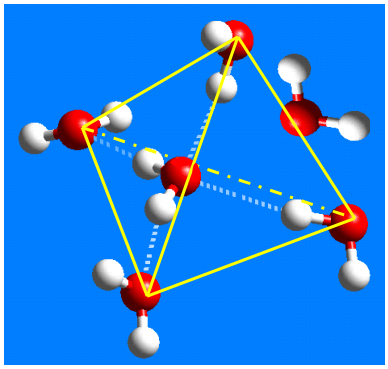
NE-M1-PRI12ENP – Integrated Nuclear Engineering Project

Molecular Modeling of Materials for Nuclear Waste Disposal Applications

Lecture 3 – Atomistic Simulations of the Properties of Water and Hydrogen Bonding



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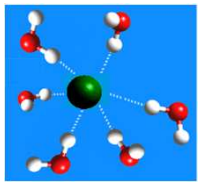

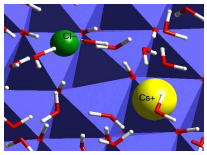

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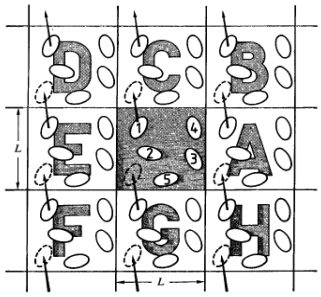
Classical MC & MD Molecular Modeling - Details

- N ~ 1,000-1,000,000 atoms / t ~ 1-10 ns / n ~ 10^6-10^7 conf.
- Typically, constant T,P or T,V statistical ensembles
- Many molecular modeling software packages currently available.
- Most important: develop efficient numerical tools for the analysis of MD-generated trajectories or MC-generated ensembles of configs.
- *Coordinates* → Equilibrium thermodynamic properties
  → Atom-atom radial distribution functions
  → Coordination numbers, hydration numbers
  → Fluid structure, hydration shells
  → Molecular cluster formation and sorption environments
- *Velocities* → Diffusion
  → Velocity autocorrelation functions
  → Power spectra; dynamic details of atomic motions
- Comparison and interpretation of spectroscopic measurements: NMR, IR, Raman, X-ray.
- Molecular mechanisms controlling the behavior of aqueous species in solution and at substrate interfaces.

Methods of Molecular Computer Simulations: Molecular Dynamics (MD) and Monte Carlo (MC)

- **MD - time averages** over a dynamic trajectory in the phase space of the simulated system
- **MC - ensemble averages** over a computer-generated random Markov chain of molecular configurations
- Periodic boundary conditions (PBC)



MD MC

$$T = \frac{2}{3Nk_B}\left\langle \sum_{i=1}^{N} \frac{m_i \mathbf{v}_i^2}{2} \right\rangle$$

$$D = \lim_{t\to\infty} \frac{1}{6Nt} \left\langle \left| \mathbf{r}(t) - \mathbf{r}(0) \right|^2 \right\rangle$$

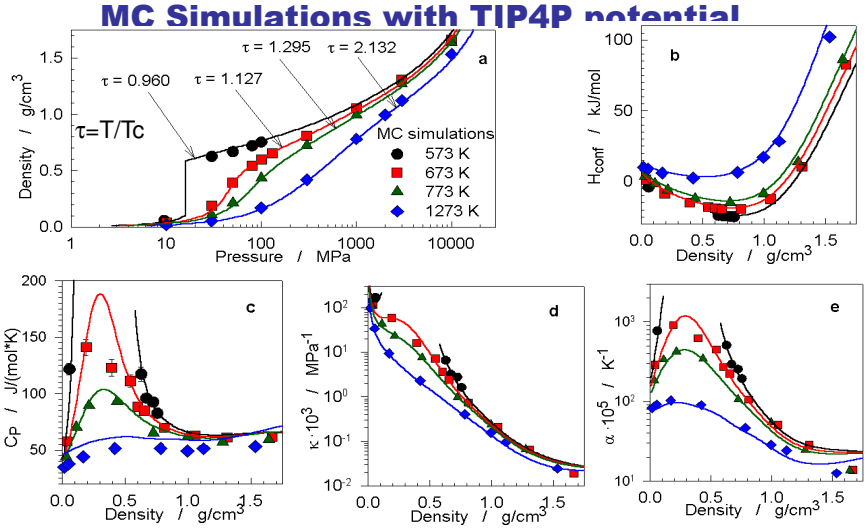
$$P = \frac{Nk_B T}{V} - \left(\frac{1}{3V}\right)\left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle$$

$$H_{conf} = \langle U \rangle + P\langle V \rangle$$

$$V_m = \langle V \rangle N_A / N$$

$$g_{ij}(r)$$

Thermodynamic Properties of Water MC Simulations with TIP4P potential



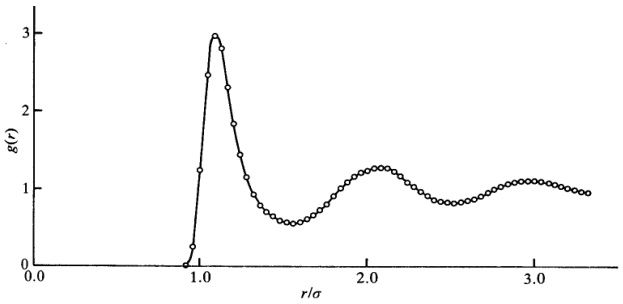
Kalinichev, *Rev. Mineral.Geochem.*, **42**, 83-129 (2001)

Fluid Structure
Radial Distribution Functions (RDFs)

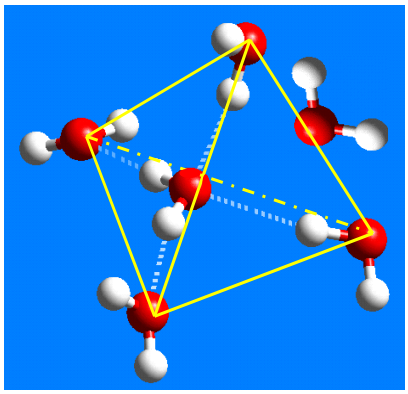
- ***Pair distribution function*** or ***radial distribution function g(r)*** – probability to find an atom *i* at a certain distance *r* from another atom *j*
- Normalized to a completely random distribution of atoms in space

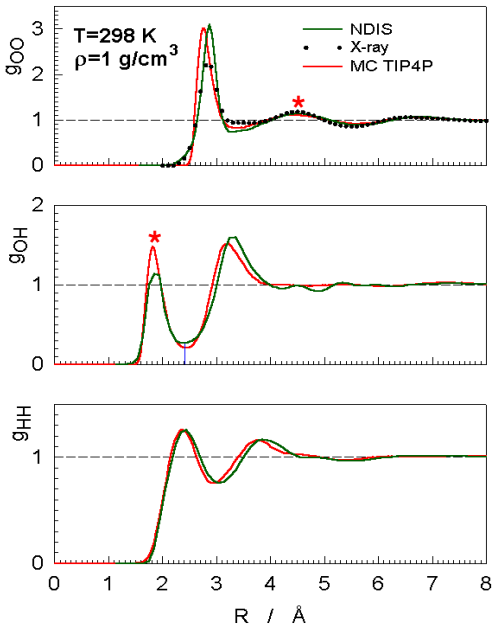
$$g(r) = \rho^{-2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r}_i)\delta(\mathbf{r}_j - \mathbf{r}) \right\rangle = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle$$

- Comparable to exp. data on X-ray or neutron diffraction
- In practice, $\delta(\mathbf{r}\text{-}\mathbf{r}_{ij})$ is replaced by a function which is non-zero in a very narrow range of **r**, and *g*(**r**) is calculated as a histogram
- *g*(**r**) = 1 for ideal gas



Structure of Water: Atom-Atom Radial Distribution Functions (RDFs)

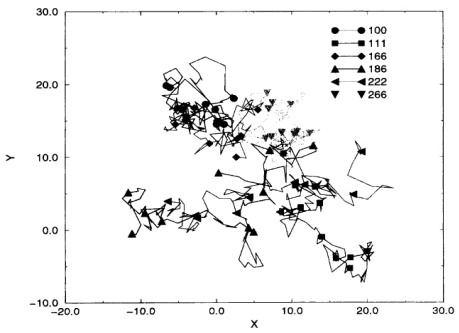


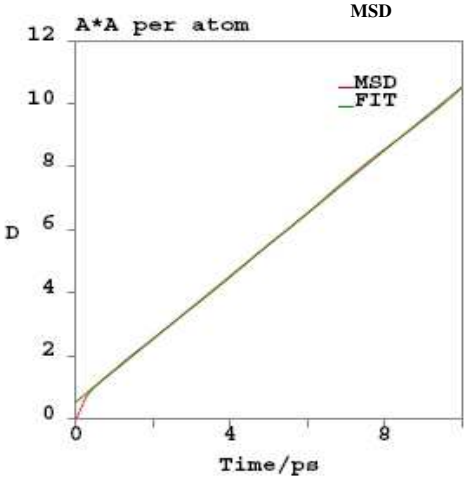


Self-Diffusion Coefficients

- Self-diffusion coefficient *D* of a species is proportional to the ***mean-squared displacement*** of this species in the limit of large *t*:

$$D = \lim_{t\to\infty} \frac{1}{6Nt} \underbrace{\left\langle \left| \mathbf{r}(t) - \mathbf{r}(0) \right|^2 \right\rangle}_{\text{MSD}}$$

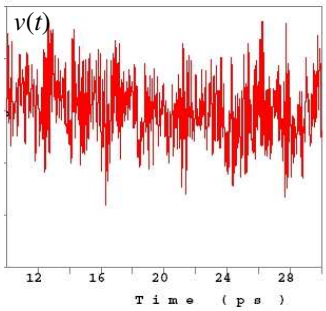




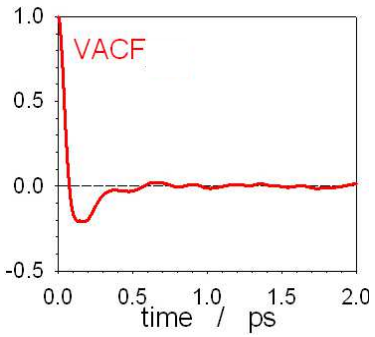
$$D = \lim_{t\to\infty} \frac{1}{3} \int_0^t \left\langle \mathbf{v}(0) \cdot \mathbf{v}(t') \right\rangle \, \mathrm{d}t'$$

Dynamics of Individual Atoms: Velocity Autocorrelation Functions

$$\mathrm{VACF} \equiv C_{vv}(t) = \frac{\left\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \right\rangle}{\left\langle \mathbf{v}(0)^2 \right\rangle} = \frac{1}{\left\langle \mathbf{v}(0)^2 \right\rangle} \int \mathbf{v}(0) \cdot \mathbf{v}(\mathrm{t}) \; d\Gamma$$



Qualitatively, the VACF reflects the relative rate with which the system or its individual atoms "forget" the velocities they had at a particular moment in time, indicated here as t = 0.

