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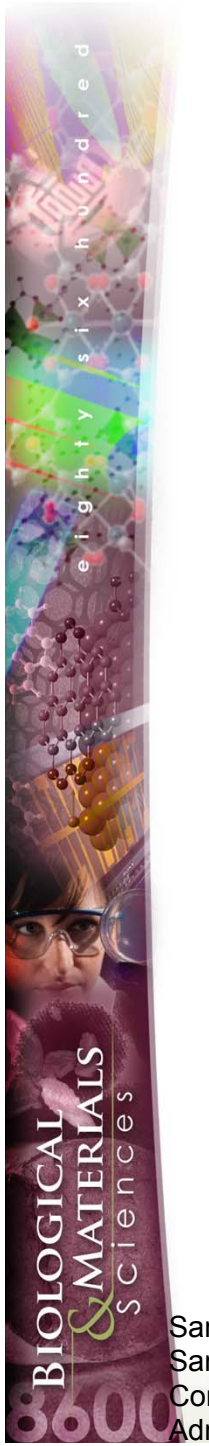

CO2 Sequestration study by Quasi-chemical Theory

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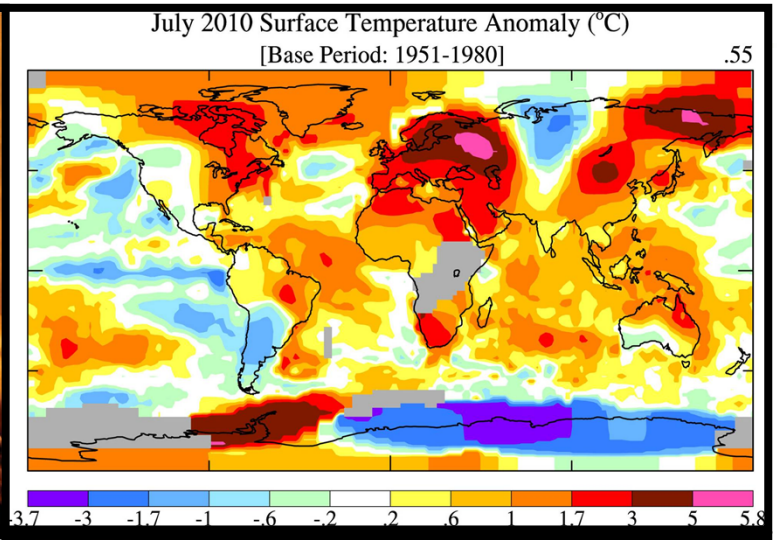
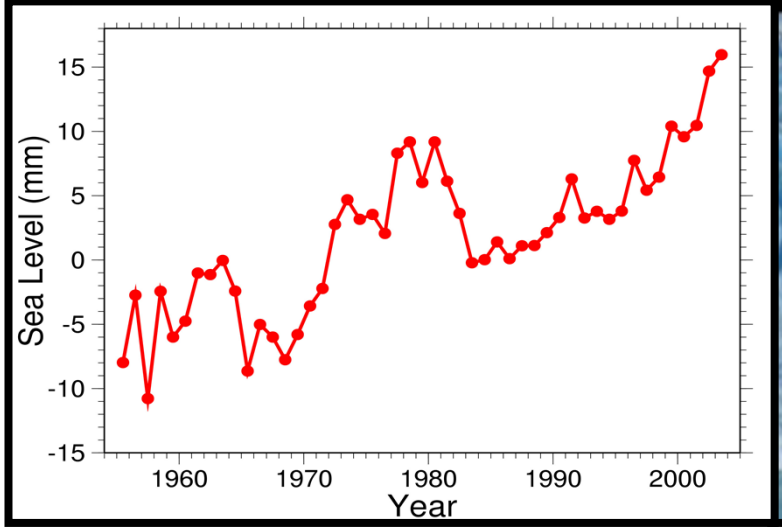
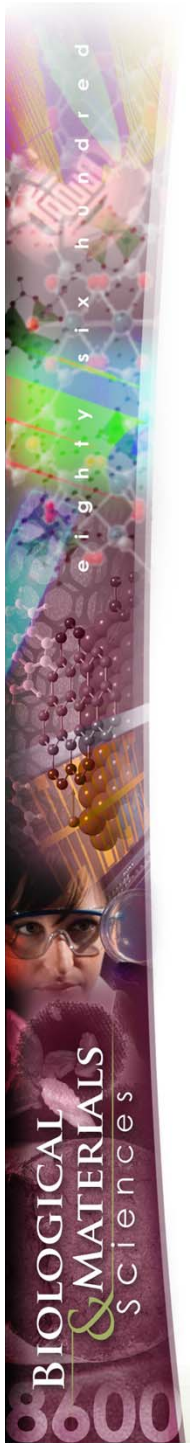
Sandia National Laboratories

