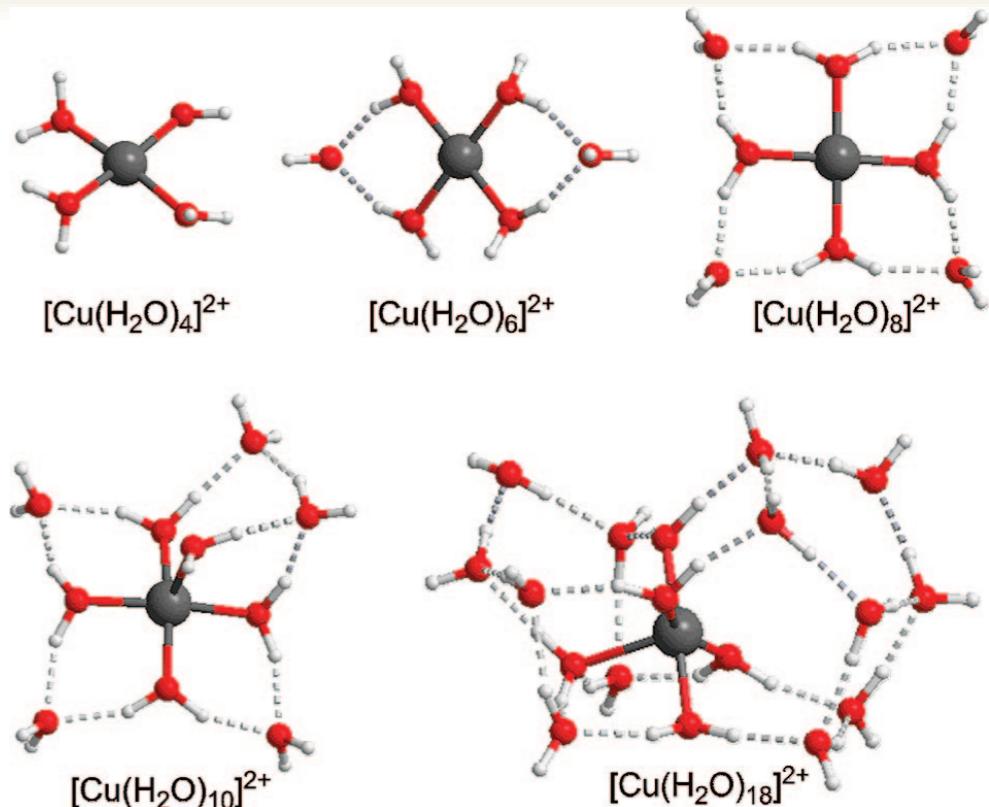
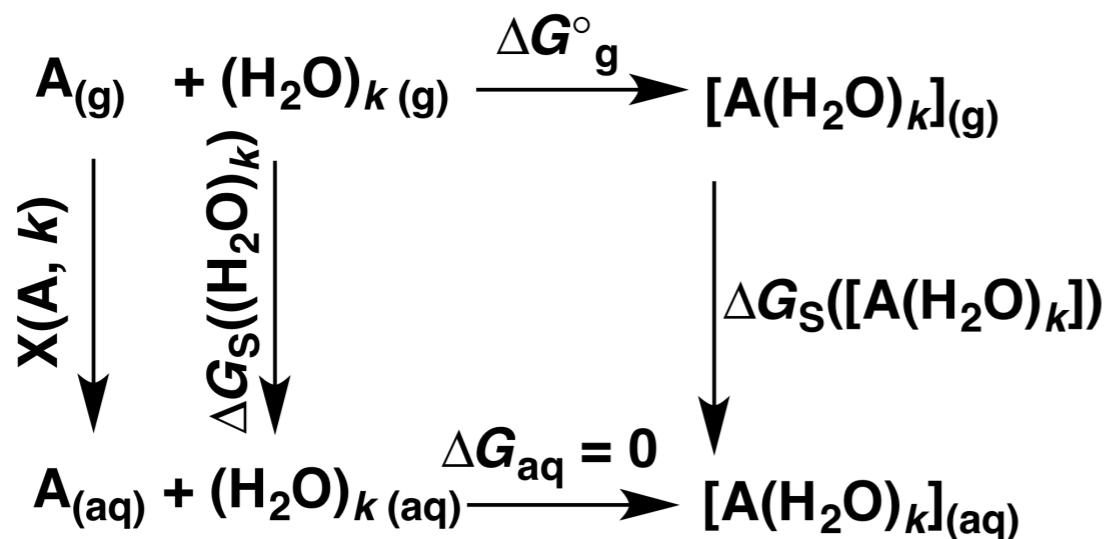
absolute predictions
usually accurate within ~ 0.2 eV
(relative data < 0.1 eV)



$$\Delta G_{\text{S,A}} = \Delta G_{298} \text{ (g)} + \Delta G_{\text{S,ASn}} - \Delta G_{\text{S,ns}}$$