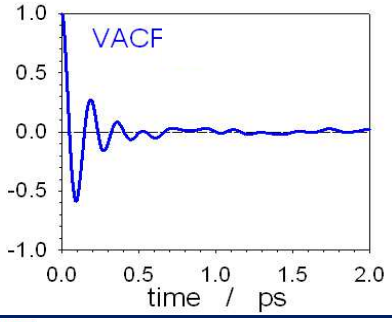


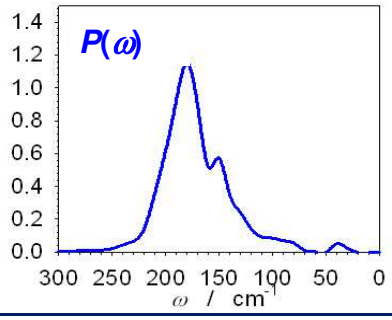
$$\left\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \right\rangle = \frac{1}{N_\tau N} \sum_{i=1}^{N_\tau} \sum_{j=1}^{N} \mathbf{v}_j(t_i) \cdot \mathbf{v}_j(t_i + t)$$

Dynamics of Individual Atoms
VACFs and Power Spectra

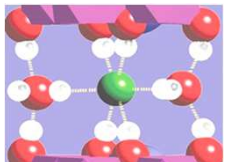
$$\text{VACF} \equiv C_{vv}(t) = \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle} = \frac{1}{\langle \mathbf{v}(0)^2\rangle}\int \mathbf{v}(0)\cdot\mathbf{v}(t)\; d\Gamma$$

$$P(\omega) = \int_0^{\infty} \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle} \cos(\omega t)\, dt$$

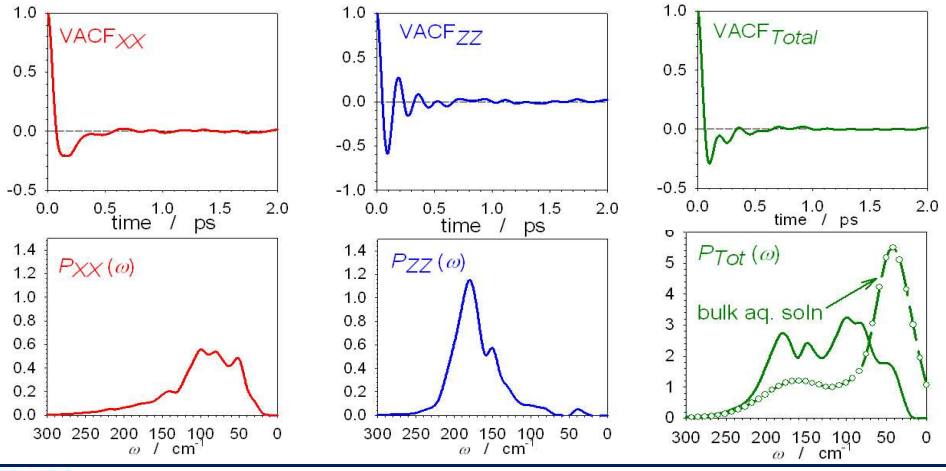




Dynamics of Individual Atoms
VACFs and Power Spectra

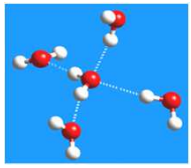


Cl^- in $LiAl_2(OH)_6Cl{\cdot}3H_2O$



Dynamics of Individual Atoms
VACFs and Power Spectra

H_2O



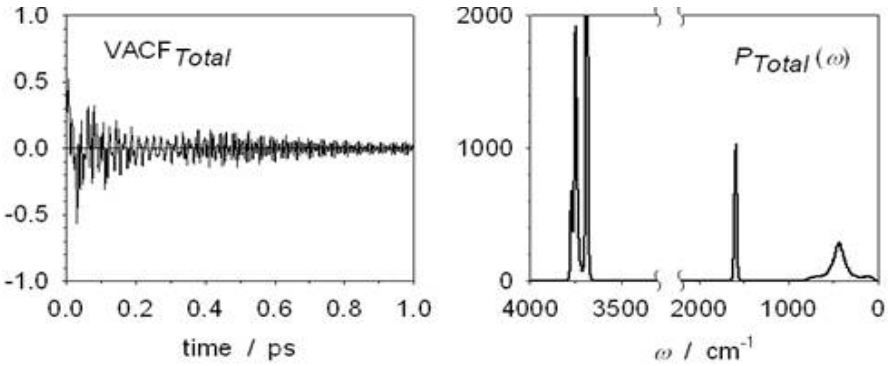
ω ~ 4000 [cm^{-1}]

$\lambda = 1/\omega = 1 / 4000$ [cm] = 2.5 ·10^{-6} [m]

c = $\lambda\nu = \lambda/\tau$

$\tau \sim \lambda/\chi$ =2.5 ·10^{-6} [m] / 3 ·10^{8} [m/s] ~10^{-14} [s]

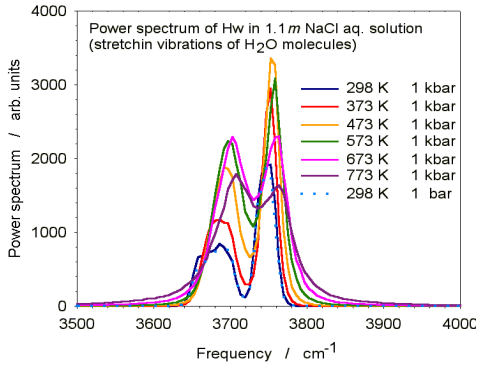
⇒ **Time step ~ τ/ 10 ~ 10^{-15} [s] = 1 [fs]**

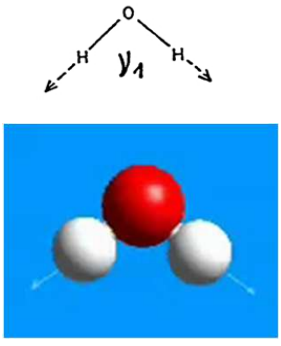


SPC: Intramolecular Stretching Vibrations of H_2O Molecules in NaCl Solutions as a Function of Temperature

$$P(\omega) = \int_0^\infty \frac{\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle}{\langle \mathbf{v}(0)^2 \rangle} \cos(\omega t)\, dt$$

symmetric stretch





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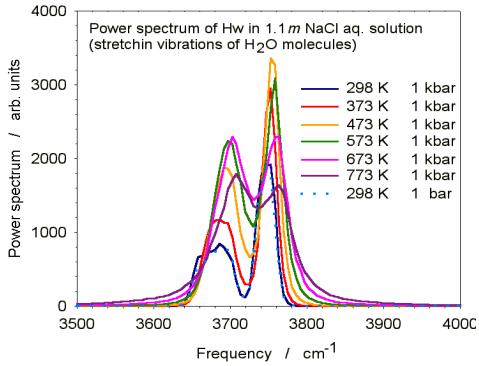
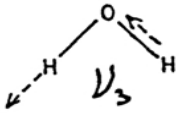
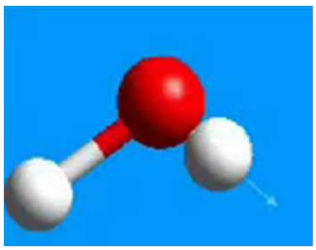


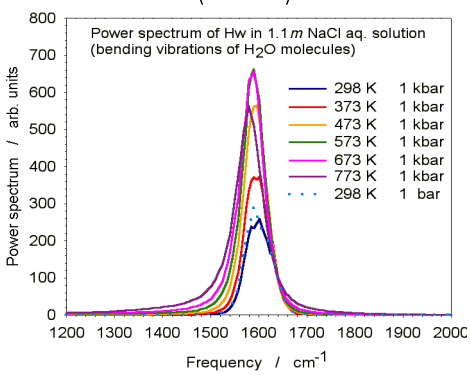
asymmetric stretch



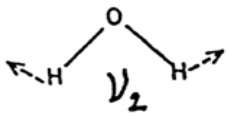


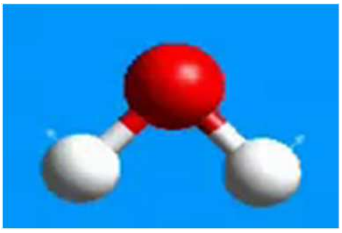
SPC: Intramolecular Bending Vibrations of H_2O Molecules in NaCl Solutions as a Function of Temperature

$$P(\omega) = \int_0^{\infty} \frac{\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle}{\langle \mathbf{v}(0)^2 \rangle} \cos(\omega t)\, dt$$



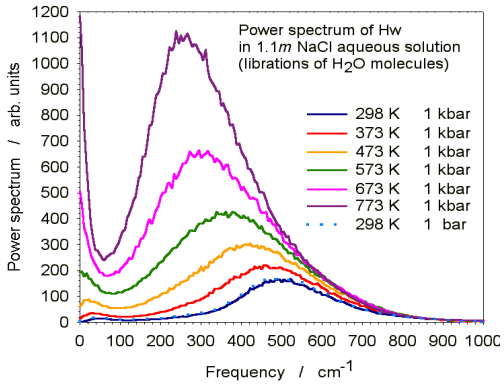
bending



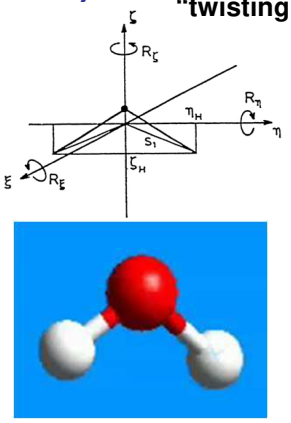


The bending spectrum is largely unaffected by the changes of temperature and density.

SPC: H_2O Molecular Librations (Hindered Rotations)

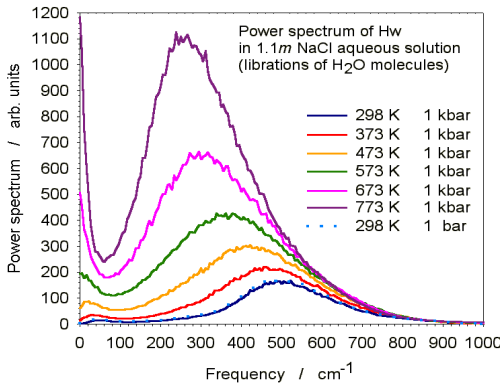


"twisting"

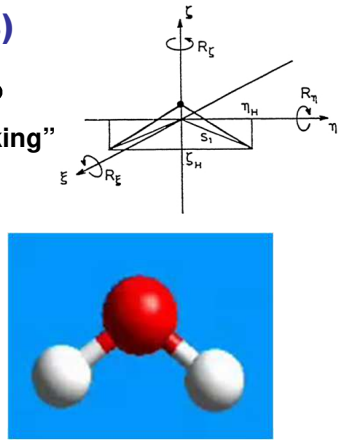


The broad frequency band of H_2O librations (hindered rotations) in the H-bonding network is centered around ~500 cm^{-1} and gradually decreases with increasing temperature and decreasing density.

