Theory and Modeling of Specific Ion Hydration

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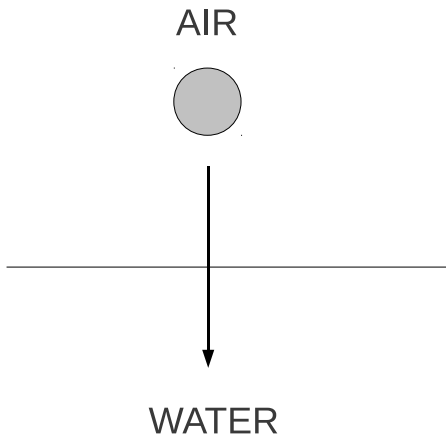
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- Not so simple as it seems
- Zhou/Stell/Friedman/Pratt theorem: if two conducting phases in contact, the interfacial potential between them is determined by the *bulk* hydration free energies of the ions in each phase (also Landau/Lifshitz vol. 8 "Galvanic cell").
- Can we extract single-ion bulk hydration free energies from available data (conventional FEs and Coe cluster data)?
- Can we learn something about specific ion hydration in the process?

Outline:

- Ion specificity: ion/water interactions involve quantum effects
- Classical models can still reveal some of the physics of hydration
- Case study in ion specificity: entropies (classical)
- Length scales and interfacial potentials in ion hydration: QM is required for accurate estimation of more collective effects, even though CM can give some insights

The water molecule (PNNL figure):

The surface potential of SPCE water is -0.6 V; QM water is 3.5 V. Neither of these is the electrochemical surface potential.

a) dipole + quadrupole
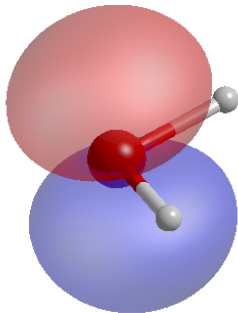
b) point charges

c) electronic structure
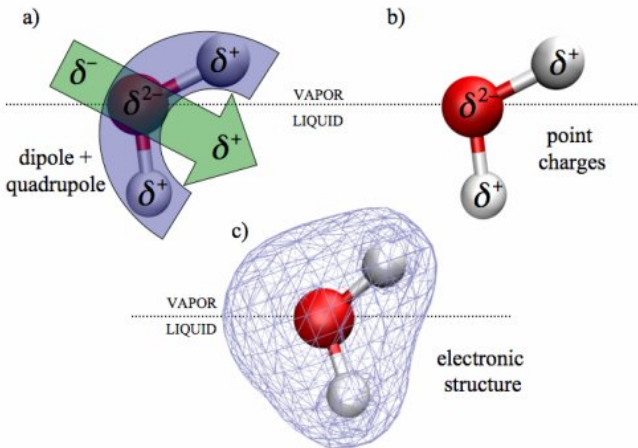
The water molecule states:
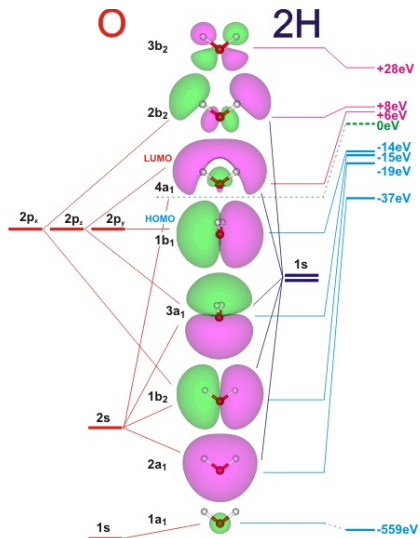
The water molecule HOMO:

Crudely speaking, the overlap of a cation s-state with the water HOMO is poor with the cation near the oxygen (small CT). Hydrogens are H-bonded to anions, greater orbital overlap and chemical character (larger CT). (The water LUMO is a Rydberg state, above).

