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Classical/Ab initio molecular dynamics and quasichemical approaches to study hydrophobic/hydrophilic hydration phenomena

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Abstract

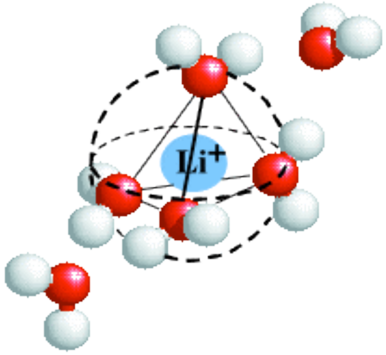
We present a computational approach to the study of hydrophobic and hydrophilic hydration based on the combination of classical/ab initio molecular dynamics and quasichemical theory. Specifically, we implement these methods to study the structural and thermal properties of small hydrophoboes and hydrophiles in water, with a special interest in krypton atom and rubidium ion as they are isolectronic species. Thermodynamic properties are evaluated by utilizing two different quasichemical approaches: `direct’ and `cluster’. In the `direct’ approach the thermodynamic property can be determined from structural information obtained by molecular simulation of the liquid state solution, while in the ‘cluster’ approach, the solute molecule of interest is successively solvated by an increasing number of surrounding solvent molecules. Both approaches have proven useful in studies of the hydration of hydrophobic/hydrophilic species that include applications to selective ion partitioning between water and biological ion channels.

Thermodynamic properties

Quasichemical theory

Basic idea - to divide a volume

- inner-shell domain
- outer-shell domain



Two approaches:

1. direct - structural information from molecular simulations is analyzed

2. cluster - first hydration shell is built one solvent molecule at the time

Thermodynamic properties

Quasichemical theory

From the potential distribution theorem

$$\beta\mu^{ex} = -ln\ \langle e^{-\beta\Delta U}\rangle$$

$$\beta\mu^{ex} = ln\ x_0 - ln\ \langle e^{-\beta\Delta U}\prod_j(1-b_j)\rangle$$

Direct approch

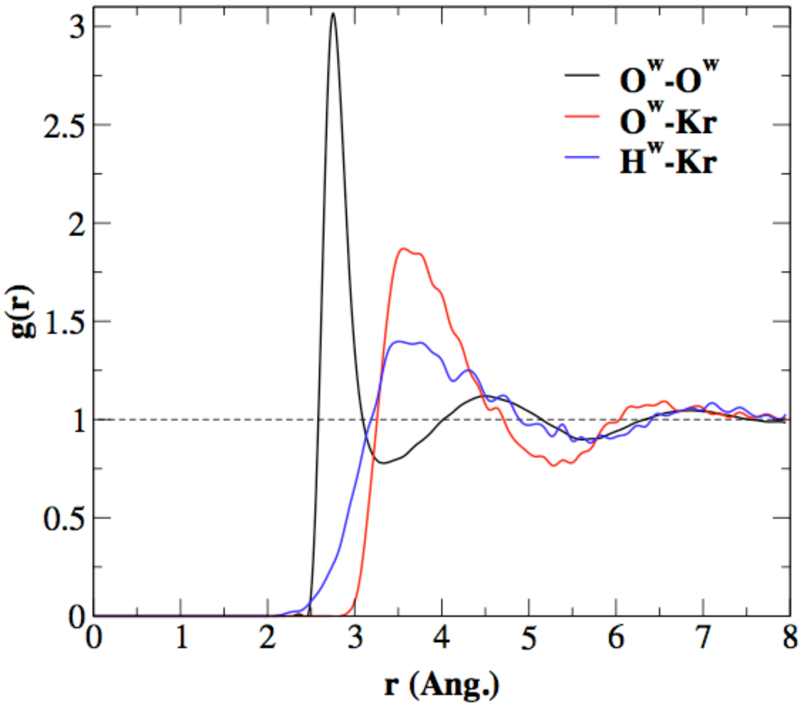
$$\mu^{ex} = RT\ ln\ x_0 - RT\ ln\ p_0 + \mu^{el} + \mu^{vdW}_{out}$$

Cluster approach

$$S + nH_2O \rightleftharpoons S(H_2O)_n$$

$$\Delta\mu^{ex} = \Delta G^{(0)} - nRT\ ln\ 1354 + \Delta\mu^{el}$$

Structural properties (classical MC): Kr(aq)