SPC: H_2O Molecular Librations (Hindered Rotations)



"rocking"



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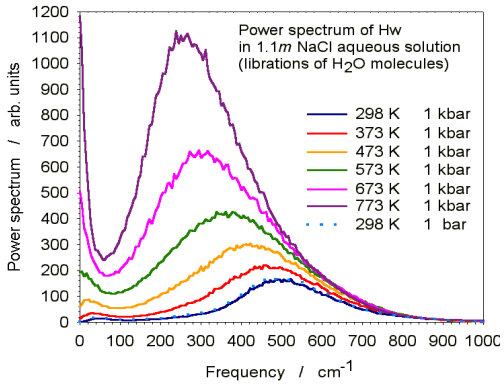
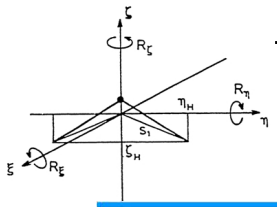
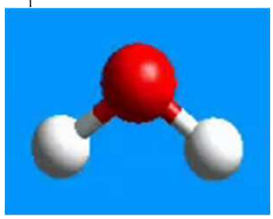


"wagging"

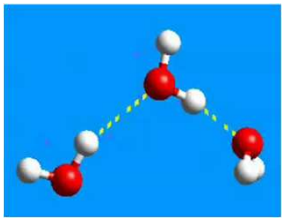


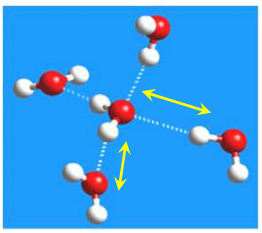


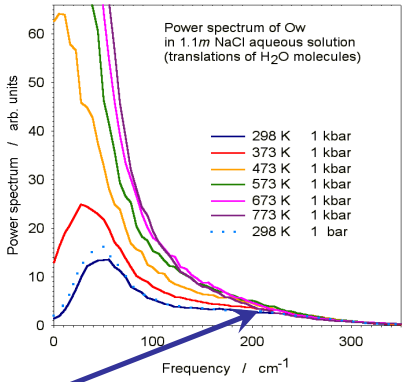
The broad frequency band of H_2O librations (hindered rotations) in the H-bonding network is centered around ~500 cm^{-1} and gradually decreases with increasing temperature and decreasing density.

Dynamics of Individual Species Power Spectra of Molecular Motions

$$P(\omega) = \int_0^{\infty} \frac{\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle}{\langle \mathbf{v}(0)^2 \rangle} \cos(\omega t)\, dt$$







H-bond stretching

The two broad bands of the translational spectra at ~50 cm^{-1} and ~200 cm^{-1} are usually assigned to H-bond **O···O···O** bending and stretching, respectively

Dynamics of Individual Species
Power Spectra of Molecular Motions

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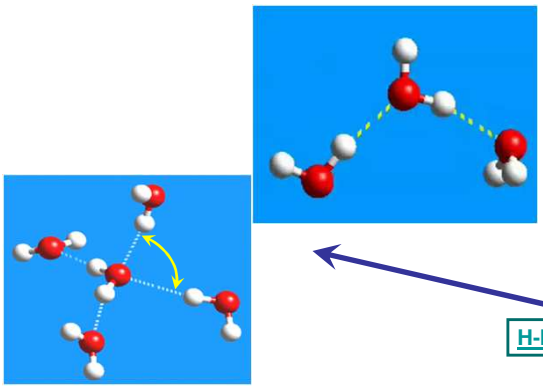

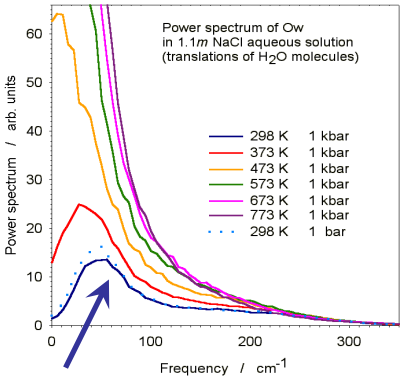

H-bond bending

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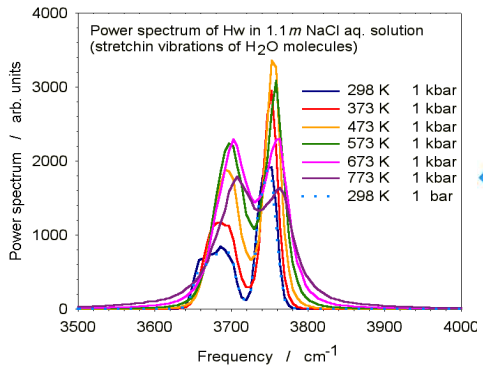
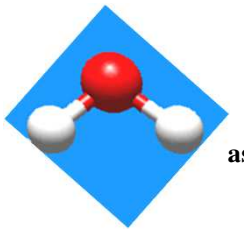
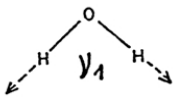
SPC: Intramolecular Stretching Vibrations of H_2O Molecules in NaCl Solutions as a Function of Temperature

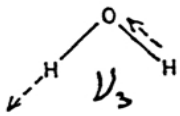




symmetric stretch

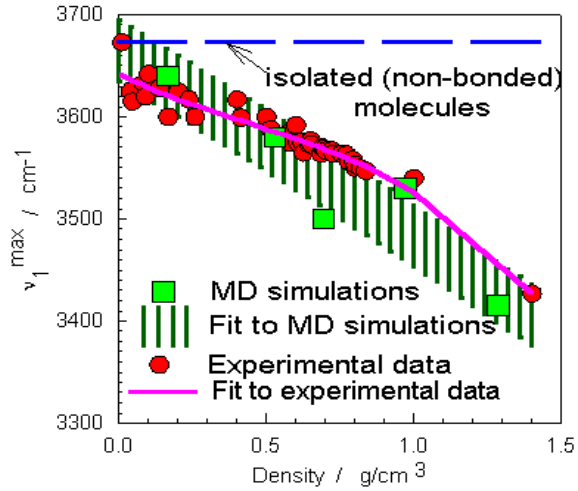


asymmetric stretch

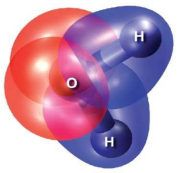


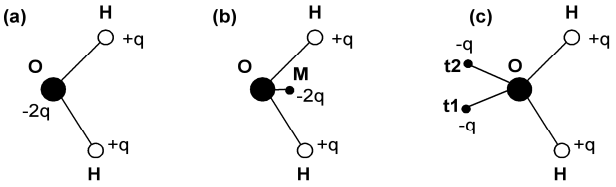
- Symmetric stretching frequencies continuously increase indicating a progressive loss of the strength of H-bonding in the solution.
- The assymetric stretching vibration frequency remains almost unaffected by the weakening of H-bonding.

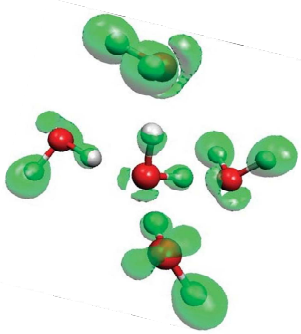
BJH: Spectral Density Maximum of the Symmetric Stretching Vibration, ν_1^{max}, as a Function of Density



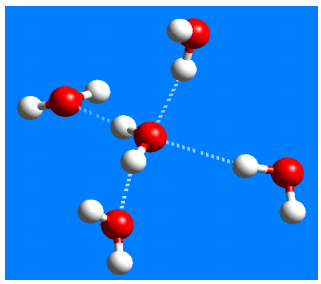
The Structure of H_2O Molecule and Intermolecular Hydrogen Bonding in Water



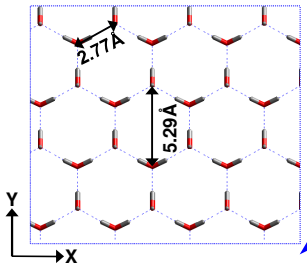


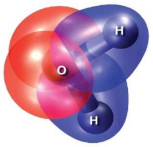


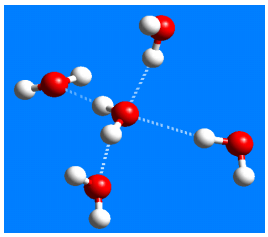
Negatively and positively charged sites of the water molecule



Hydrogen Bonding and Local Tetrahedral Ordering in Water

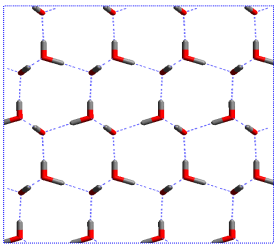




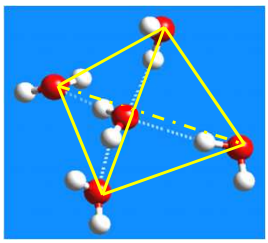


Ice Ih structure

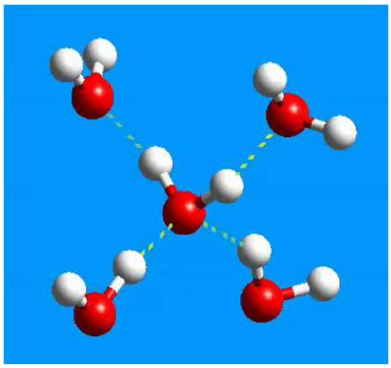
Liquid water structure



- Tetrahedrally ordered O positions in the diamond-like network
- H positions are disordered
- Proton diffusion
- Proton hopping
- Long-range order is destroyed upon melting
- Short-range tetrahedral ordering remains in liquid



The name is Bond, H-Bond

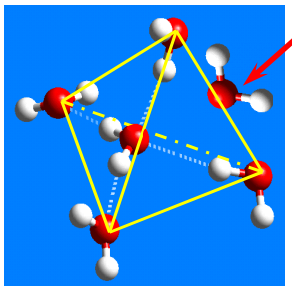


Ideally, each H_2O molecule in the H-bonding network can *donate* 2 H-bonds to its neighbors and *accept* 2 H-bonds from other neighbors

Hydrogen Bonding is the Most Important Phenomenon Governing the Properties of All Aqueous Systems

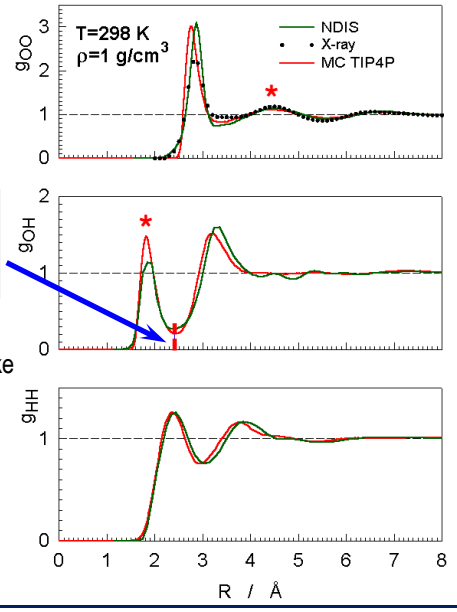
- **H-bonding** is ubiquitous, as water itself
- **H-bonding** is responsible for the anomalous properties of water
- All processes in water as a solvent are strongly affected by **H-bonding**
  - *hydration of species*
  - *adsorbtion*
  - *diffusion*
  - *intercalation*
- **H-bonding** stabilizes many inorganic and organic hydrous materials
- Inter- and intra-molecular **H-bonding** is important aspect of the bio-molecular behavior and functions

Structure of Water: Atom-Atom Radial Distribution Functions (RDFs)