Method // Ion	K^+	Na^+	Li^+	Br^-	Cl^-	F^-
AIMAll	0.021	0.027	0.033	-0.059	-0.060	-0.079
Henkelman	0.017	0.025	0.030	-0.052	-0.052	-0.064

AIM-derived charge transfer values (in e), computed with AIMAll and the grid-based Henkelman method. Positive means ion gets some electron density. Collective effects in bulk (ongoing); total for $Cl^- \approx -0.2$ e (Zhao, Rogers, Beck; Asher expt).

- Cations: water oxygen gains some electron density, hydrogens lose electron density symmetrically. Net loss of electron density.

- Anions: water oxygen gains more electron density, H-bonded hydrogen *loses* electron density, distant hydrogen gains some electron density. Net gain of electron density.

- This is only for one water, condensed phase shows collective effects.

- Interestingly for anions, first-shell waters are slightly underpolarized relative to bulk (Masia, JCTC, 2009)

QTAIM analysis of ion/water bond critical point

- At bond critical point, $\nabla \rho = 0$
- Charge density is relatively low, F^- is higher
- $\nabla^2 \rho$ is positive $\rightarrow$ 'closed shell' character
- Energy per electron is positive for cations, negative for anions (more chemical)
- Eigenvalues of Hessian of ρ indicate closed shell character, but anions more chemical; again F^- anomalously chemical
- Conclusion: ion/water interactions for anions show more CT, more chemistry, with F^- anomalously chemical (Collins et al 2007, McCoy et al 2006, Thompson/Hynes 2000).
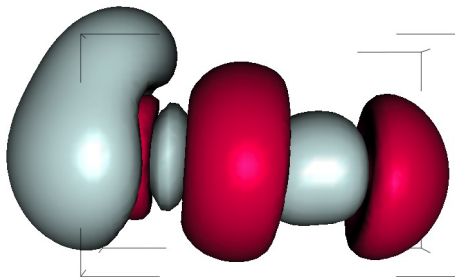
$$\Delta q(z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{z} dz' \Delta\rho(x,y,z') \qquad (1)$$

F^- (blue), Cl^- (green), Br^- (red)
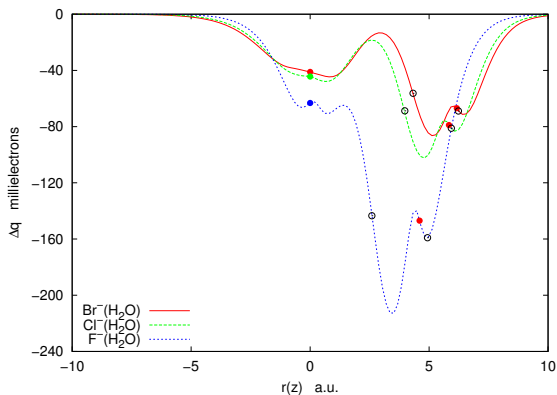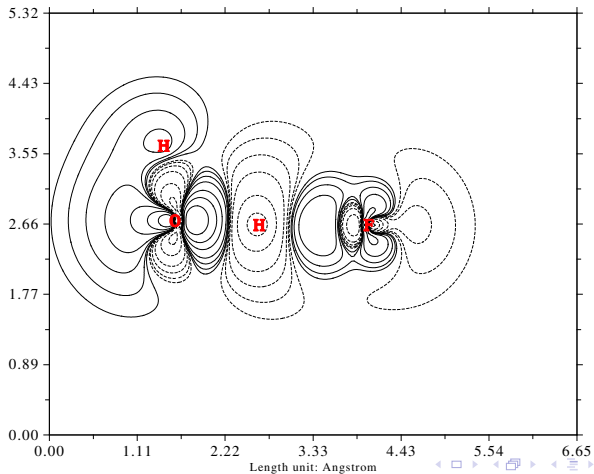
This is what a polarizable model attempts to mimic (the resulting potential outside the molecule). Water is on the left, F^- on the right. Gray is enhanced electron density, red is depletion (.001 au).