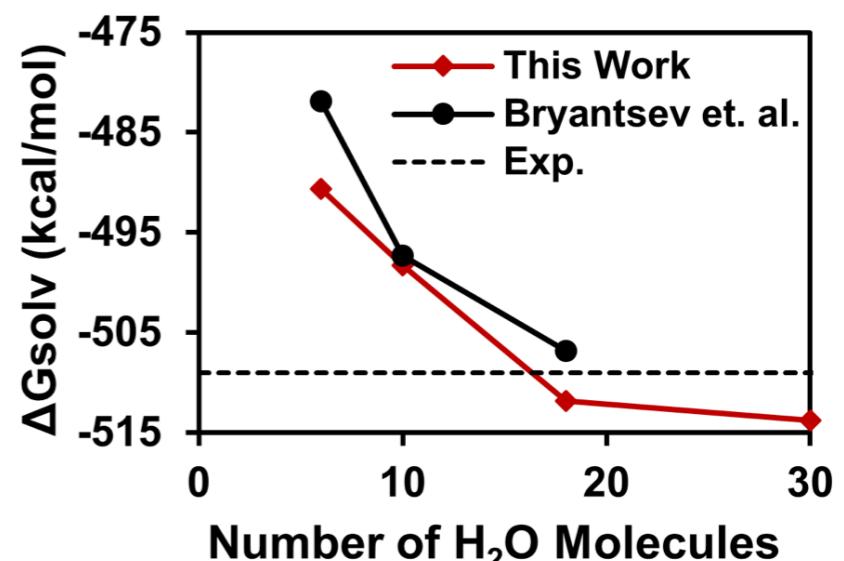
absolute predictions
usually accurate within 2% of experimental measurements

Cluster continuum modeling: thermodynamic cycle to solve for 'X'