Global Warming and Greenhouse Gas







Overview

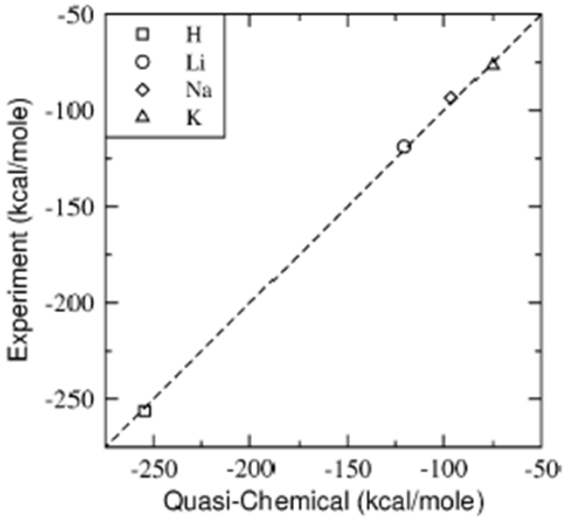
- Introduction
- Thermodynamic study of CO2 solvation in water
- Prediction of pKa shift in Carbonic Anhydrase
- Goal: Help design programmable polymer for CO2 sequestration.

Quasi-Chemical Theory

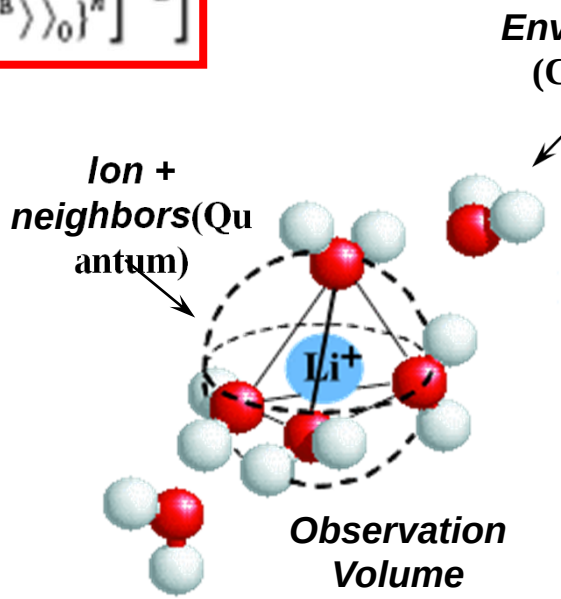
$$\beta\mu_A^{ex} = -\ln\left[\sum_{n\geq 0} K_{n,\Gamma}^{(0)}\left[\frac{\langle\langle e^{-\beta\Delta U_{AB_n}}\rangle\rangle_{0,\Gamma}}{\{\langle\langle e^{-\beta\Delta U_B}\rangle\rangle_0\}^n}\right]C_B^n\right]$$

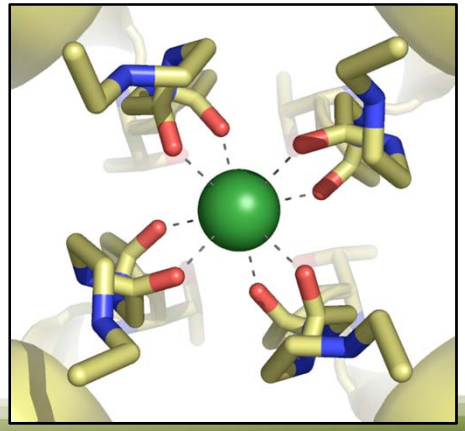
QCT provides a robust framework for 'QM/MM' division