Length unit: Angstrom

SAPT partitioning of interaction energies:

Ion	Elst	Exch	Disp	Ind	CT	ΔE_{SAPT}	ΔE_{CP}^{rlx}
K^+	-19.61	8.37	-2.28	-4.63	-0.24	-18.14	-17.70
Na^+	-25.32	8.67	-1.35	-6.50	0.10	-24.28	-23.87
Li^+	-33.36	12.75	-1.08	-13.81	0.59	-35.35	-34.43
Br^-	-16.52	12.79	-4.29	-5.41	-1.47	-12.96	-12.77
Cl^-	-19.46	15.83	-4.72	-7.31	-1.84	-15.05	-14.75
F^-	-45.13	49.59	-8.59	-27.88	-7.09	-27.49	-27.05

SAPT2+3-CT energy decomposition analysis of the ion-water dimers with accompanying supermolecular and perturbation theory binding energies. CT estimate from method by Stone. Units in kcal mol^{-1}.
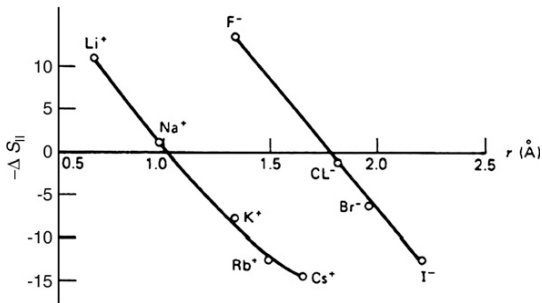
Water models:

- Classical point charge models: electrostatics and ion size
- Addition of higher distributed multipoles (Stone)
- Polarization in classical models (most previous pol models have over-polarized anions by 2x). New CT models (Rick).
- The form of the LJ repulsive core is too repulsive (Cahill/Parsegian), and induction/dispersion only at crude level
- Quantum models get the charge density right, but are severely limited
- What to do?

- Ion specificity is relatively local
- Far-field response is relatively Gaussian
- Local interactions are specific and can have chemical aspect
- We can partition free energies (QCT, LMFT), atoms in molecules (QTAIM-Bader, Partition Theory-Wasserman), interactions (SAPT)
- Partitioning helps reveal origins of collective behavior
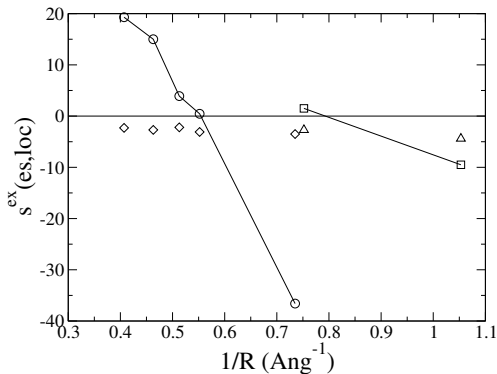- Classical models can still be helpful (below)

Ion specificity (expt entropy):

Kosmotropes and chaotropes: entropy change to convert a water molecule into an ion (K. Collins, et al., 2007).
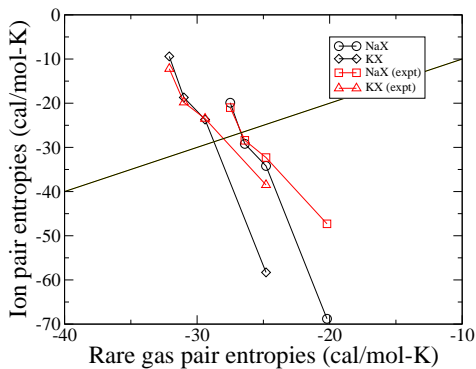
LMFT partitioning of $\Delta S_{solv}(ES)$: local and far-field parts. Cations are 'more chaotropic', what keeps them from the water surface?