Interstitial H_2O molecule

Distance criterion for H-bonding



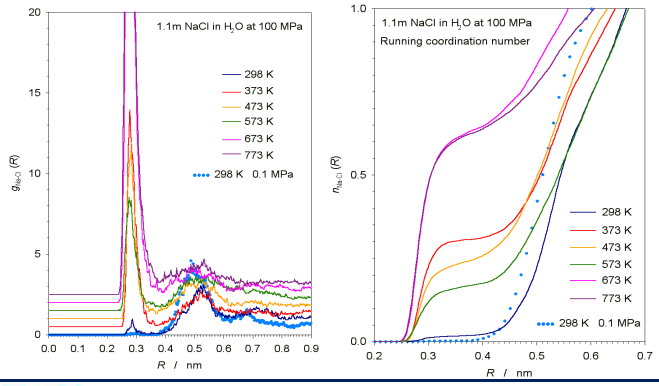
- **Ice:** Tetrahedrally ordered O in the diamond-like network
- H positions are disordered
- Proton diffusion
- Proton hopping
- **Liquid:** Only short-range tetrahedral ordering remains

Fluid Structure - Running Coordination Numbers

Average number of atoms *i* within a sphere of radius *r* from another atom *j* :

$$n_{ij}(r) = 4\pi\rho_i \int_0^r g_{ij}(r)\, r^2 dr = 4\pi \frac{N_i}{V} \int_0^r g_{ij}(r)\, r^2 dr$$

RDFs and running coordination numbers for Na^+-Cl^- Ion pairs in solution



- At $T < 373$ K only water-separated Na^+-H_2O-Cl^- ion pairs can be found in the solution
- At 373 K < T < 573 K ~25% of ions participate in contact ion pairs
- At $T > 673$ K the number of contact ion pairs increases very quickly involving the majority of ions

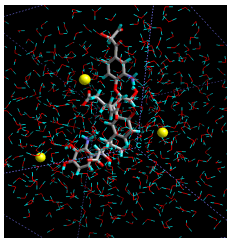
Radial Distribution Functions and Running Coordination Numbers

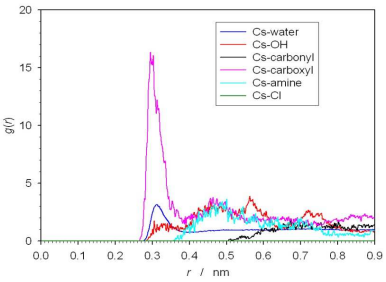
- Importance of $g(r)$ normalization
- Height of the $g(r)$ peaks is not necessarily an indication of high population
- Average density or concentration of species is equally important

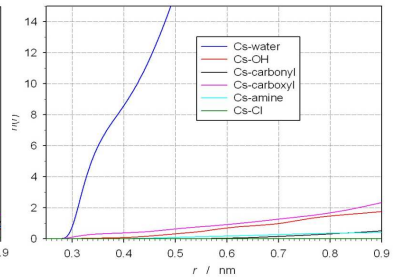
$$g_{ij}(r) = \frac{1}{N_j \rho_i} \left\langle \sum_i \sum_j \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle$$

$$n_{ij}(r) = 4\pi\rho_i \int_0^r g_{ij}(r)\, r^2 dr$$

3 Cs^+ ions in aqueous solution with humic acid (NOM anion)







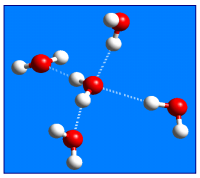
Hydrogen Bonding in Aqueous Systems and the Characteristic Scales Molecular Processes

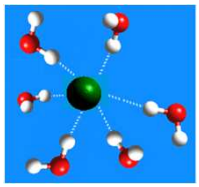
- Characteristic H-bond lifetime (300K) ~2-5ps ~3Å
  - " - " - (600K) ~0.2ps
  - " - " - (200K) ~200ps
- O-H vibrations; individual acts of H-transfer among water molecules ~0.2ps ~1Å
- Local H-bonding rearrangement (300K) ~10-20ps ~10Å
- Lifetime in ionic hydration shell (300K)

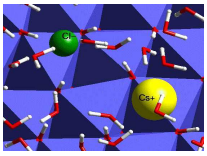
K^+, Cl^-	~5ps	~10Å
Na^+	~10ps	
Li^+, F^-	~30-50ps	
Ca^{2+}, Mg^{2+}	~50-100ps	

- H_2O, Cl^-, K^+ surface site residence times

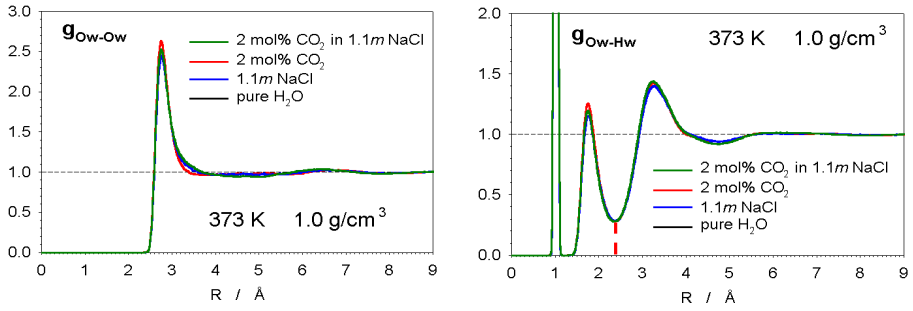
neutral surface	~ 20 ps
charged surface	> 100 ps





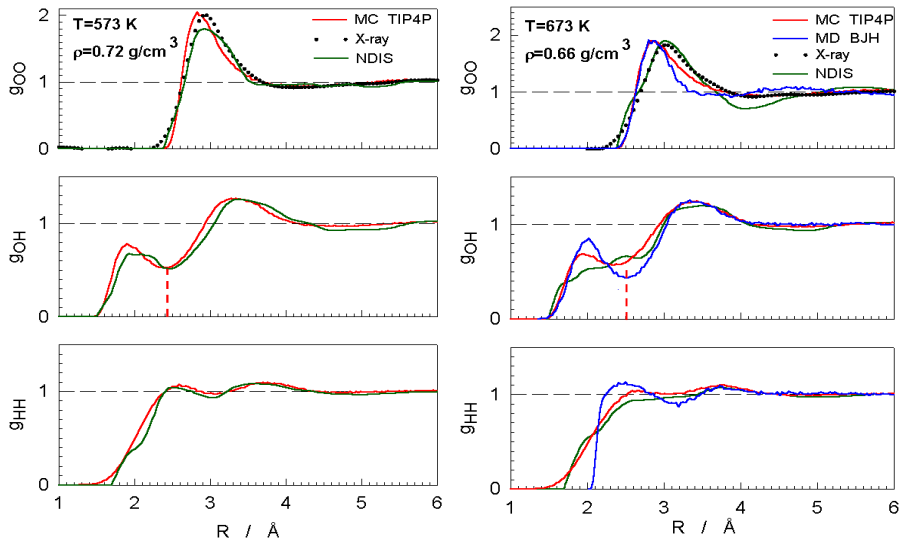


The Effect of Small Amounts of Electrolyte and Non-electrolyte Solutes on the Structure of Water

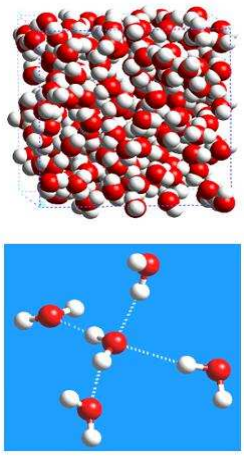


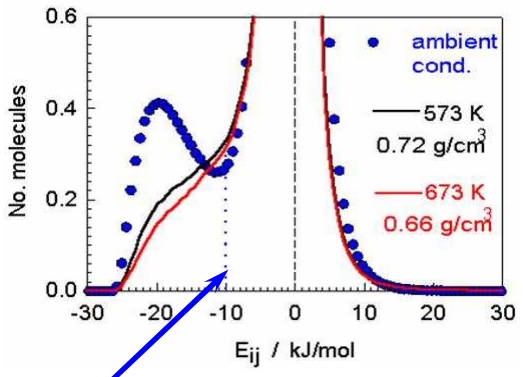
At low concentrations, the water structure represented by atom-atom radial distribution functions, is not strongly affected by the presence of any solute, and the general solution structure is in good agreement with recent X-ray diffraction measurements.

Water Structure under Hydrothermal Conditions



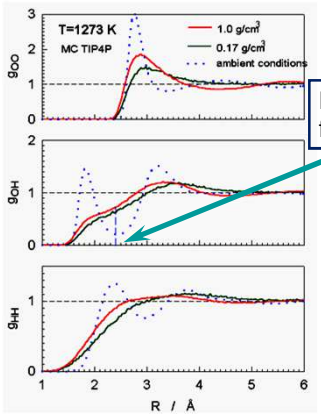
Micro-Thermodynamic Properties: Molecular Pair Energy Distributions



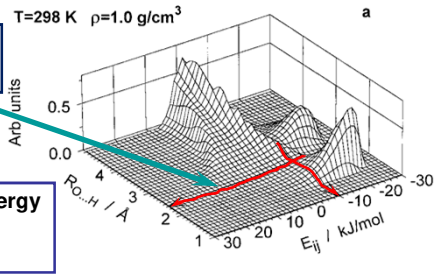


Energy criterion for hydrogen bonding

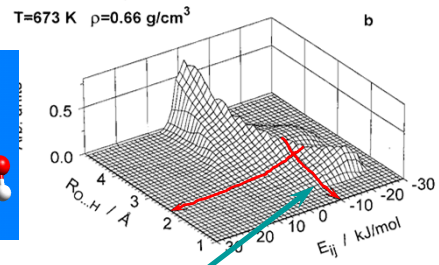
H-bond Definitions

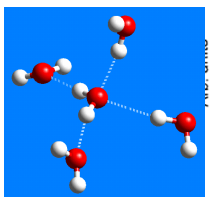


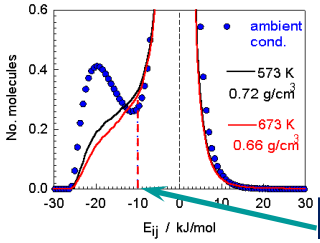
Distance criterion for H-bonding



Distance-Energy Distribution Functions

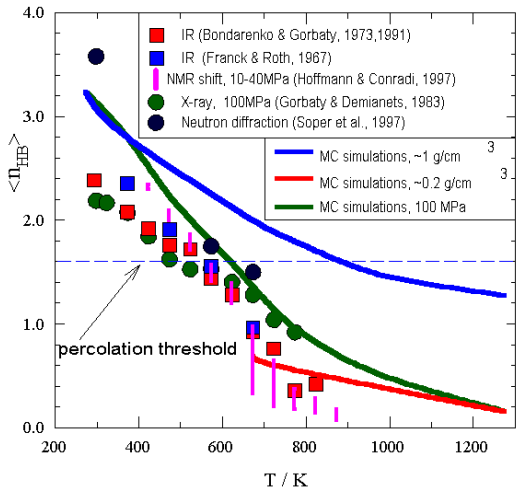




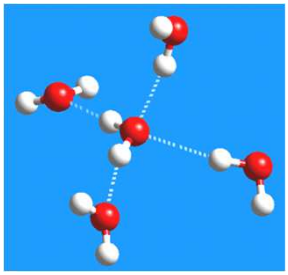


Energy criterion for H-bonding

Temperature and Pressure Dependence of the Number of H-bonds per Water Molecule

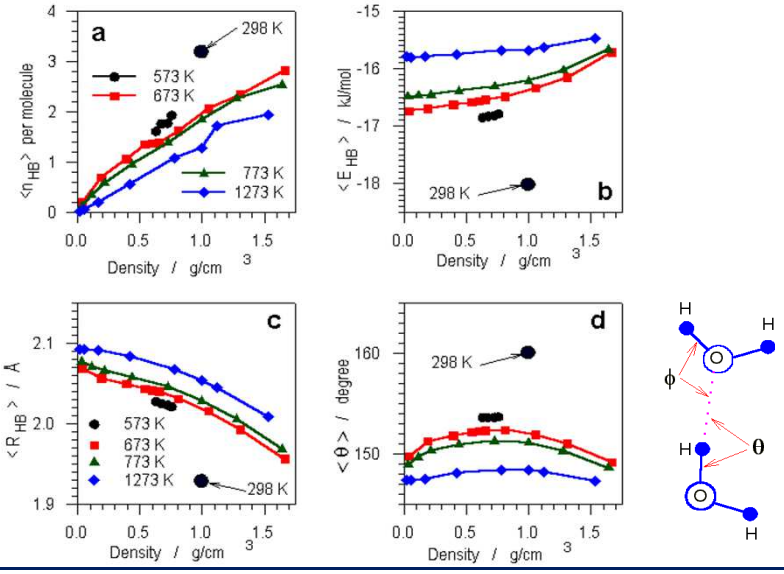


H-bonding:
molecular simulations ***vs*** spectroscopic and diffraction evidence from various sources