-validated by ion hydration studies



Pratt &LaViolette (1998);
Pratt & Rempe (1999);
Beck, *et al* (2004)



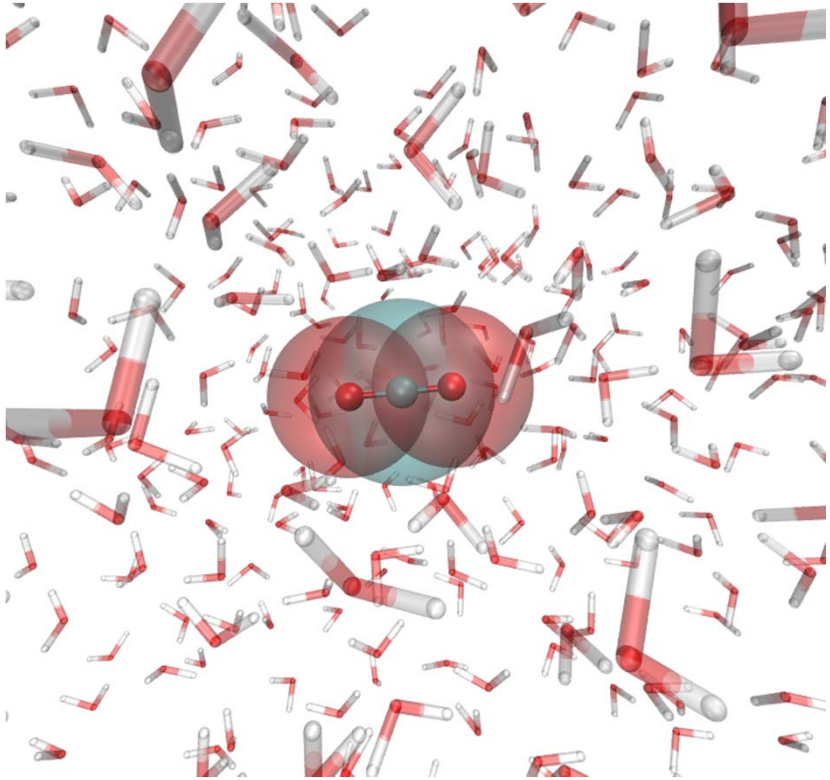


Varma&Rempe (2007)

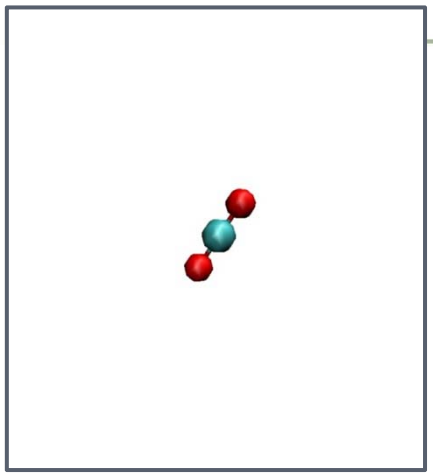
CO_2 Solvation – Direct Method

$$\mu_{CO_2}^{ex} = \overbrace{RT \ln x_0}^{inner-shell} - \overbrace{RT \ln p_0 + \mu^{el} + \mu^{vdw}}^{outer-shell}$$

- x0 – probability of finding solute in the inner shell
- p0 – probability of finding a vacuum size of inner shell