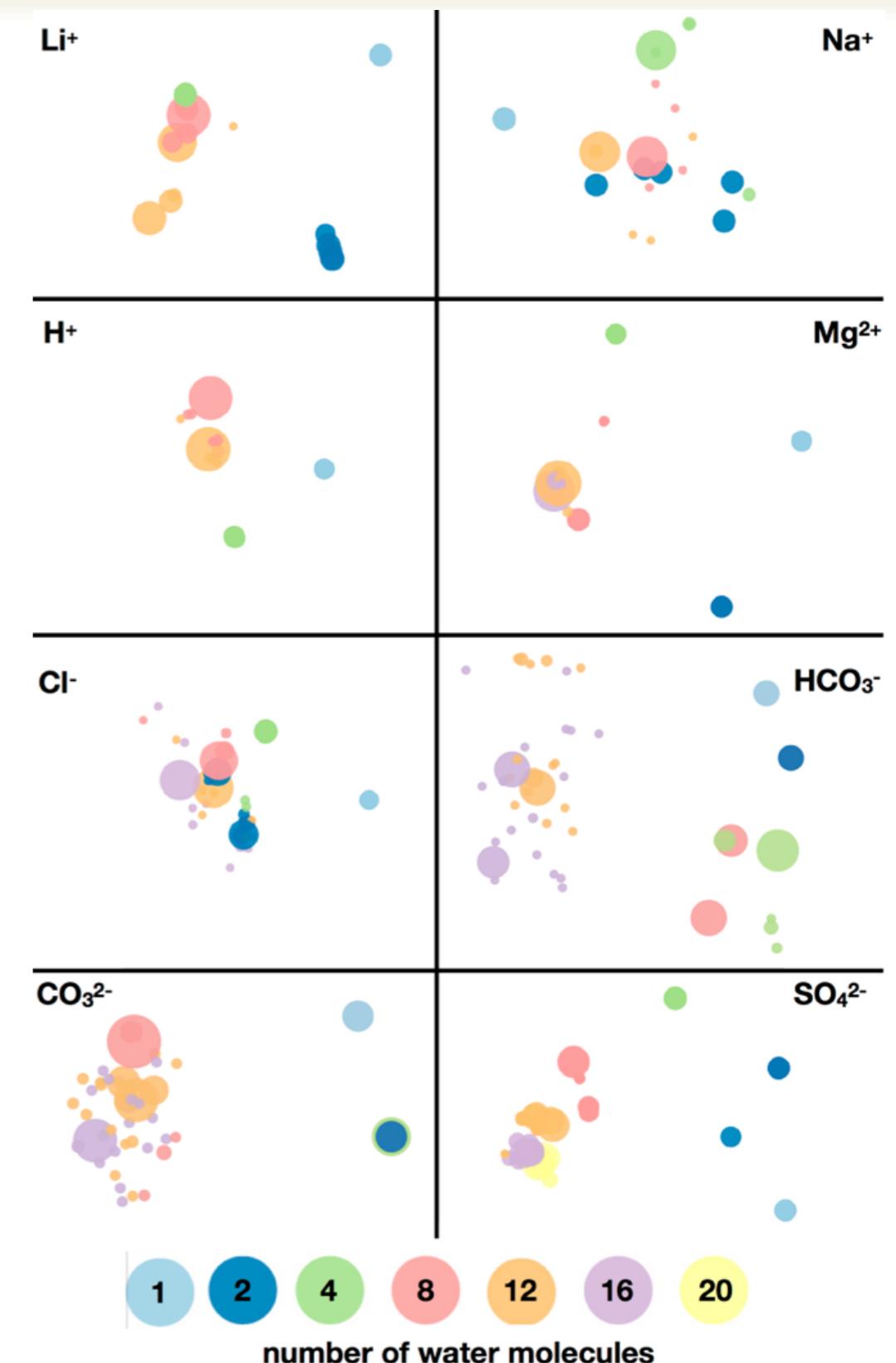
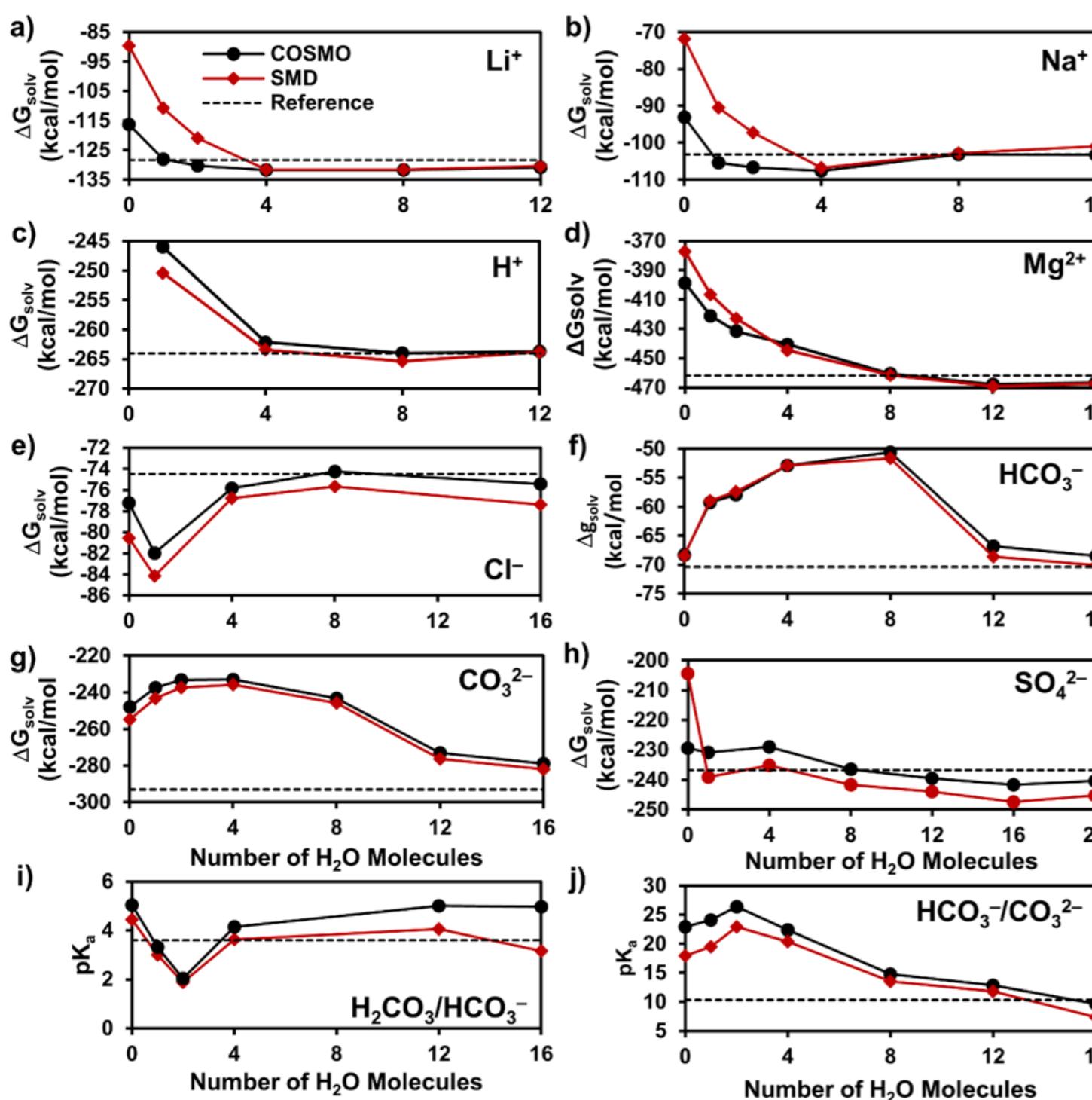
V.S. Bryantsev, M.S. Diallo, W.A. Goddard, III,
J. Phys. Chem. B, 2008, 112, 9709-9719

- Step 1. Automate cluster generation using global optimization code: ABCluster.¹
- Step 2. Filter ca 5,000 clusters down to lowest 20 structures according to semi-empirical QM.
- Step 3. Use QM and Boltzmann weight five lowest energy structures using B3LYP/Def2-TZVP//BP86/Def2-SVP



¹Zhang, J.; Dolg, M.
Phys. Chem. Chem. Phys. 2015, 17, 24173-24181.

Converging solvation energies?