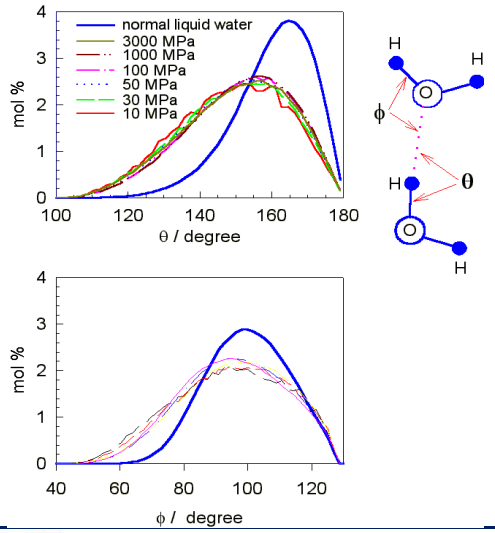
Kalinichev, *Rev. Mineral. Geochem.*, **42**, 83-129 (2001)

Average Parameters of H-bonds

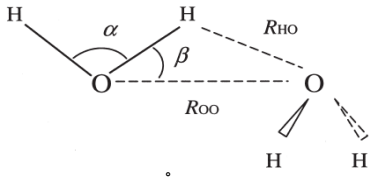


Angular Distributions of H-bonds

Distributions of HB angles at 773 K

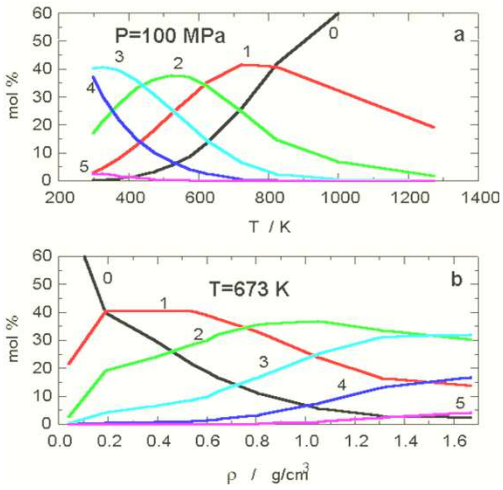


Angular criterion of H-bonding can in many cases be used instead of the energetic criterion

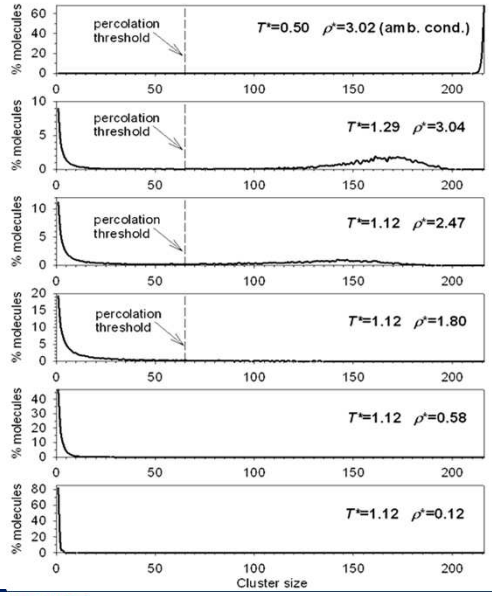


$R_{OO} \leq$ 3.3-3.5 Å
or
$R_{OH} \leq$ 2.45-2.5 Å
and
$\beta \leq 30^{o}$

Distributions of Water Molecules, Participating in a Given Number of H-bonds

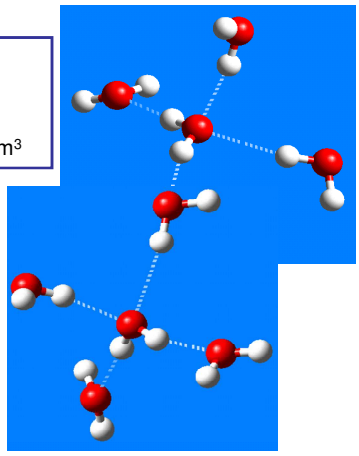


Topology of H-bonding Network in Water



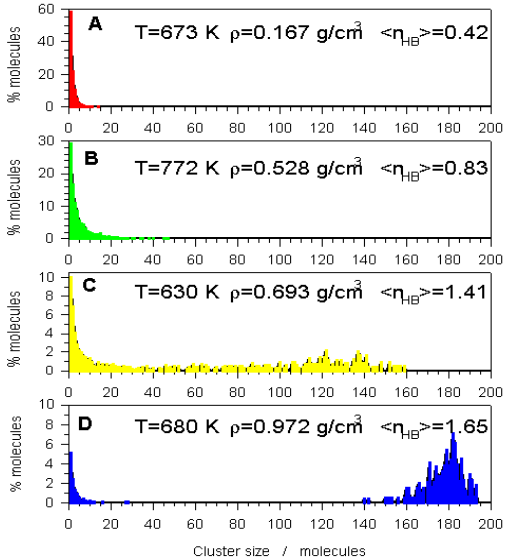
Percolating H-bond network *vs* H_2O molecular clusters

$T^*=T/T_c$
$\rho^*=\rho/\rho_c$
T_c=647 K
ρ_c=0.31 g/cm^3

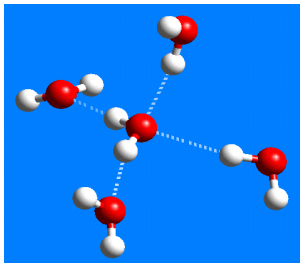


Percolation threshold $\langle n_{HB}\rangle$ ~ 1.6

Molecular Clusterization in Supercritical Water



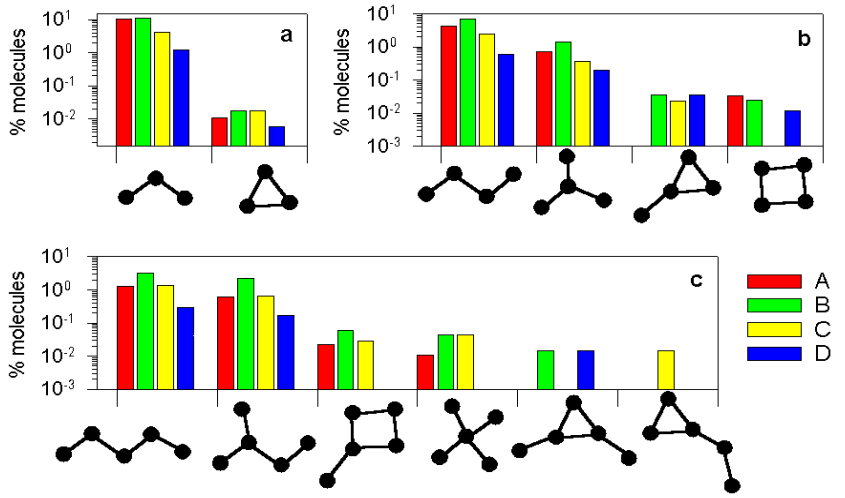
H-bonded cluster size distributions



Kalinichev & Churakov, 1999, 2001

Molecular Clusterization in Supercritical Water

Abundance of topologically different H_2O clusters



Kalinichev & Churakov, 1999, 2001

Molecular Clusterization in Supercritical Water

Average Parameters of H-bonded Clusters

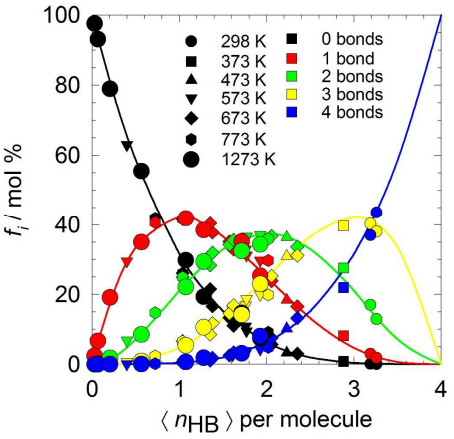
Cluster topology	3a	3b	4a	4b	4c	4d	5a	5b	5c	5d	5e
$\langle \angle O\cdot\cdot\cdot O\cdot\cdot\cdot O_1 \rangle$ / °	109	60	110	107	114	87	110	108	112	107	105
$\langle \angle O\cdot\cdot\cdot O\cdot\cdot\cdot O_2 \rangle$ / °					60				86	60	
$\langle \angle O\cdot\cdot\cdot O\cdot\cdot\cdot O_3 \rangle$ / °										119	
$\langle R_{O\cdot\cdot\cdot H} \rangle$ / Å	2.04	2.07	2.04	2.04	2.06	2.03	2.04	2.04	2.05	2.06	2.05
$\langle R_{O\cdot\cdot\cdot O} \rangle$ / Å	2.90	2.89	2.91	2.91	2.90	2.90	2.91	2.91	2.91	2.90	2.92
$\langle \angle O\cdot\cdot\cdot H–O \rangle$ / °	149	143	150	150	146	150	150	150	149	146	150
$\langle U_{HB} \rangle$ / kJ/mol	-16.9	-16.4	-16.9	-16.7	-16.3	-17.0	-16.9	-16.8	-16.7	-16.3	-16.8

Distributions f_i of H_2O Molecules Involved in i H-bonds in Liquid and Supercritical Water as a Function of the Average Number of H-bonds per Molecule in the System, $\langle n_{HB} \rangle$

It has long been established that the interconnected percolating network of H-bonds in liquid water can be quite accurately described by a simple binomial distribution

$$f(i) = \left(\frac{m}{i}\right)\left(\frac{\langle n_{HB}\rangle}{m}\right)^{i}\left(1-\frac{\langle n_{HB}\rangle}{m}\right)^{m-i}$$

Blumberg et al. (1984) Connectivity of hydrogen bonds in liquid water. *J. Chem. Phys*, **80**, 5230-5241



Lifetime of H-bonds in Supercritical Water

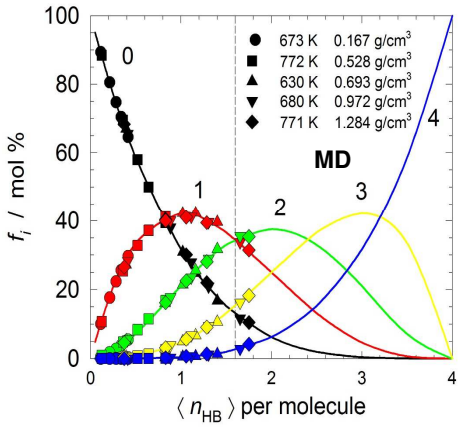
Average number of H-bonds per water molecule and concentration of H-bonded species in supercritical BJH water at 630 K and 0.692 g/cm^3 as a function of a lifetime criterion for H-bonds.