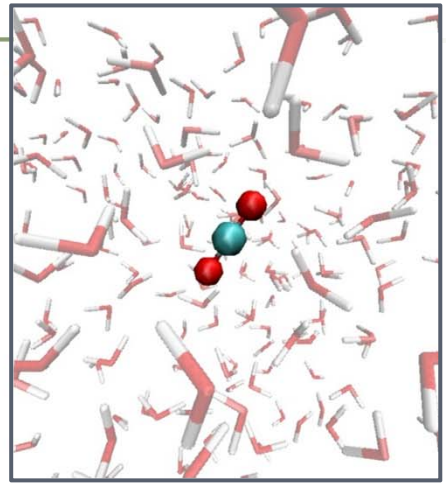


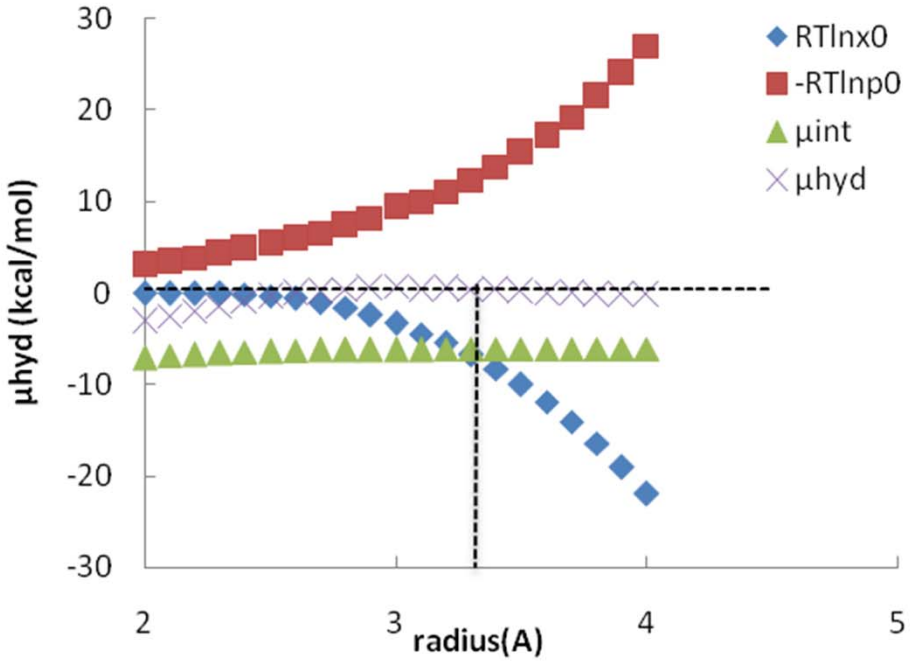
CO_2 Solvation – Direct Method



ΔGexp= 0.24 kcal/mol

ΔGqct= 0.06 kcal/mol





CO_2 Solvation – Cluster Method

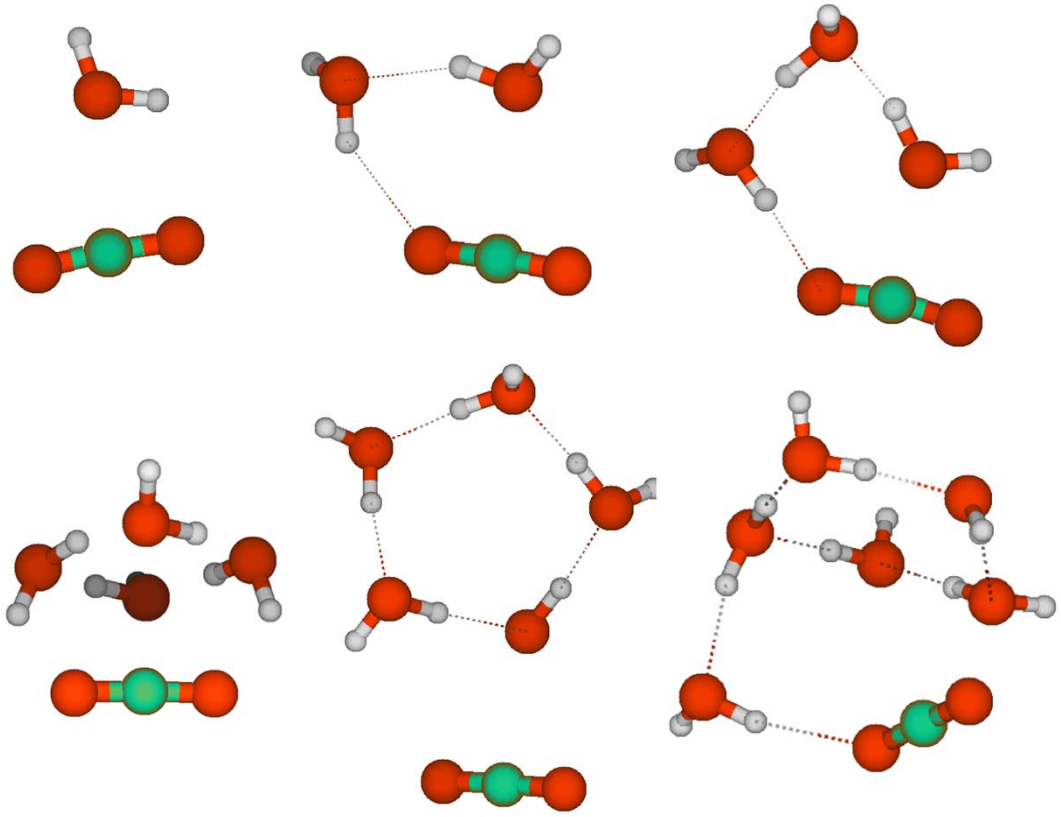
- Inner shell – gas phase (QM)