Ion specificity (computed, classical):

Ion pairs vs. rare gas pairs, ΔS_{solv}

Length-scale partitioning of free energy

$$\beta\mu^{ex} = \ln\left\langle e^{-\beta U_{HS}(\lambda)}\right\rangle - \ln\left\langle e^{-\beta U_{HS}(\lambda)}\right\rangle_0 - \ln\left\langle e^{-\beta\Delta U}\right\rangle_{U_{HS}(\lambda)} \tag{2a}$$
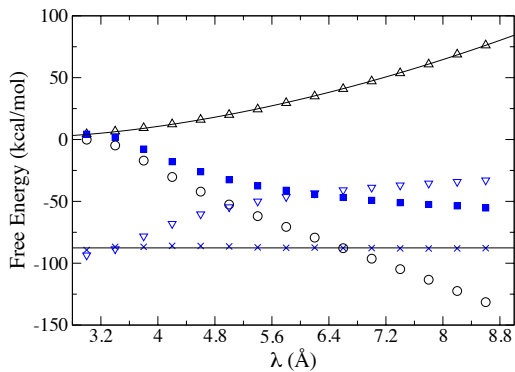
$$= \ln x_0(\lambda) - \ln p_0(\lambda) - \ln\left\langle e^{-\beta\Delta U}\right\rangle_{U_{HS}(\lambda)} \tag{2b}$$

$$= \beta[\mu_{IS}^{ex}(\lambda) + \mu_P^{ex}(\lambda) + \mu_{LR}^{ex}(\lambda)] = -\ln\left\langle e^{-\beta\Delta U}\right\rangle_0 \tag{2c}$$

1) Inner-shell 2) Packing 3) Long-ranged terms (total λ indepedent)

Cl- all terms:

SPC/E water, Horinek/Netz ions

Anion IS data:

Ion specificity followed by linearity (ion-dipole, not macroscopic). Macroscopic should be sum of λ^2 and λ^{-1} terms to balance P and LR. The 'universal' length scale occurs at the cavity size where the cavity formation free energy cancels a Born model estimate of the LR term.
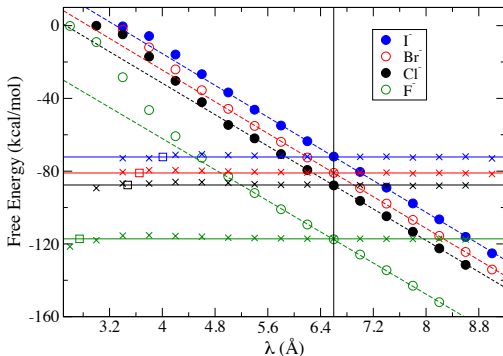
- Cations and anions show consistent length scale where IS equals the total free energy, but length differs between cations and anions
- That free energy in periodic boundaries is termed the 'intrinsic' free energy
- It includes information from the ion-water boundary, but does not include a distant water liquid-vapor interface
- When the cation/anion data is shifted by ± 9.5 kcal/mol-e all IS free energies collapse to a single length scale of 6.15 Å. This is the cavity potential in PBC (SPCE).

The electrochemical potential

- Electrochemical definition

$$\mu = kT \ln \left[\rho \Lambda^3 \right] + \mu^{ex} = kT \ln \left[\rho \Lambda^3 \right] + \mu^{ex}_{int} + q\phi_{sp} \qquad (3)$$

- ϕ_{sp} is large positive in real water (3.5 V)
- Re-definition (Harder and Roux, Vorobyov and Allen)

$$\mu^{ex} = \mu^{ex}_b + q\phi_{np} \qquad (4)$$

- $\phi_{np} = \phi_{lp} + \phi_{sp} = -11.6$ kcal/mol-e (-0.5 V) is net potential at center of uncharged ion (LPS approach, Ashbaugh and Asthagiri, 2008)
- This is the 'electrochemical surface potential': yields exact shift between Marcus (-253.4 kcal/mol) and Coe (-265.9 kcal/mol) proton free energies.
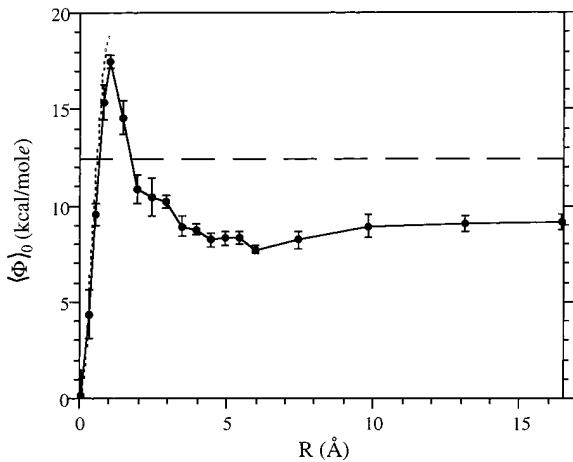
Results