Revisiting how local solvation effects affect multistep reactions



Article

DOI: 10.1021/ja5111392

pubs.acs.org/JACS

J. Am. Chem. Soc. 2015, 137, 3811–3826

A Case Study of the Mechanism of Alcohol-Mediated Morita Baylis–Hillman Reactions. The Importance of Experimental Observations

R. Erik Plata and Daniel A. Singleton*

Department of Chemistry, Texas A&M University, College Station, Texas 77842, United States

Supporting Information

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By [Stuart A. Borman](#)



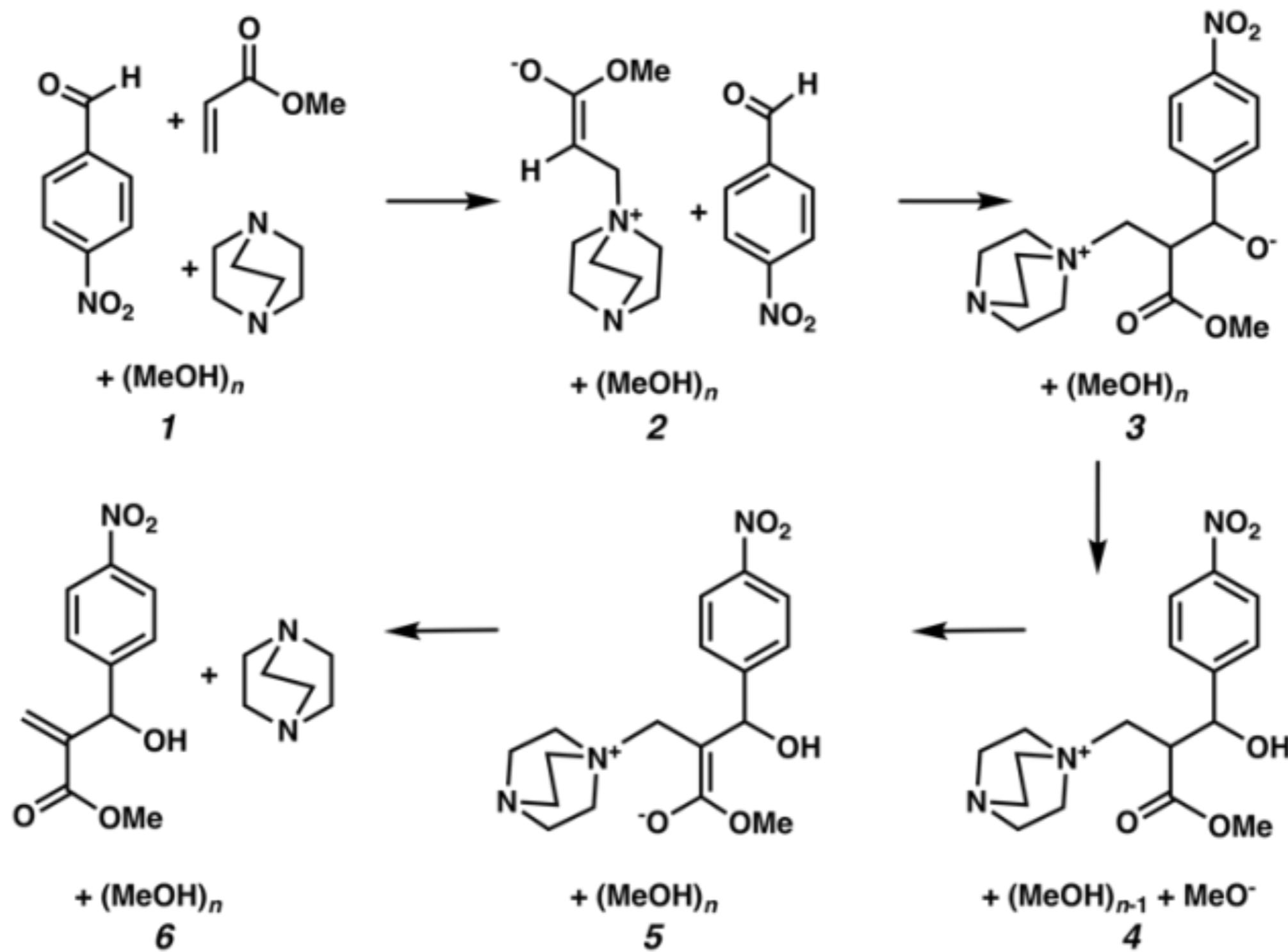
NATURE CHEMISTRY | NEWS AND VIEWS

Computational chemistry: Making a bad calculation

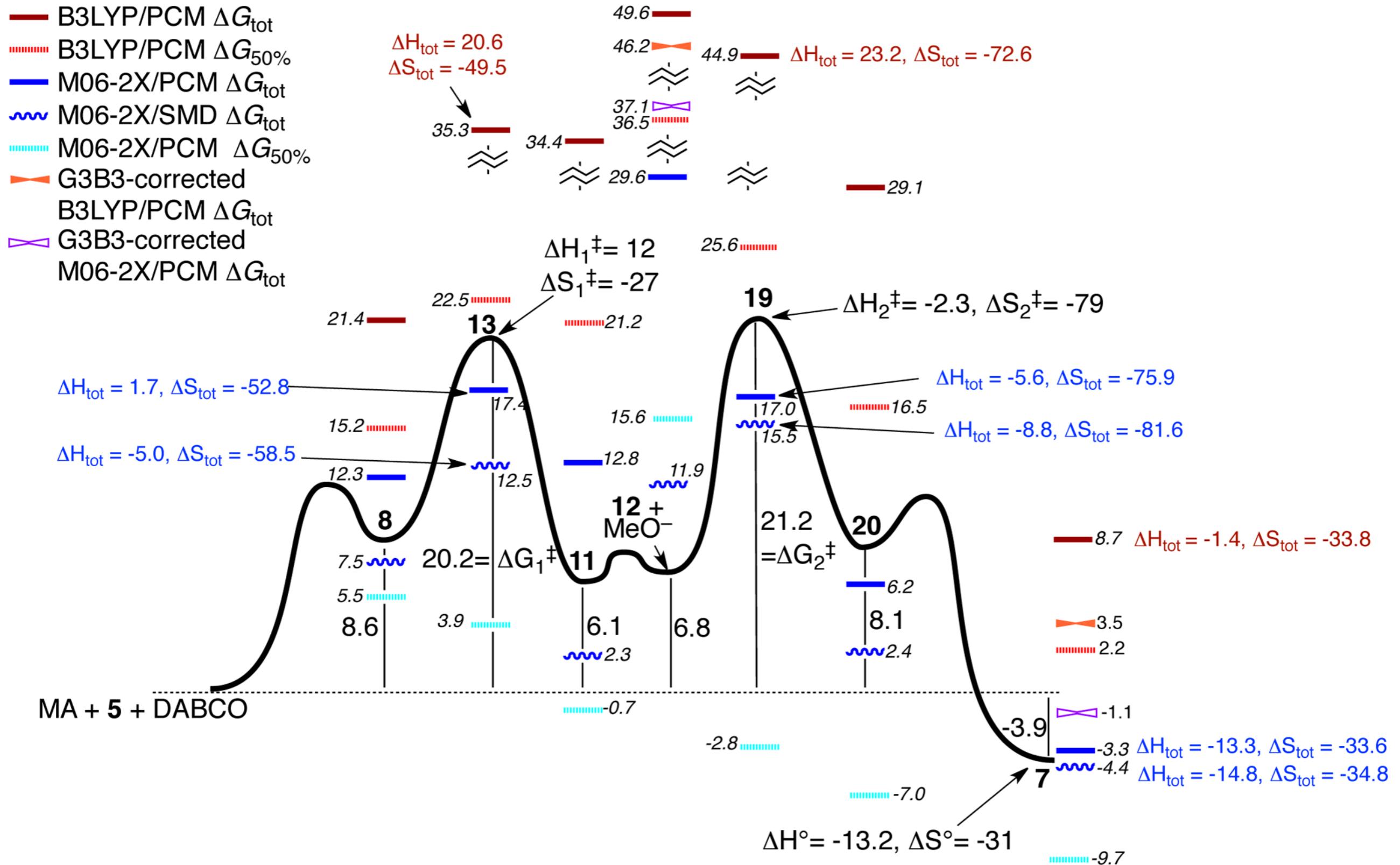
Arthur Winter

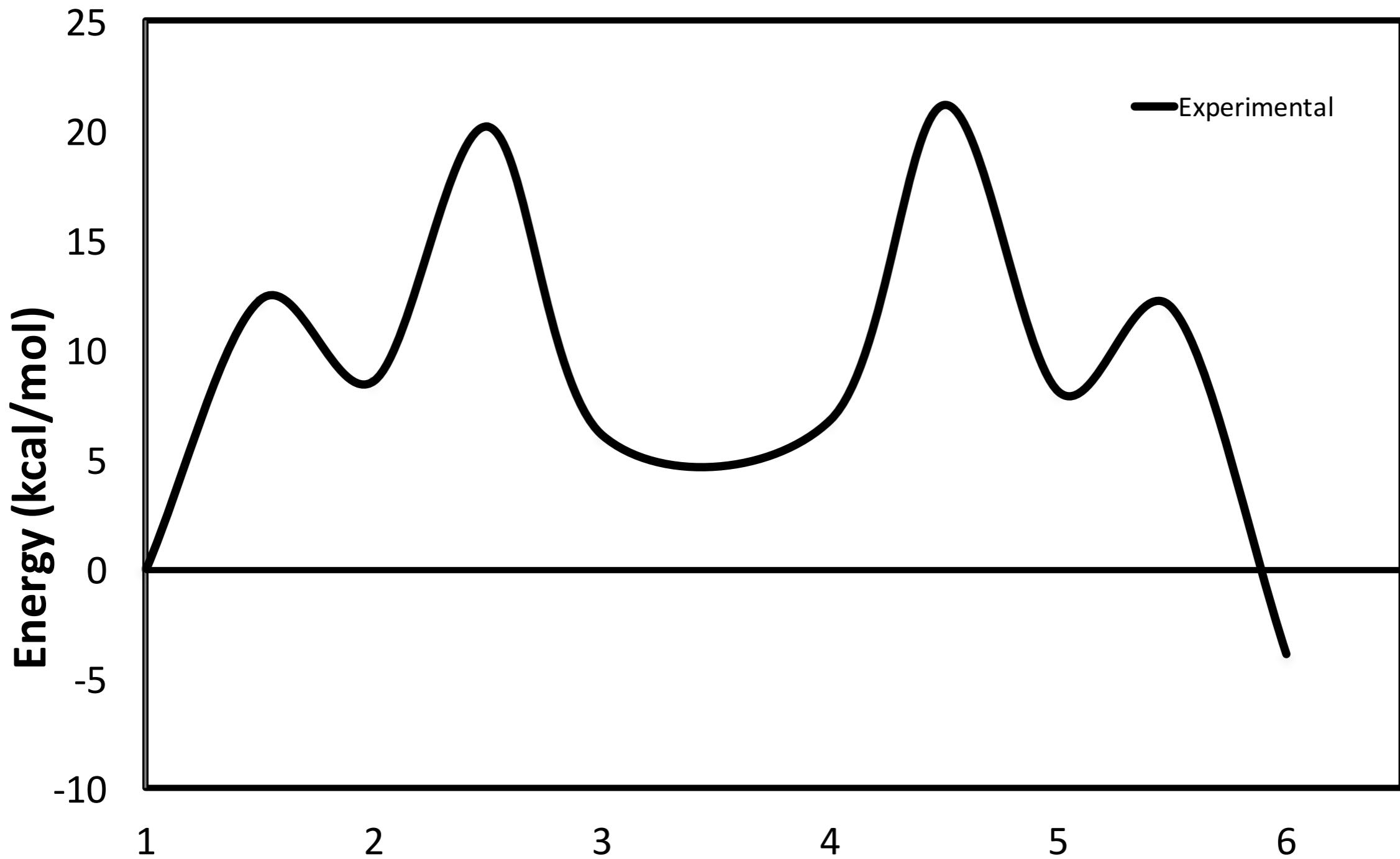
Nature Chemistry 7, 473–475 (2015) | doi:10.1038/nchem.2267
Published online 20 May 2015