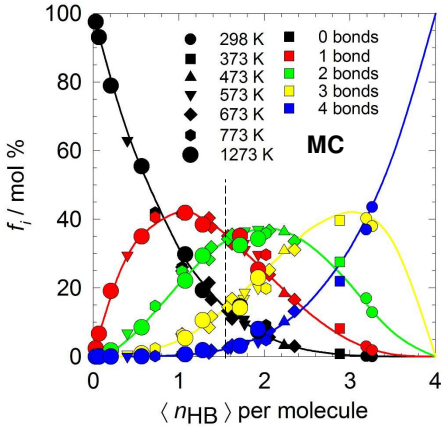
$\Delta\tau$ / ps	$\langle n_{HB}\rangle$	% of monomers (0 bonds)	% of dimers (1 bond)	% of trimers (2 bonds)	% of tetramers (4 bonds)
0.01	1.41	16.6	39.4	31.9	10.7
0.1	0.83	40.2	40.2	16.3	3.0
0.2	0.57	55.0	34.2	9.5	1.2

Distributions f_i ($\langle n_{HB} \rangle$) from MC and MD Simulations with TIP4P and BJH Potentials

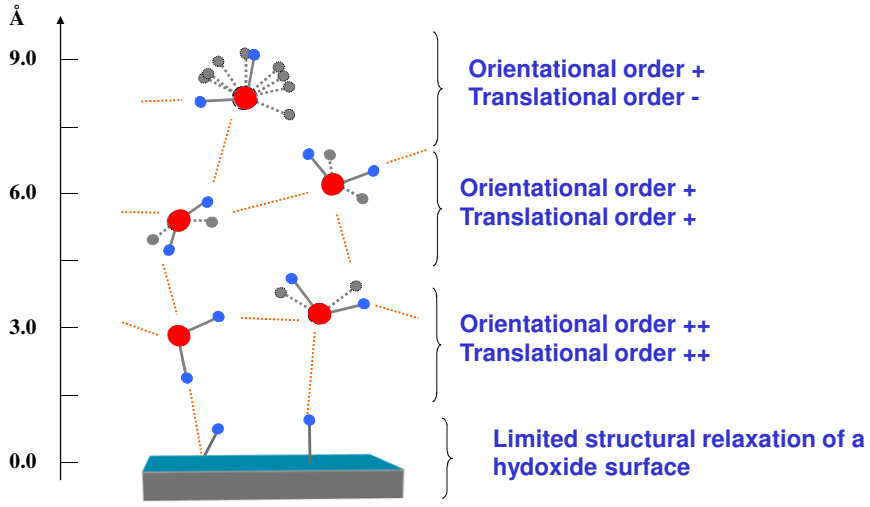
$$f(i) = \binom{m}{i} \left(\frac{\langle n_{HB} \rangle}{m} \right)^i \left(1 - \frac{\langle n_{HB} \rangle}{m} \right)^{m-i}$$

Kalinichev (2017) Universality of hydrogen bond distributions in liquid and supercritical water. *Journal of Molecular Liquids*, **241**, 1038-1043



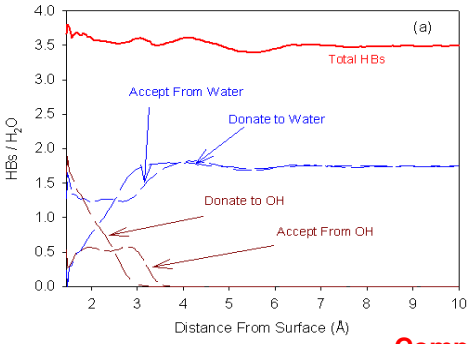


H-Bonding of Water at a Hydroxylated Surface, e.g., $Mg(OH)_2$, $Ca(OH)_2$

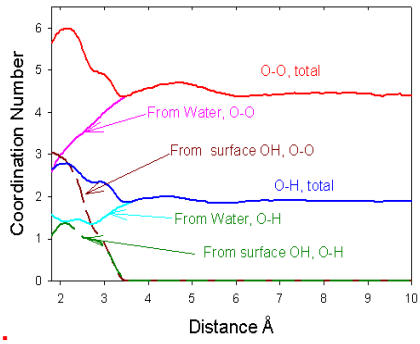


Water Structure at the Brucite, $Mg(OH)_2$, Surface

Hydrogen Bonds



Coordination Numbers



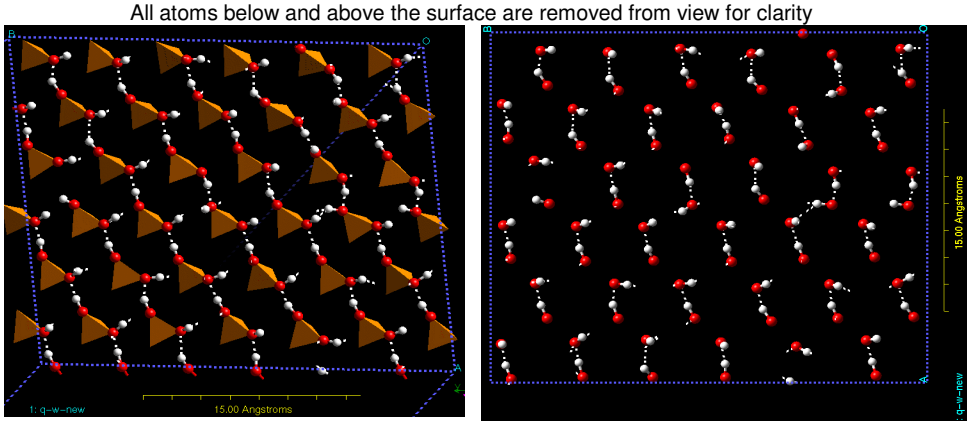
Compare to:

Bulk water under pressure:
- Nearest neighbors: ↑
- Hydrogen-bonds: ~
- Ice VIII: NN=8, HB=4

Supercooled bulk water:
- Nearest neighbors: ↓
- Hydrogen-bonds: ↑
- Ice Ih: NN=4, HB=4

H-Bonding at a Fully Protonated α-Quartz-Water Interface (Low pH)

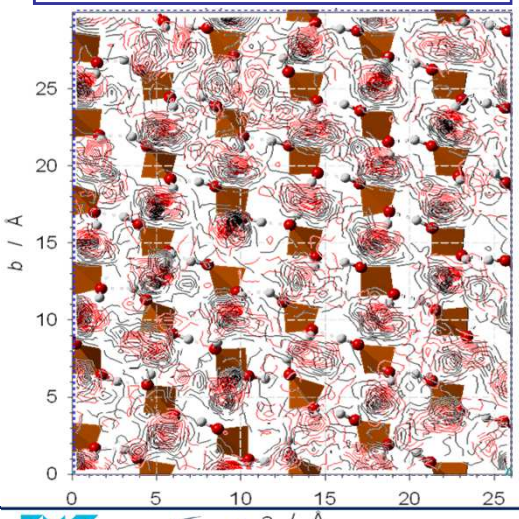
All atoms below and above the surface are removed from view for clarity

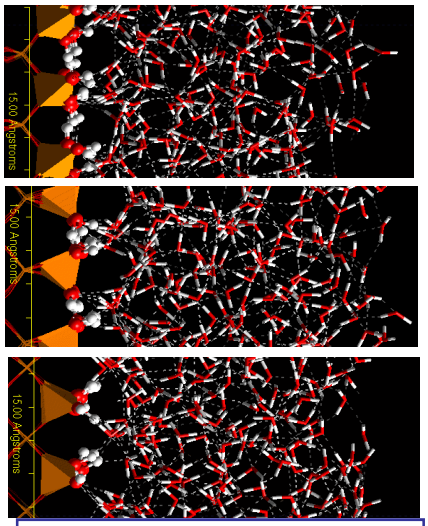


- ~50% of the surface OH groups are oriented parallel to the surface, form H-bonds to other surface OHs, and accept H-bonds from interfacial H_2O molecules.
- The other ~50% of the surface OH groups are oriented perpendicular to the surface and donate H-bonds to interfacial H_2O.

Surface Atomic Density Contours and H-bonding at the Protonated α-Quartz (0001) - Water Interface

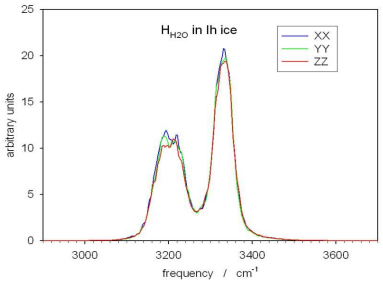
H (black) and O (red) contours of H_2O above the fully protonated quartz surface





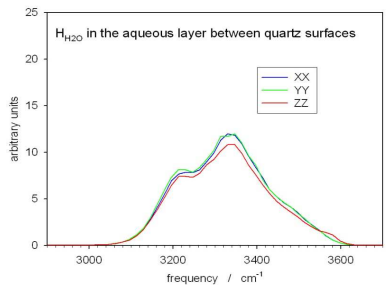
H-bonded "grooves" on the surface viewed from different directions

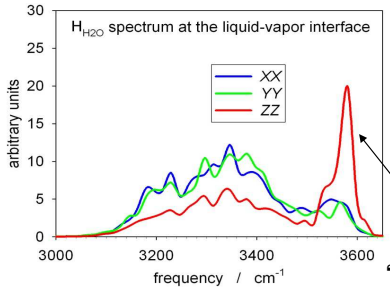
O-H Stretching Power Spectra of H_2O



$$\mathrm{VACF} \equiv C_{vv}(t) = \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle} = \frac{1}{\langle \mathbf{v}(0)^2\rangle}\int \mathbf{v}(0)\cdot\mathbf{v}(t)\, d\Gamma$$

$$P(\omega) = \int_0^{\infty} \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle} \cos(\omega t)\, dt$$

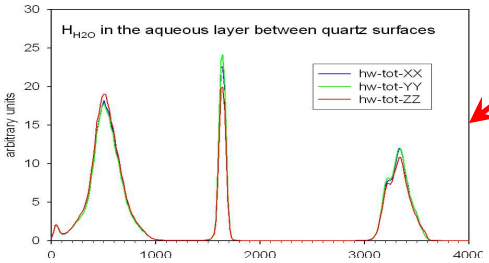




Velocity Autocorrelation Functions and Vibrational Spectra of Surface H_2O

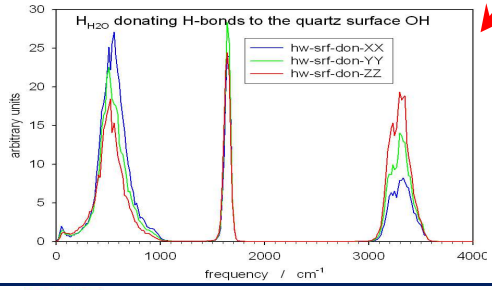
$$\mathrm{VACF} \equiv C_{vv}(t) = \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle} = \frac{1}{\langle \mathbf{v}(0)^2\rangle}\int \mathbf{v}(0)\cdot\mathbf{v}(t)\,d\Gamma$$