- Based on above analysis, ϕ_{np} for SPC/E is -4.3 kcal/mol-e (-0.20 V)
- Crude QM prediction: scale by $3.1/2.35 \rightarrow$ -5.7 kcal/mol-e
- Correct sign but factor of 2 off
- This suggests SPC/E water orientations near the cavity are decent but not perfect
- Expt: including a cavity repulsion for water H's pushes ϕ_{np} much closer to experiment, -10.5 kcal/mol-e vs. -11.6 kcal/mol-e (-0.5 V). Also almost perfectly Gaussian
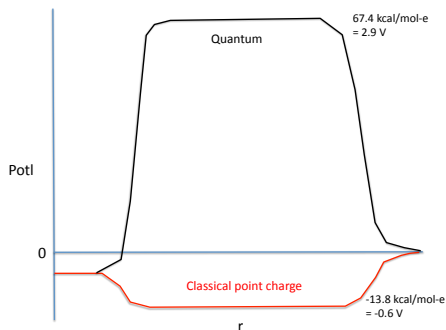
Partitioning the cavity potential

Figure: Black: QM potential profile. Red: CM potential profile. The mean potential at the cavity center is -0.5 V (expt). Quadrupole trace makes the difference. QM necessary for accurate ϕ_{np} and correct ϕ_{sp}.

Quasi-chemical theory (QCT):

Rearranging the QCT, a fundamental formula for the free energy that links accurate QM for the inner-shell with Ninham/Parsegian approach for interaction of inner-shell cluster with medium (Pratt et al.):

$$\mu_X^{ex} = -kT \ln K_n^{(0)} \rho_W^n + kT \ln p_X(n) + \mu_{XW_n}^{ex} - n\mu_W^{ex} \qquad (5)$$

Terms:

- Accurate QM for formation of XW_n cluster in *gas phase*.
- Probability of inner-shell occupation in the medium
- Solvation free energy of the cluster: continuum dielectric response (all frequencies)?
- Free energy of water in water, known

Summary:

- Ion specificity is relatively local
- Classical models incorporate some of the physics
- But the interactions, especially near the ion, involve complex charge rearrangements, some chemistry, and QM dispersion
- Partitioning of interactions is a first step (Parsons, Duignan, Ninham)
- The QCT is a helpful theoretical framework for partitioning
- Future: Partitioning and The Law of Matching Water Affinities

- Even with the Zhou/Stell/Friedman/Pratt theorem...
- Crucial in setting consistent scale for single-ion bulk hydration free energies: electrochemistry
- Larger magnitude than changes in surface potl due to changing ion concentration
- If such a net (electrochemical) surface potential exists (-0.5 V), it results in one part of FE driving force: pushes anions toward water surface, cations away (protons are special).
- The potential can alter the near-surface auto-ionization of water
- Are there longer-ranged collective effects? Exclusion zone of Pollock: protons expelled, anions remain behind?

Papers:

- D. M. Rogers and T. L. Beck, Quasi-Chemical and Structural Analysis of Polarizable Anion Hydration, J. Chem. Phys. **132**, 014505 (2010).
- *Z. Zhao, D. M. Rogers, and T. L. Beck, Polarization and Charge Transfer in the Hydration of Chloride Ions J. Chem. Phys. **132**, 014502 (2010).
- T. Beck, Hydration Free Energies by Energetic Partitioning of the Potential Distribution Theorem, J. Stat. Phys. **145** 335 (2011).
- *T. Beck, A local entropic signature of specific ion hydration, J. Phys. Chem. B **115**, 9776 (2011).
- A. Arslanargin and T. L. Beck, Free energy partitioning analysis of the driving forces that determine ion density profiles near the water liquid-vapor interface , J. Chem. Phys. **136**, 104503 (2012).
- *T. L. Beck, The influence of water interfacial potentials on ion hydration in bulk water and near interfaces, Chem. Phys. Lett. **561-562**, 1 (2013).
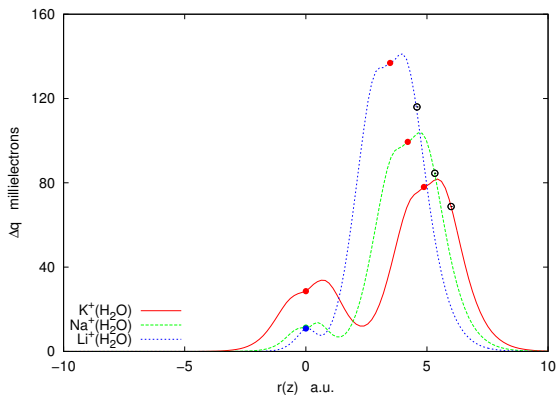- *Y. Shi and T. L. Beck, Length scales and interfacial potentials in ion hydration, J. Chem. Phys., in press (2013).

A larger density isosurface (0.005 au vs. 0.001 above)
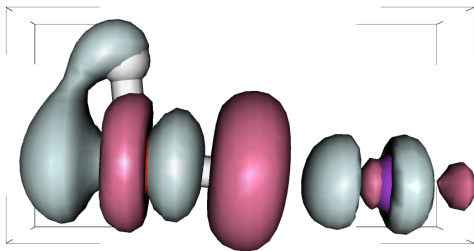
$$\Delta q(z) = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{z} dz' \Delta \rho(x, y, z') \qquad (6)$$

Li^+ (blue), Na^+ (green), K^+ (red)

Water atomic basin CT:

Atom // Ion	K^+	Na^+	Li^+	Br^-	Cl^-	F^-
O (AIMAll)	0.065	0.081	0.113	0.095	0.107	0.187
O (Henkelman)	0.071	0.082	0.105	0.102	0.111	0.187
H_{bond} (AIMAll)	-0.043	-0.054	-0.073	-0.057	-0.074	-0.172
H_{bond} (Henkelman)	-0.044	-0.054	-0.068	-0.069	-0.084	-0.183
H_{far} (AIMAll)	-0.043	-0.054	-0.073	0.022	0.028	0.063
H_{far} (Henkelman)	-0.044	-0.054	-0.068	0.019	0.025	0.060

For cations, the water oxygen has enhanced electron density while the two hydrogens show depletion (symmetrically). For anions, the water oxygen shows a larger enhancement, the H-bonded hydrogen shows a depletion, and the distant hydrogen shows some enhancement.

QTAIM analysis of ion/water bond critical point

Ion	r(H$_2$O-bcp)	ρ	$\nabla^2\rho$	H/ρ	G/ρ	V/ρ	$|V|/G$	$|\lambda_1/\lambda_3|$
K$^+$	1.28	0.02133	0.11071	0.17206	1.12564	-0.95359	0.84715	0.16
Na$^+$	1.22	0.02626	0.18296	0.23305	1.50876	-1.27609	0.84578	0.16
Li$^+$	1.15	0.03898	0.29118	0.22140	1.64597	-1.42458	0.86549	0.18
Br$^-$	0.74	0.02354	0.04840	-0.09813	0.61215	-0.71028	1.16031	0.26
Cl$^-$	0.68	0.02980	0.06402	-0.12785	0.66510	-0.79295	1.19223	0.27
F$^-$	0.40	0.08925	0.10227	-0.58611	0.87249	-1.45860	1.67176	0.41