$$CO_2 + nH_2O \leftrightarrow CO_2(H_2O)_n$$

- Outer shell – implicit/explicit solvent (MM)

$$\Delta\mu^x = \mu^x_{CO_2(H_2O)_n} - n\mu^x_{H_2O}$$

CO2-H2O Clusters



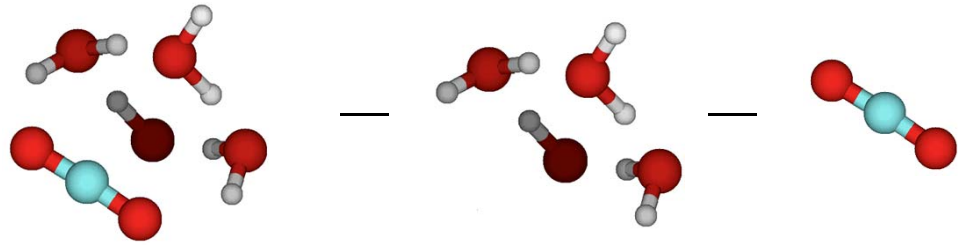
Anharmonicity

- Weak interaction between solute and ligands and h-bonding between ligands.

$$G^{anharm} = G^{(0)}_{(H_2O)_n} - nG^{(0)}_{H_2O}$$

- Preformed cluster

$$\Delta G^{(0)}_{pre-formed} =$$



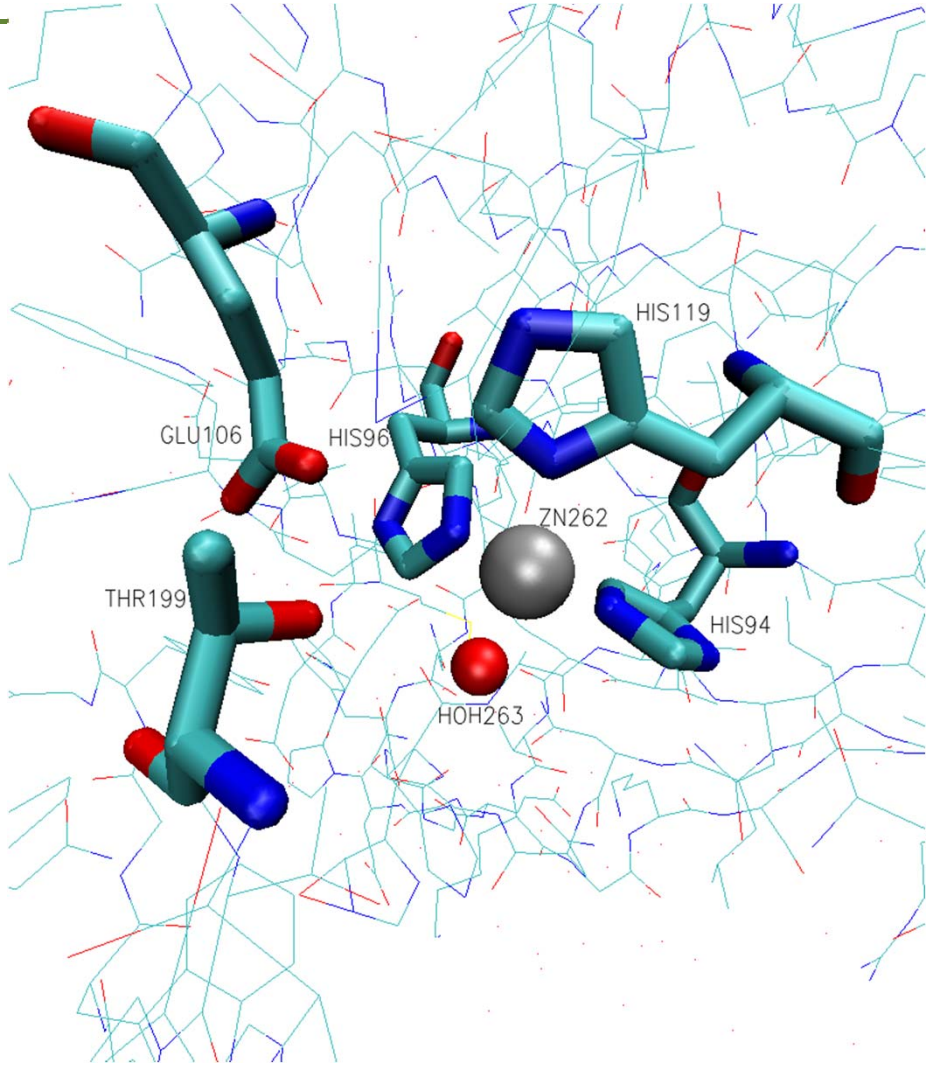
Cluster method

n	$\Delta G^{(0)}$	G^{anharm}	μ_{IS}	μ^{den}	$\Delta\mu^{el}_{out}$	μ_{OS}	μ^{ex}
1	8.79	0	6.47	-4.27	-0.87	-2.30	4.17
2	15.09	3.34	9.60	-8.54	-0.21	-6.22	3.38
3	**20.65**	**5.26**	**13.15**	**-12.81**	**-0.18**	**-10.79**	**2.36**
4	24.62	4.53	17.70	-17.08	2.83	-12.48	5.32
4[a]	**20.09**	**0**	**17.70**	**-17.08**	**-0.03[b]**	**-15.23**	**2.47**