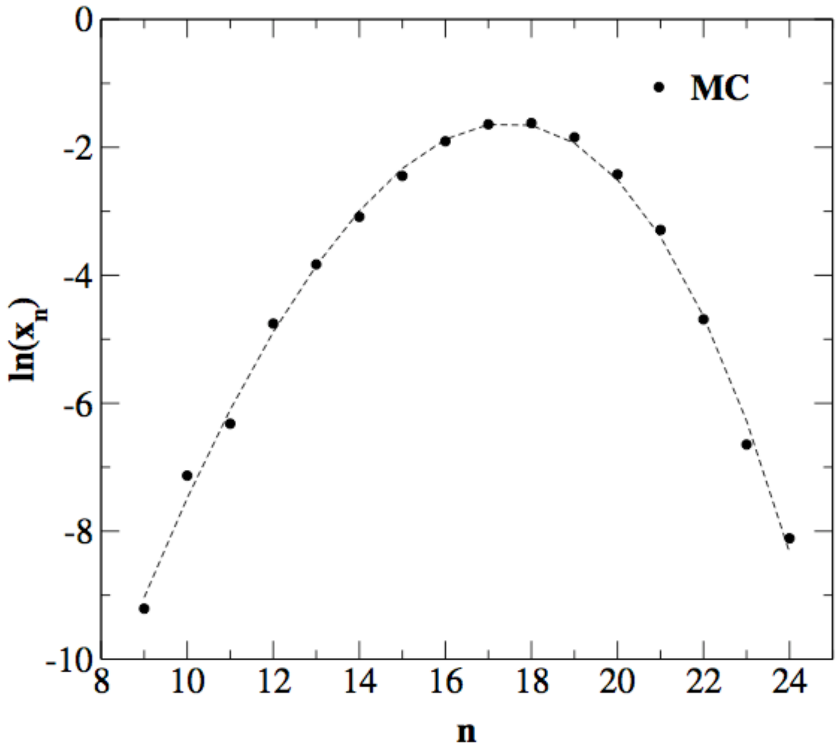


<n> = 18 waters

Experiment: PRL **81** 4164 (1998)

<n> = 18 waters

<n> = 17.6 ± 0.5



Thermal properties: Kr(aq)

Simulation (MC):

μ^{ex}=2.3 ± 0.4 kcal/mol

Experiment:

μ^{ex}=1.7 kcal/mol

Direct approach:

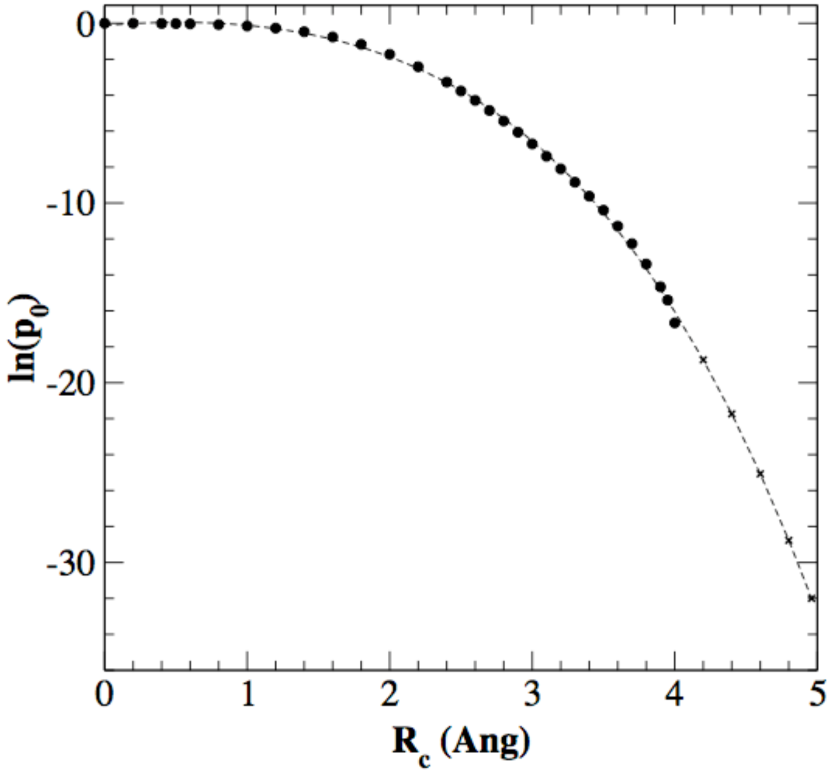
RT ln x_0=-18.9 kcal/mol

RT ln p_0= 20.8 kcal/mol

μ^{vdW} = -1.4 kcal/mol

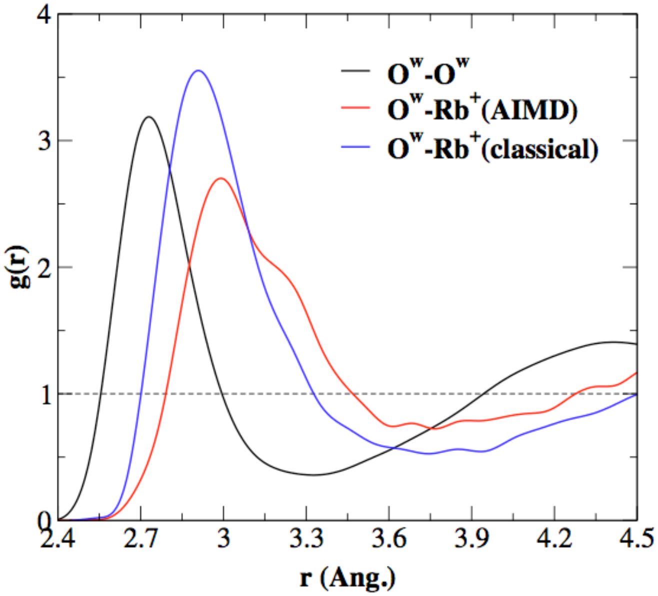
μ^{ex} = 0.5 kcal/mol

Cavity hydration free energy

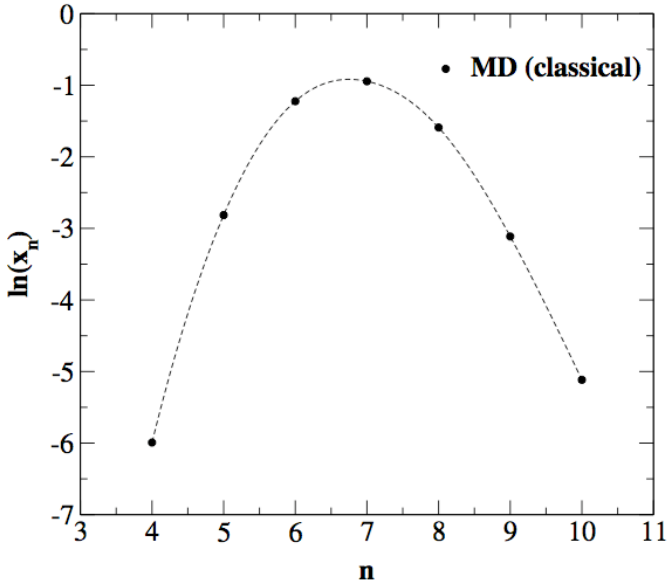


Extrapolation error ~ 1.4 kcal/mol

Structural properties: $Rb^+(aq)$



<n> = 6.9 ± 0.2

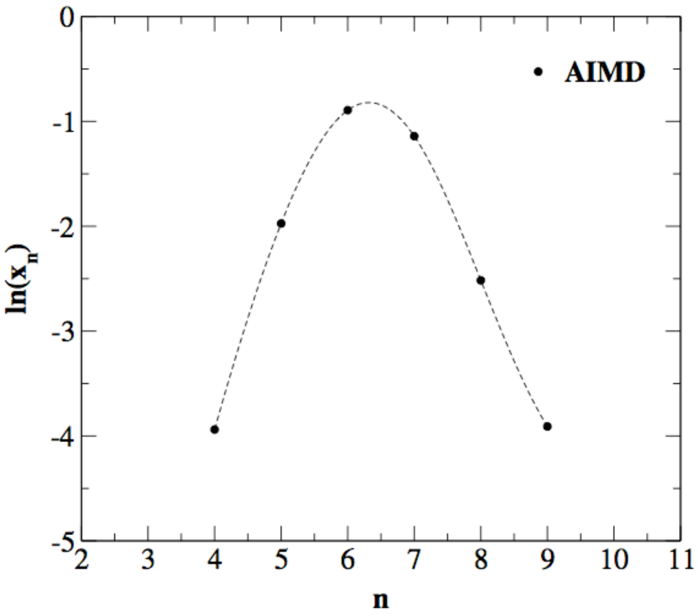


<n> = 6.2 ± 0.2

$\langle n\rangle_c$ = 6.9 waters

$\langle n\rangle_{aimd}$= 6.1waters

R_c=3.6 Å



Experiment:

Chem.Phys. **258,** 171 (2000)

<n> = 6.9 ± 0.5

JCP **105** 2161 (1996)

<n> ~ 6

Thermal properties: $Rb^+(aq)$

Experiment:

μ^{ex}=-69.5 kcal/mol

Cluster approach

Direct approach (classical MD):

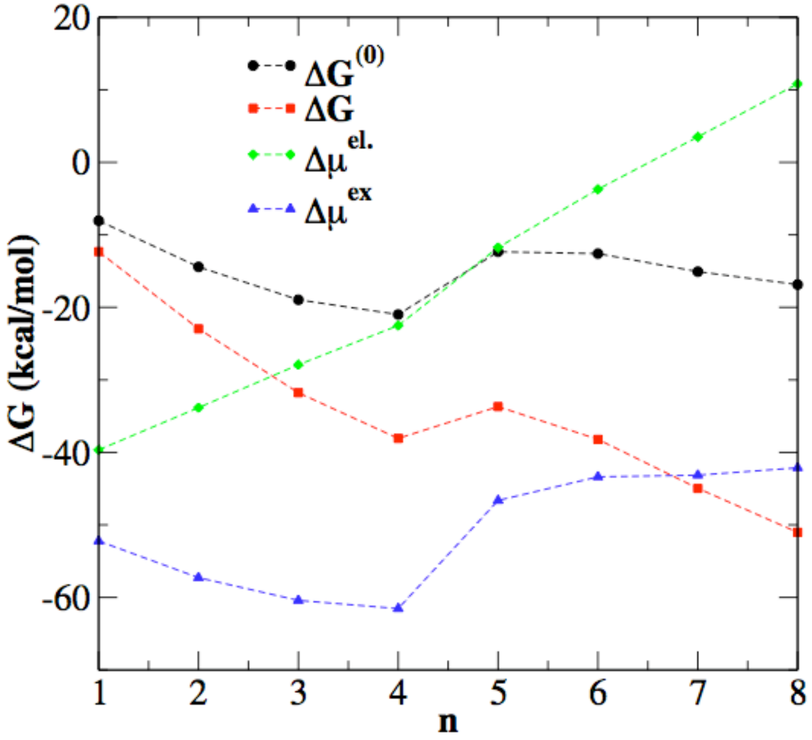
RT ln x_0=-23.2 kcal/mol

RT ln p_0= 6.7 kcal/mol

μ^{vdW} = -0.5 kcal/mol

μ^{el} = -45.6 kcal/mol

μ^{ex} = -62.6 kcal/mol



Conclusions

Structural properties of Kr(aq):

- water structure further away from solute; bulk-like
- vicinity of solute; water pushed further away from solute
- on average H & O atoms located at the same r from solute
- average and most probable coordination # is 18
- good agreement with experiment

Thermodynamic properties of Kr(aq):

- very good agreement between simulation and experiment

Structural properties of Rb^+(aq):

- classical MD vs AIMD; classical more structured than AIMD
- classical coordination # slightly larger than AIMD
- good agreement with experimental value

Conclusions

Thermodynamic properties of $Rb^+(aq)$:

- **good agreement between simulation and experiment**

Acknowledgements

Software

- Classical Molecular Dynamics simulations - GROMACS v3.1
  (Lindahl *et al*., J Mol. Mod. 2001)
- *Ab initio* Molecular Dynamics simulations - VASP v4.6
- *Classical Monter Carlo simulations* - MCCCS v4.11.7
- Quantum Chemical calculations - Gaussian03 (Gaussian Inc.)
- Implicit Solvent Simulations - APBS (Baker *et al*., PNAS 2001)

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DOE