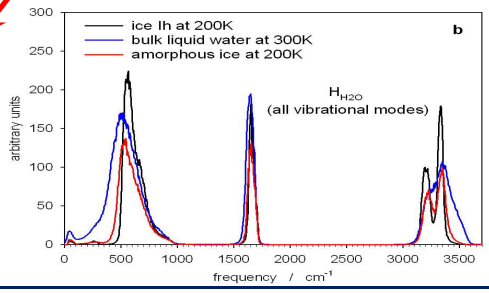
$$P(\omega) = \int_0^{\infty} \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle}{\langle \mathbf{v}(0)^2\rangle}\cos(\omega t)\,dt$$



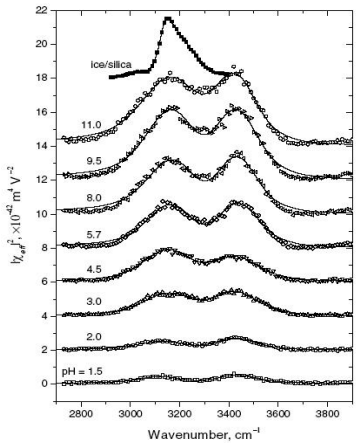
Total H_2O

Surface H_2O
- Narrower spectral bands
- More anisotropic
- Closer to 'ice-like"



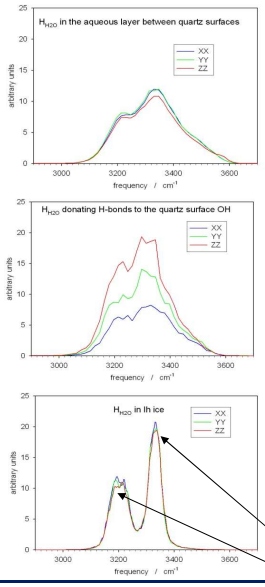


O-H Stretching Power Spectra of Surface H_2O



"… ordered H-bonding network with regions that are highly ice-like, and spanning several quartz unit cells."

Ostroverkhov et al., *Chem.Phys.Lett.*, **386** (2004) 144



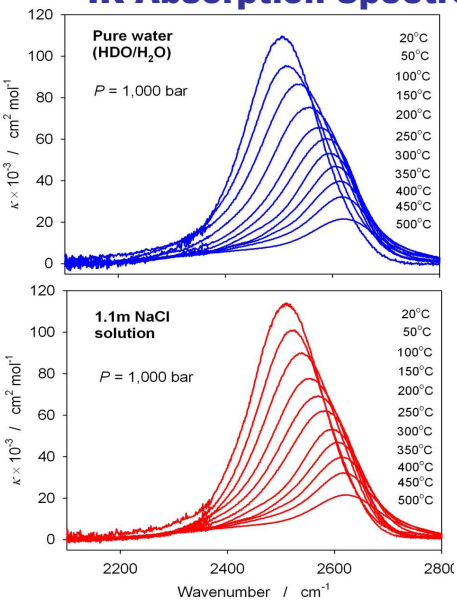
Bulk Water
Isotropic
Broad bands (disordered)
More weak H-bonding

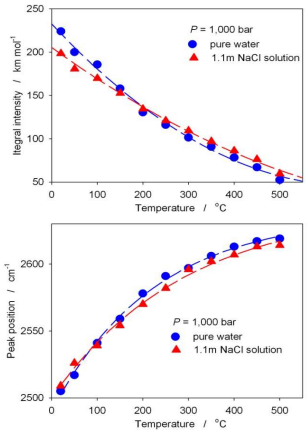
Interfacial Water
Anisotropic
Narrower bands
Stronger H-bonding ⊥ Surface

Bulk Ice
Isotropic
Narrow bands (ordered)
Strong H-bonding

Asymmetrical
Symmetrical

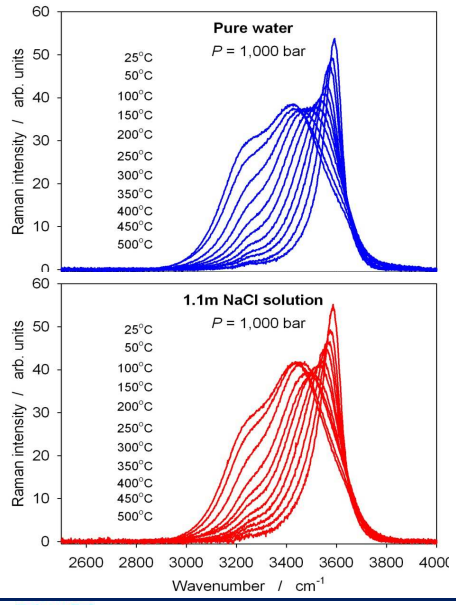
IR Absorption Spectroscopy: H_2O-NaCl Solution

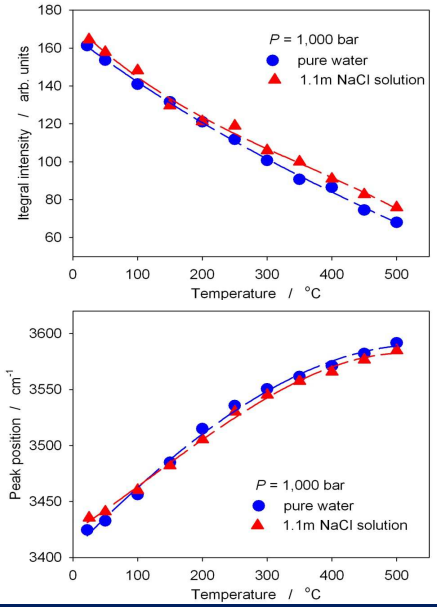




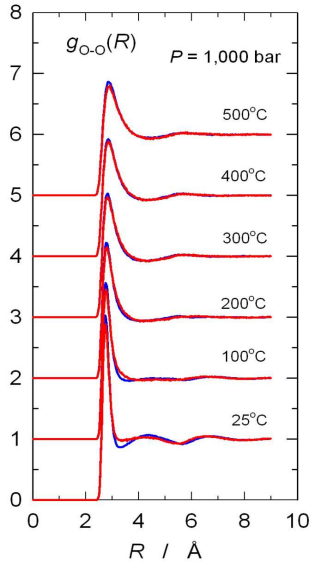
The differences in the behavior of IR spectra of pure water and 1.1*m* NaCl solution at heating to high temperatures is surprisingly small !

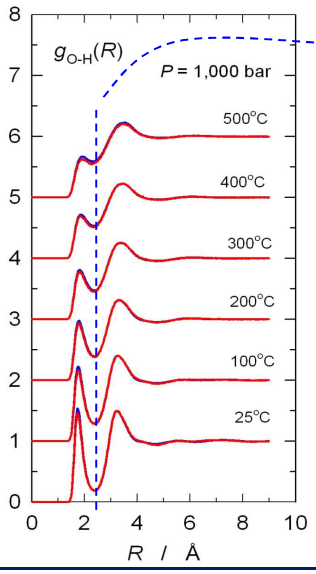
Raman Spectroscopy: H_2O-NaCl Solution

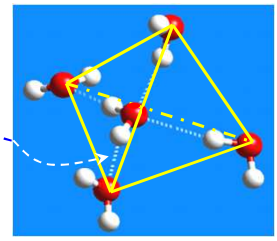




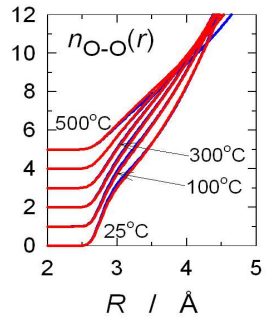
H_2O Molecule Coordination in High Temperature H_2O-NaCl Solutions



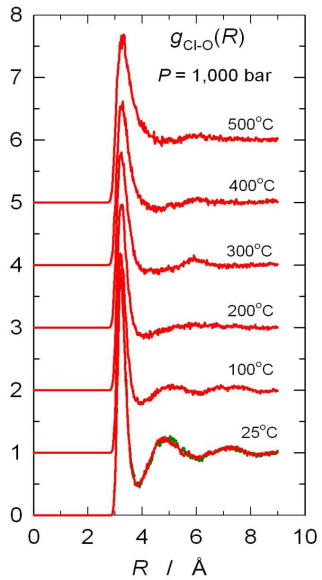


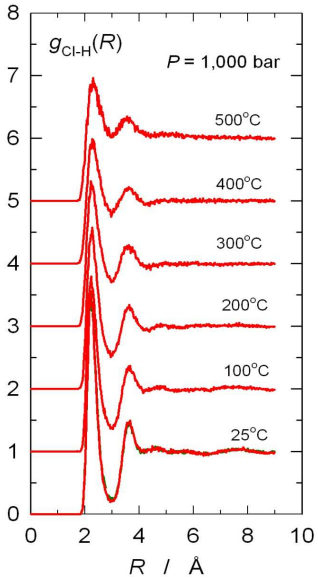


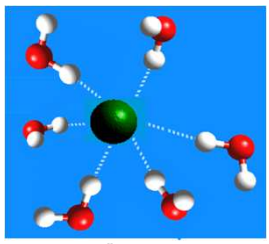
$$n_{ij}(r) = 4\pi\rho_i \int_0^r g_{ij}(r)\, r^2 dr$$



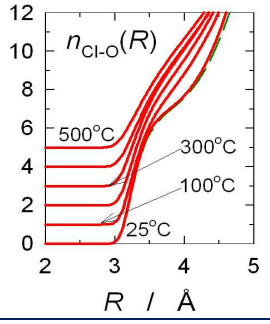
Hydration of Cl^- Ion



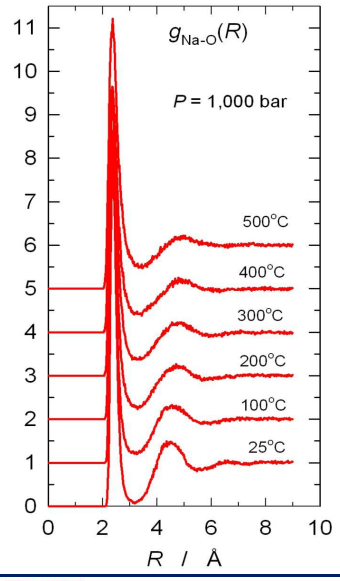


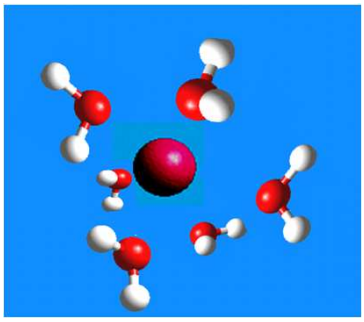


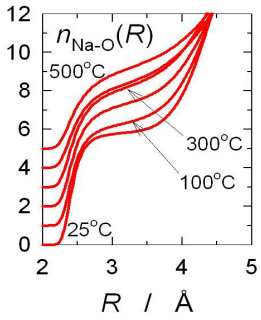
$$n_{ij}(r) = 4\pi\rho_i \int_0^r g_{ij}(r)\, r^2 dr$$