a. **Preformed cluster**
b. **Implicit solvent**

pKa of Zinc-bound water

- Native enzyme: 6.8
- His → Asp/Glu: 8.5

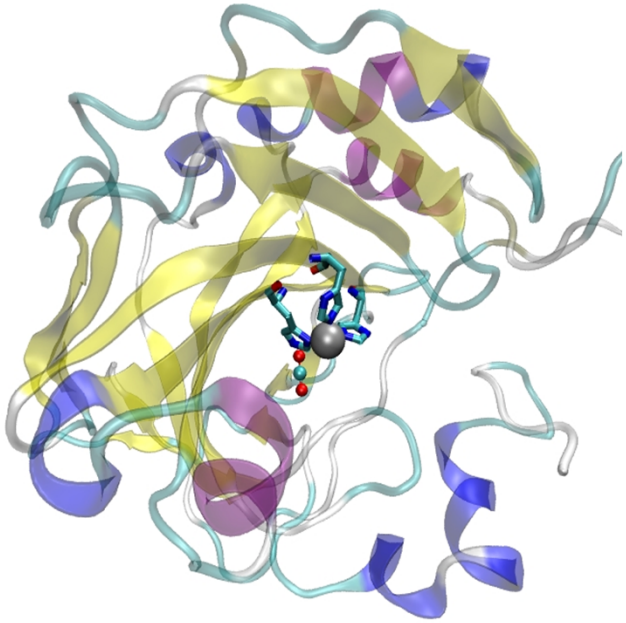


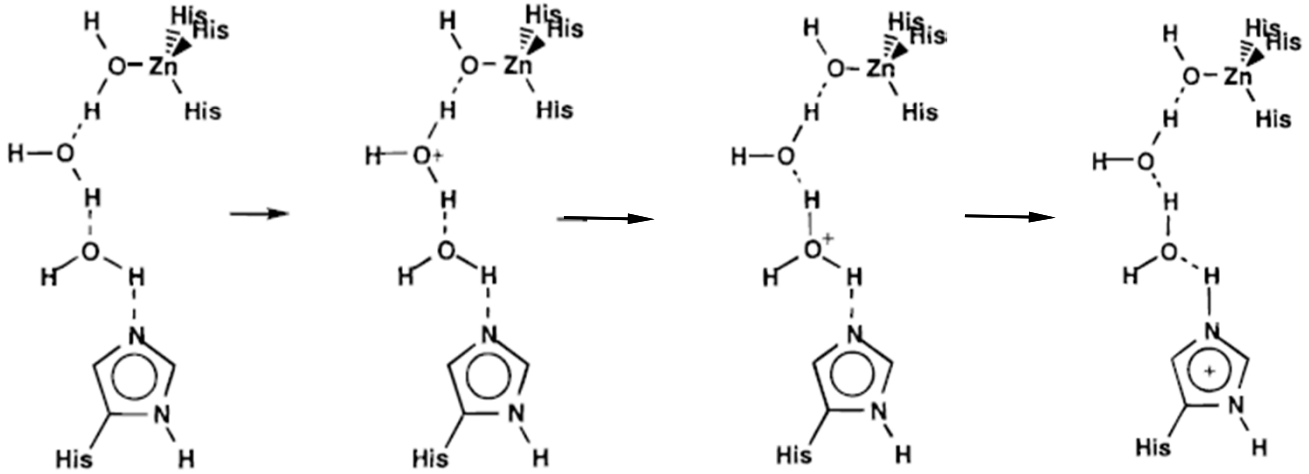