Atoms in molecules (AIM) data at the X-W bond critical point:
chemical or closed shell? Ion/water bonds have closed shell
character (positive Laplacian), but anion/water (H-bond) case is
'more chemical', especially F$^-$ (ratio of potential to kinetic energy,
per electron). Eval ratios (perp/par) of ρ Hessian give similar
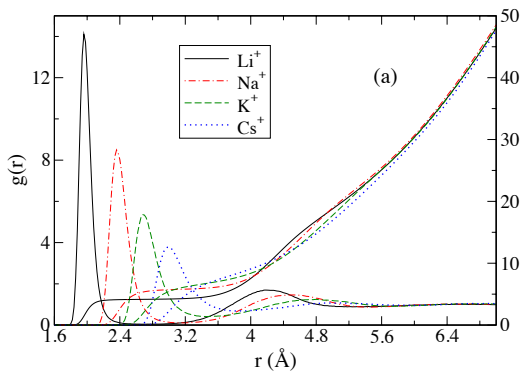picture; if ratio > 1, then strongly chemical.

Classical and quantum ϕ_{np}

Figure: Black full: QM potential distribution. Black dash: CM potential distribution. The mean potential at the cavity center is between -9.9 (QM) and -7.5 (CM) kcal/mol-e at cluster center. Red curves: near cluster surface.
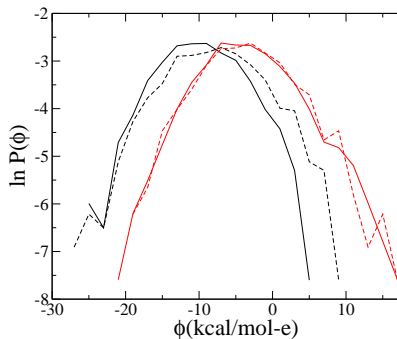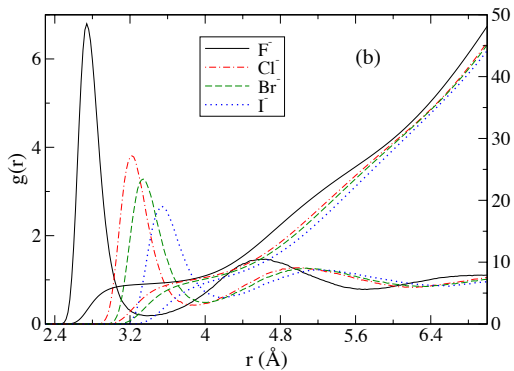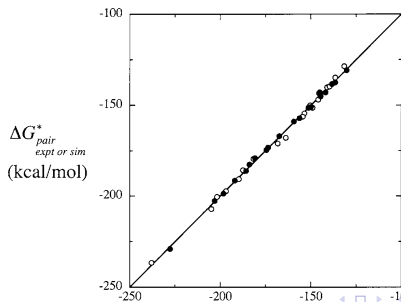
Cation X-O rdfs:

SPC/E water, Horinek/Netz ions

What is ϕ_{np}?

Ashbaugh and Asthagiri (building on Latimer, Pitzer, Slansky) $\rightarrow$ -11.6 kcal/mol-e. Agrees exactly with shift between Marcus and Coe et al. estimates of free energy of the proton.

$$\mu^{ex}(\text{pair}) = -\frac{q^2}{2}\left(1 - \frac{1}{\epsilon}\right)\left(\frac{1}{r_+ + \delta_+} + \frac{1}{r_- + \delta_-}\right) + 2\lambda \quad (7)$$

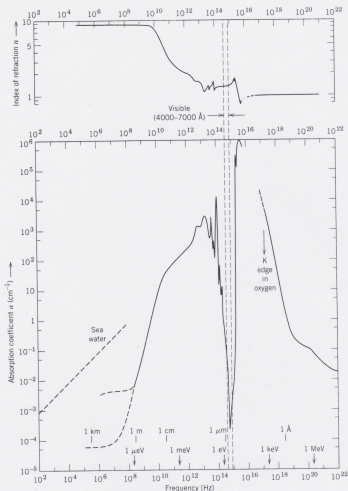# Water index of refraction:

Figure 7.9   The index of refraction (top) and absorption coefficient (bottom) for liquid water as a function of linear frequency. Also shown as abscissas are an energy scale (arrows) and a wavelength scale (vertical lines). The visible region of the frequency