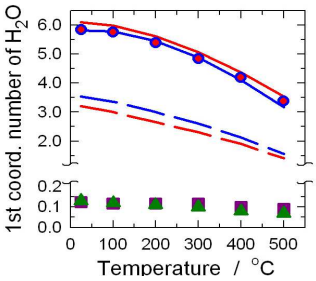
Hydration of Na^+ Ion

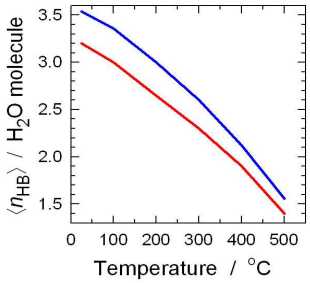


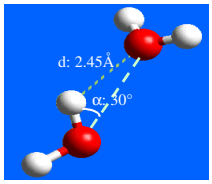




Comparison of Hydrogen Bonding Numbers

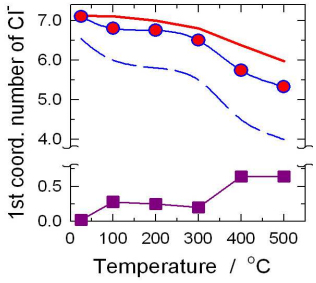


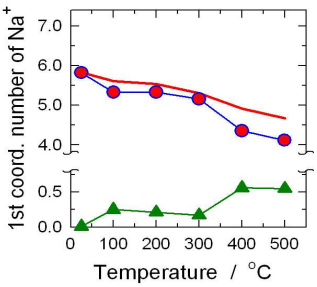




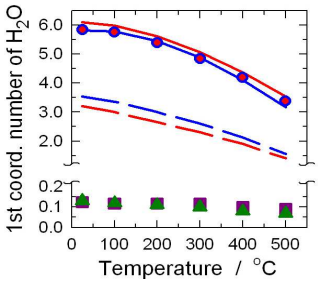
H... O distance: < 2.45Å *
OH... O---O angle : < 30°

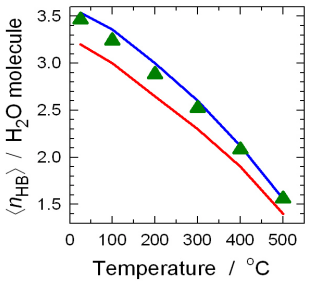
Luzar (2000) *J.Chem.Phys.*, **113**, 10663-10675

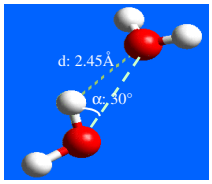




Comparison of Hydrogen Bonding Numbers

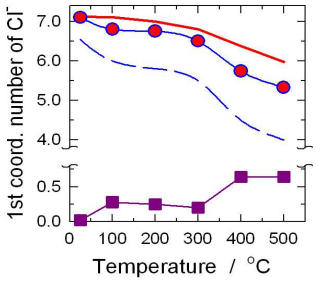


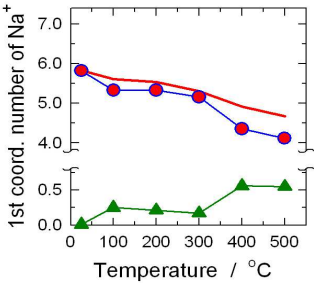




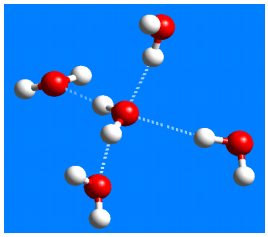
H... O distance: < 2.45Å *
OH... O---O angle : < 30°

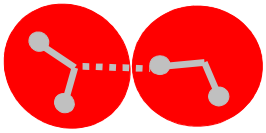
Luzar (2000) *J.Chem.Phys.*, **113**, 10663-10675





Comparison of H-Bonding Strength





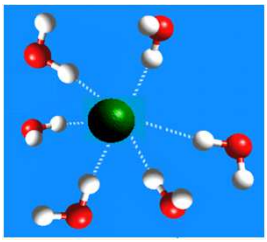
q_O = -0.82e

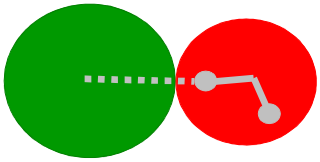
q_H = +0.41e

σ_{H2O} ~ 1.6 Å

$R_{O...H}^{max}$ ~ 1.82 Å

$F_{HB} \sim q_O q_H / R_{O...H}^2 = 0.10$





q_{Cl} = -1.0e

q_H = +0.41e

σ_{Cl} ~ 1.95 Å

$R_{Cl...H}^{max}$ ~ 2.23 Å

$F_{HB} \sim q_{Cl} q_H / R_{Cl...H}^2 = 0.09$

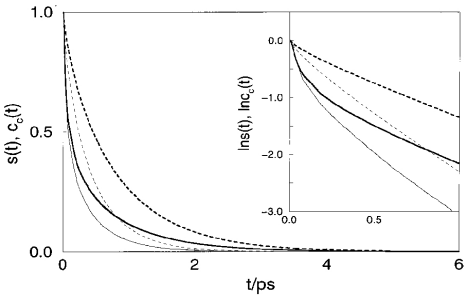
H-bond Dynamics in Water

$$C_{\mathrm{HB}}(t) = \frac{\sum_{\langle i,j \rangle} s_{i,j}(t_0) s_{i,j}(t_0 + t)}{\sum_{\langle i,j \rangle} s_{i,j}(t_0)}$$

Two definitions possible:

1) Autocorrelations for molecular pairs bonded *continuously*, i.e., *without interruptions* over the entire interval from 0 to t (continuous HB correlation function).

2) Autocorrelations for molecular pairs *irrespective of intervening interruptions*, i.e., of possible prior H-bond breaking and reforming events (intermittent HB correlation function).



Exponential fit to estimate the H-bond relaxation time, τ:

$$C_{\mathrm{HB,c}}(t) = \exp(-t/\tau_{\mathrm{HB}})$$

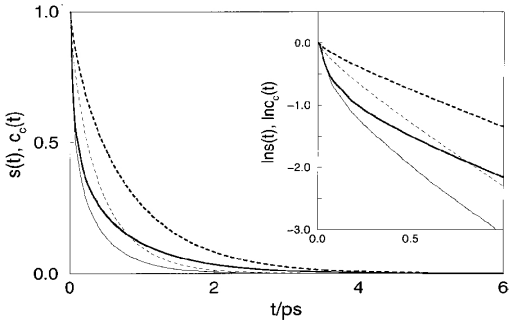
A.Luzar (2000) Resolving the hydrogen bond dynamics conundrum. *J.Chem.Phys.*, **113**, 10663-10675.

H-bond Dynamics in Water

$$C_{\mathrm{HB}}(t) = \frac{\sum_{\langle i,j \rangle} s_{i,j}(t_0) s_{i,j}(t_0 + t)}{\sum_{\langle i,j \rangle} s_{i,j}(t_0)}$$

Exponential fit to estimate the H-bond relaxation time, τ:

$$C_{\mathrm{HB,c}}(t) = \exp(-t/\tau_{\mathrm{HB}})$$



Survival probabilities for a newly generated bond, $s(t)$ (solid lines) and for an average bond, $C_{\mathrm{HB,c}}(t)$ (dashed lines), for stricter HB definition (thin lines) and for less strict HB definition (thick lines).

Inset represents the short time behavior of all functions on a semi-log plot.

A.Luzar (2000) Resolving the hydrogen bond dynamics conundrum. *J.Chem.Phys.*, **113**, 10663-10675.

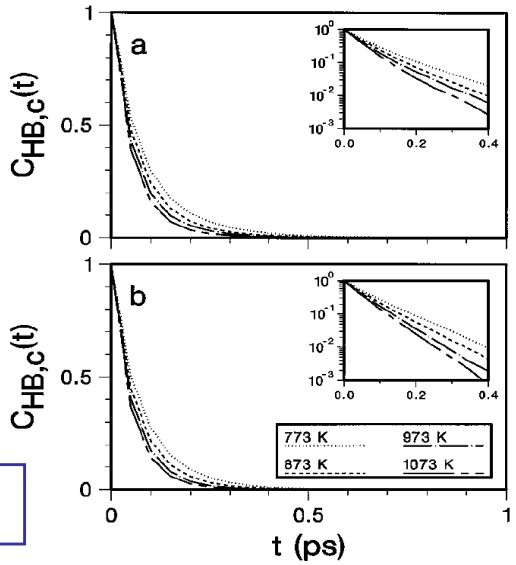
H-bond Dynamics in Water at High Temperature

$$C_{HB}(t) = \frac{\sum_{\langle i,j \rangle} s_{i,j}(t_0) s_{i,j}(t_0 + t)}{\sum_{\langle i,j \rangle} s_{i,j}(t_0)}$$

Exponential fit to estimate the H-bond relaxation time, τ:

$$C_{HB,c}(t) = \exp(-t/\tau_{HB})$$

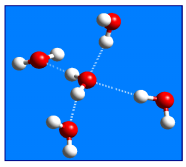
T.Mizan et al. (1996) Temperature dependence of hydrogen bonding in supercritical water. *J.Phys. Chem.*, **100**, 403-408.

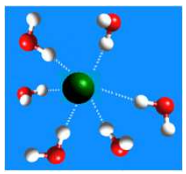


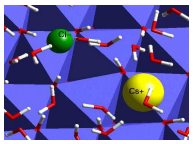
Hydrogen Bonding in Aqueous Systems and the Characteristic Scales Molecular Processes

- Characteristic H-bond lifetime (300K) ~1-2ps ~3Å
  - " - " - (600K) ~0.2ps
  - " - " - (200K) ~200ps
- O-H vibrations; individual acts of H-transfer among water molecules ~0.2ps ~1Å
- Local H-bonding rearrangement (300K) ~10-20ps ~10Å
- Lifetime in ionic hydration shell (300K)

  K^+, Cl^- ~5ps ~10Å
  Na^+ ~10ps
  Li^+, F^- ~30-50ps
  Ca^{2+}, Mg^{2+} ~50-100ps
- H_2O, Cl^-, K^+ surface site residence times
  neutral surface ~ 20 ps
  charged surface > 100 ps







Additional Reading

#1 Finney JL (2004) Water? What's so special about it? *Phil. Trans. R. Soc. Lond. B* **359**, 1145–1165

#2 Guillot B (2002) What we have learnt during three decades of computer simulations on water. *Journal of Molecular Liquids* **101**, 219-260.

#3 Kalinichev AG (2001) Molecular simulations of liquid and supercritical water. *Rev Mineral Geochem* **42**, 83–129.

Questions for the final paper / report on one of the 21 topics, e.g., 1 – clays; 2 – cement; 3 – TiO_2 surfaces; 4 – corrosion; 5 – organics, etc. (Please use only as a guidance)

- What molecular modeling method was used and why?
- Was it a fully atomistic simulations, or some simplified models were used?
- What other approximations were used in the modeling?
- What was the number of particles in the simulations? Was it big enough for the specific problem? Was it small enough to make the simulations computationally efficient?
- How long-range electrostatic interactions were handled in the simulations? Was it important for the given problem?
- What kind of boundary conditions were applied to the simulation box? Why?
- What properties of the system were calculated from the molecular simulation?
- Make a qualitative assessment of the accuracy for the calculated properties given the number of atoms in the simulated system and the duration of the simulation.
- What other properties would you additionally calculate from the same simulations for the same system?
- Formulate 2 or 3 strong points of the given molecular simulation paper and 2 or 3 weak points of the paper.