Carbonic Anhydrase

$$(E)Zn^{2+}(OH_2) = (E)Zn^{2+}(OH^-) + H^+$$

$$(E)Zn^{2+}(OH^-) + CO_2 = (E)Zn^{2+}(HCO_3^-)$$

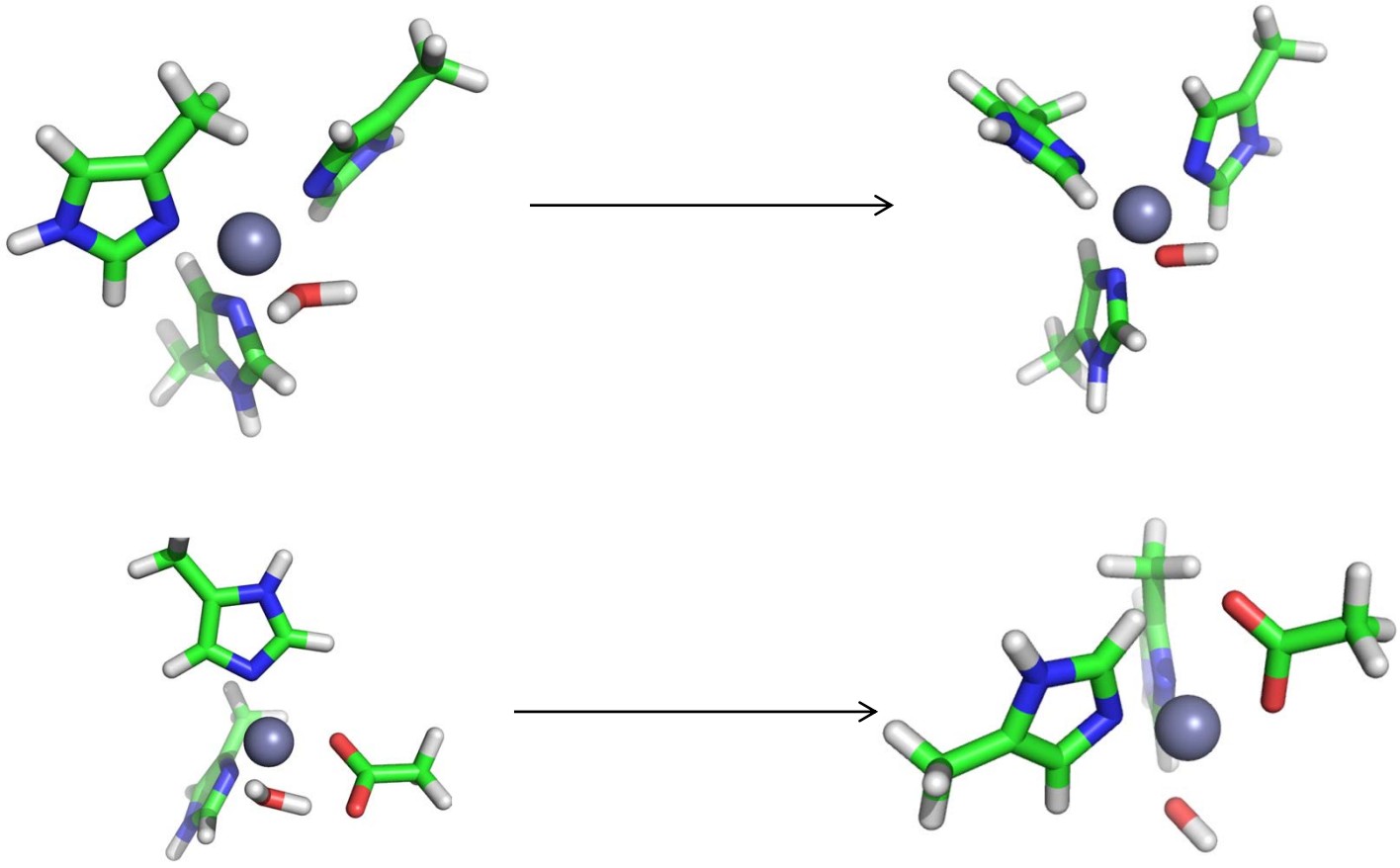
$$(E)Zn^{2+}(HCO_3^-) + H_2O = (E)Zn^{2+}(OH_2) + HCO_3^-$$