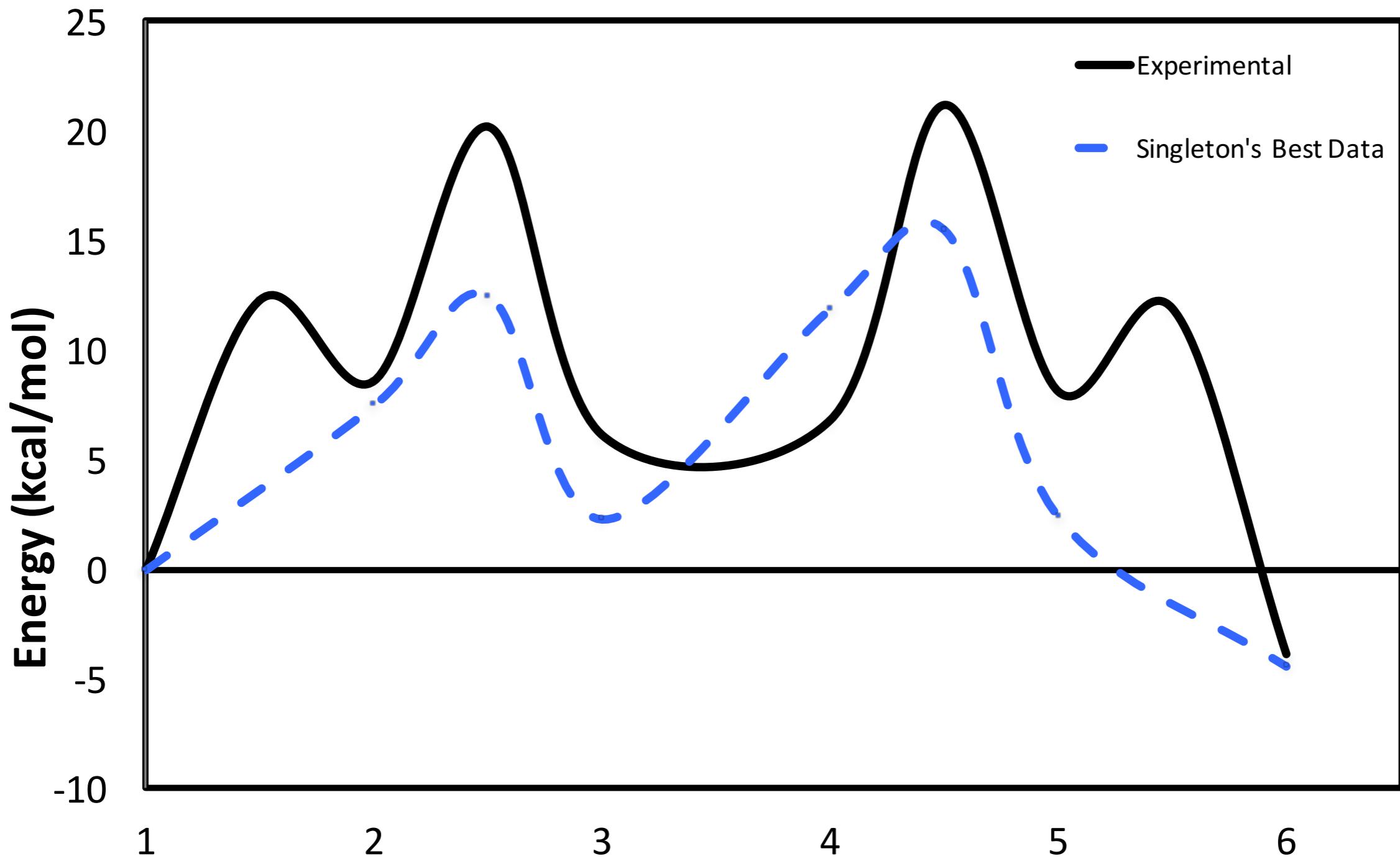
Morita-Baylis Hillman Reaction Steps

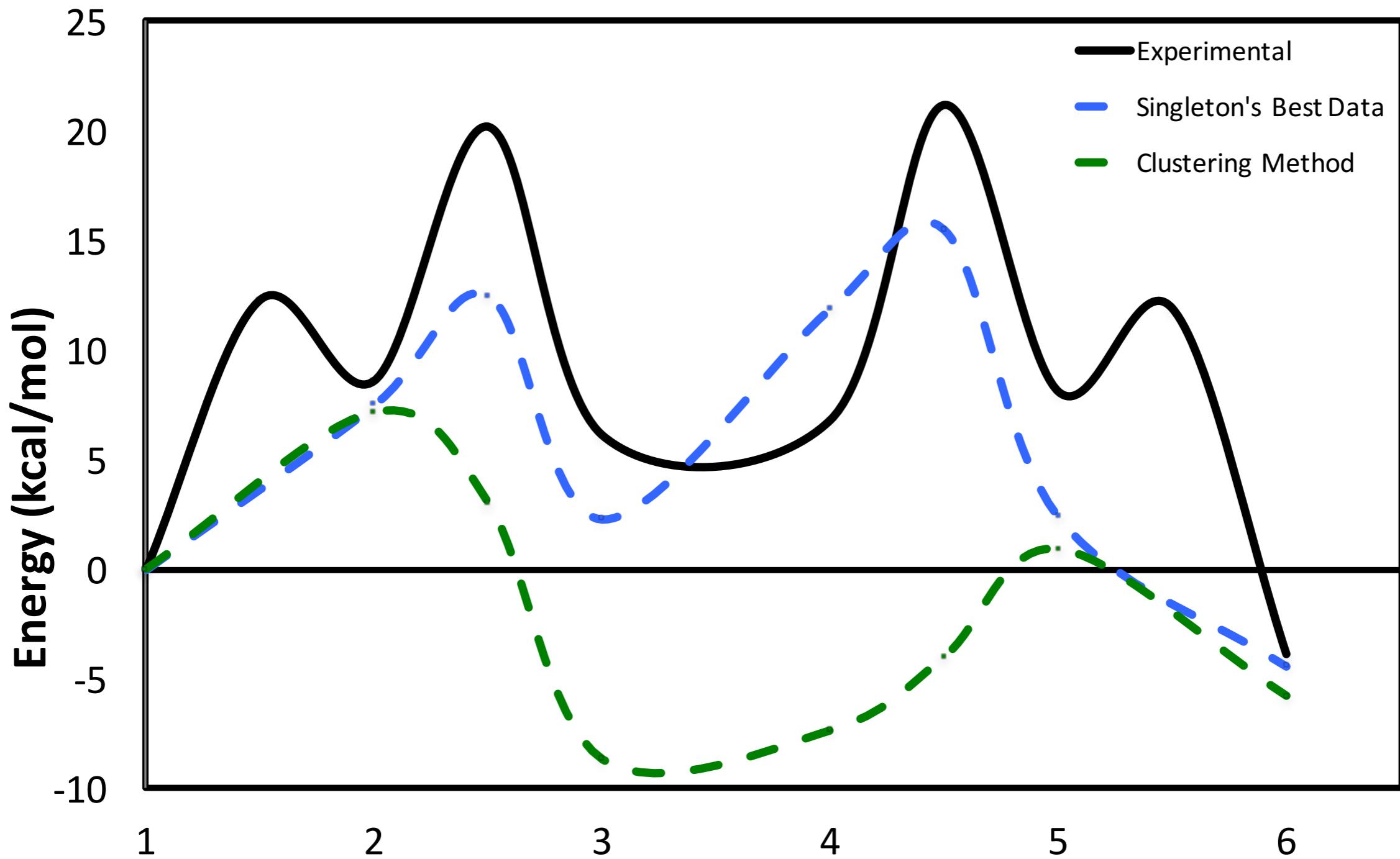


models using continuum solvent and different model chemistries