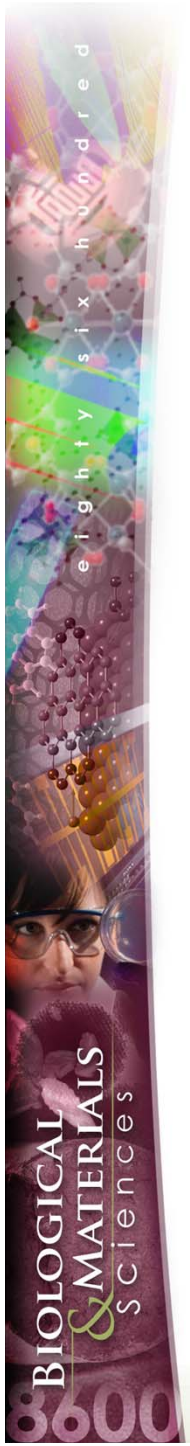




Results

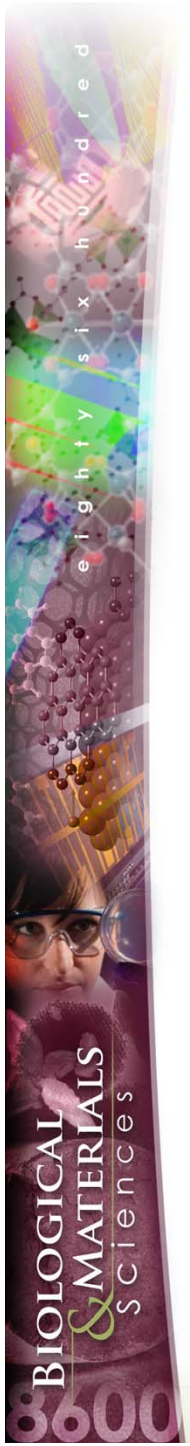
$pKa = \Delta G^{deprot}(aq)/RT\ln 10$





Conclusion

- Both approaches provide reasonable estimation of solvation free energy.
- Inner shell chemical contribution cancel out with outer shell packing term (direct).
- Independence of radius (direct).
- Asymmetric hydration shell
- Uncertainty from anharmonicity and solvent treatment.



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