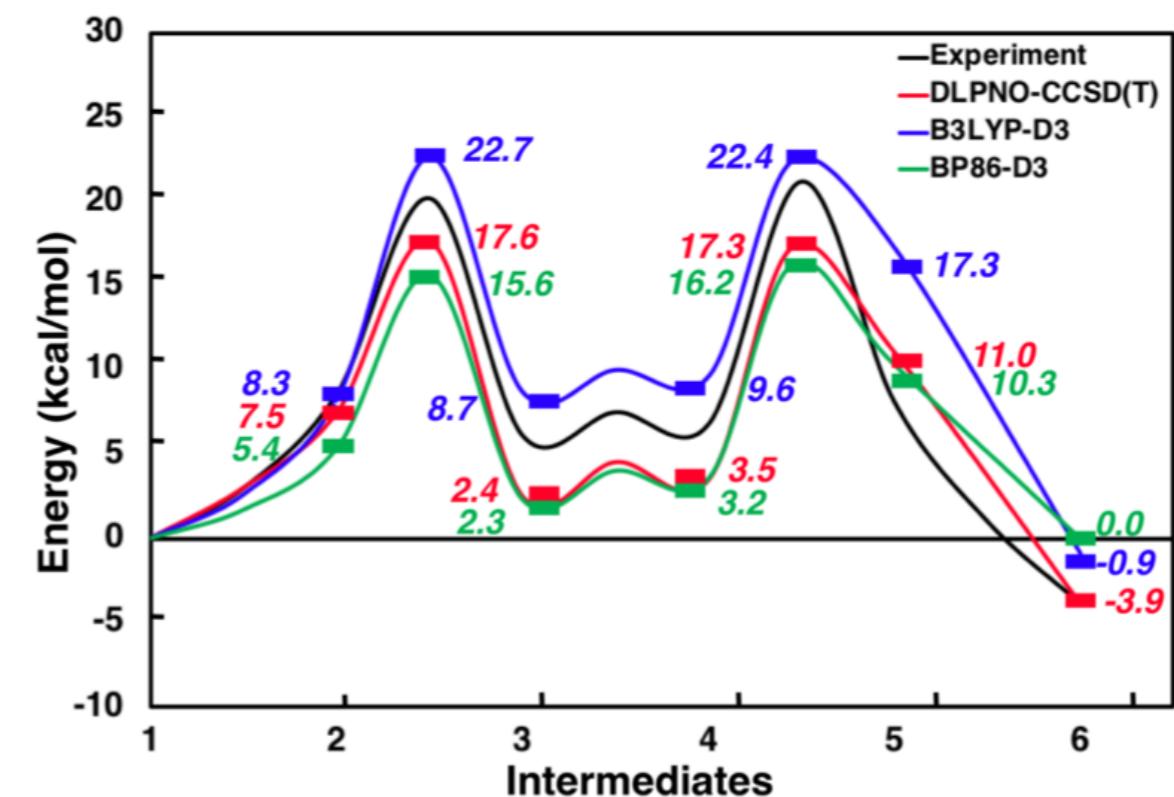
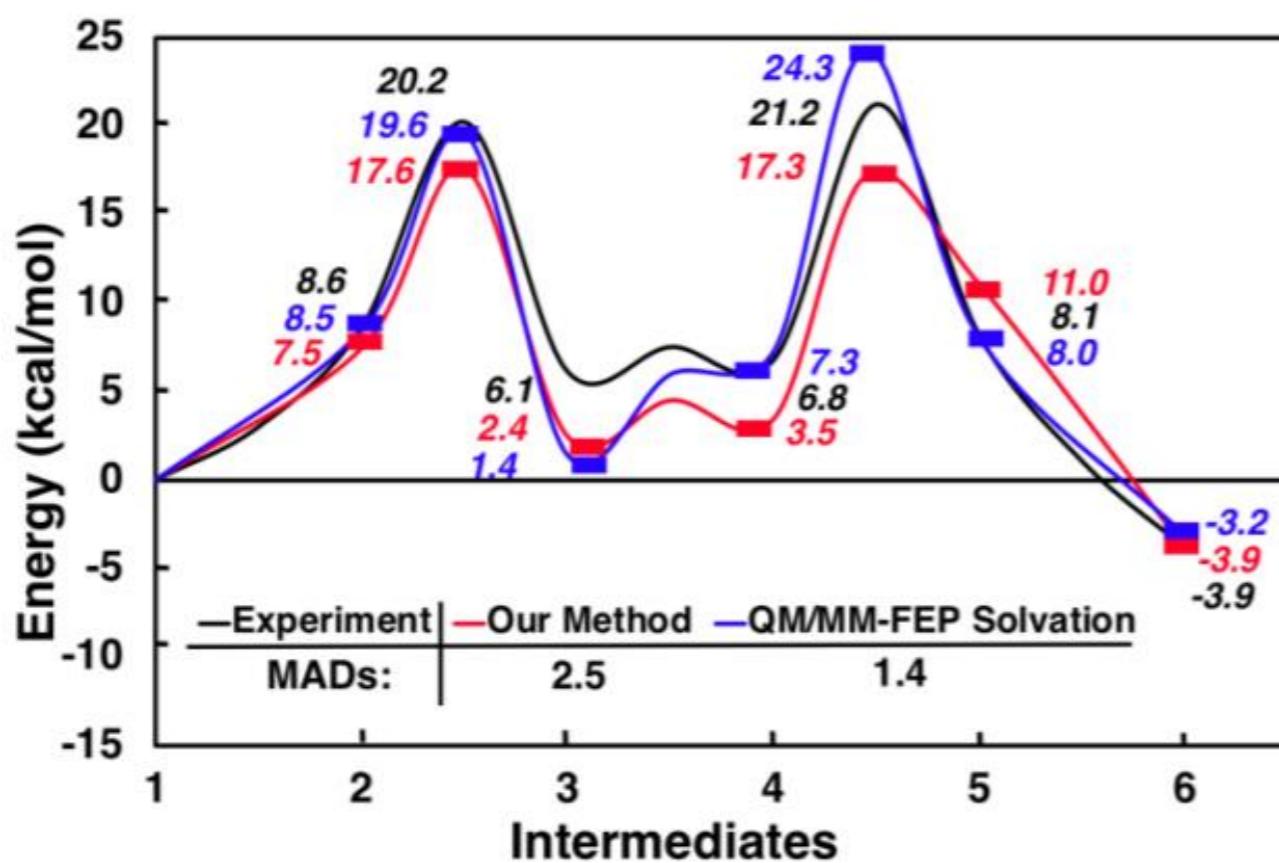








Reaction mechanism explored using Paul Zimmerman's growing string methods with five methanol molecules...



Reaction energetics somewhat dependent on level of theory used.

Keith
Group
Spring
2018

Karthi Saravanan

Mitch Groenenboom



Thank you for your attention!