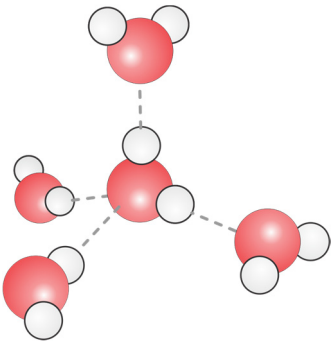
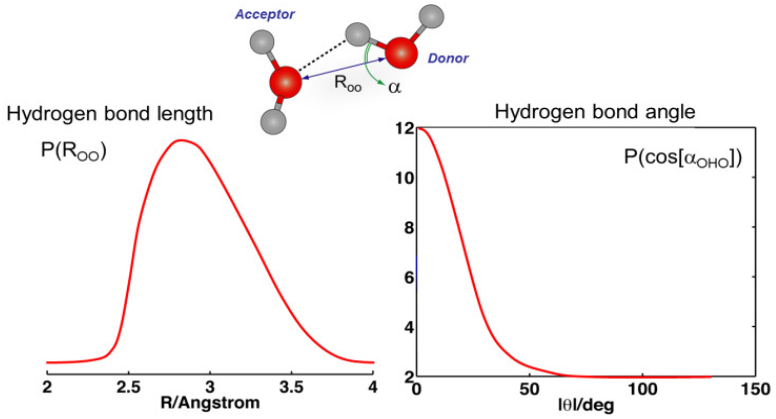
3. Water's Physical Properties

Water Structure

Water is a structured liquid. Its unique physical properties stem from its hydrogen bond network.

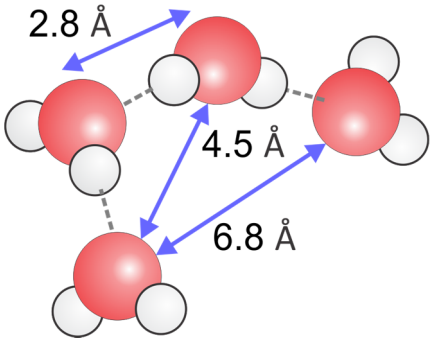
- On average, each molecule can donate two hydrogen bonds and accept two hydrogen bonds.
- Strong hydrogen bond (HB) interactions give preferential directionality along tetrahedral orientation.
- Large variation in HB distances and angles.



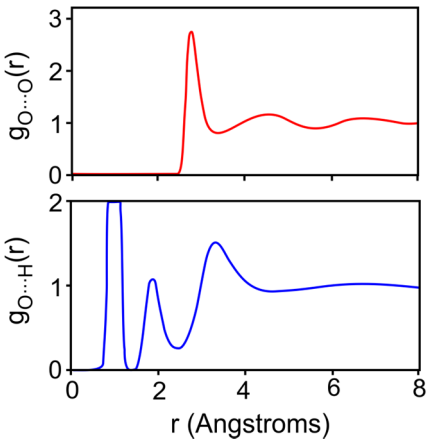


Water HB probability densities

- Structural correlations last about 1–2 solvent shells, or <1 nm.

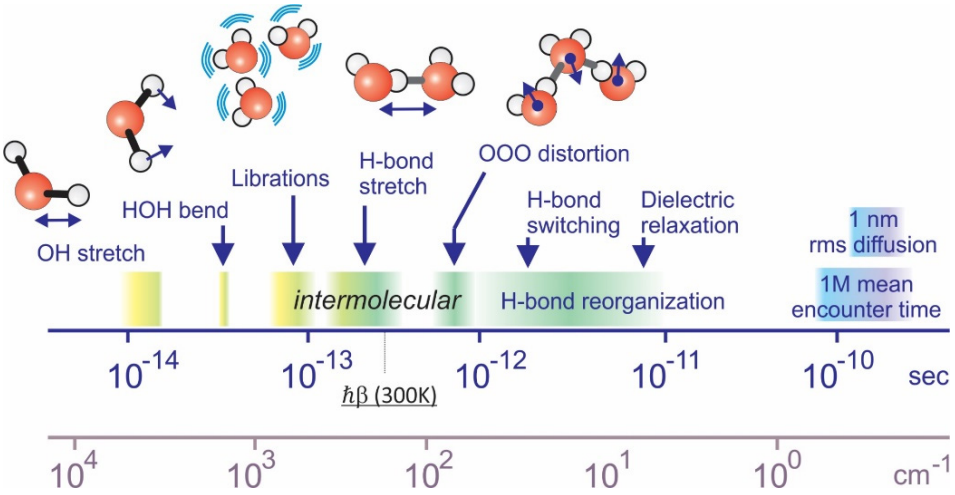


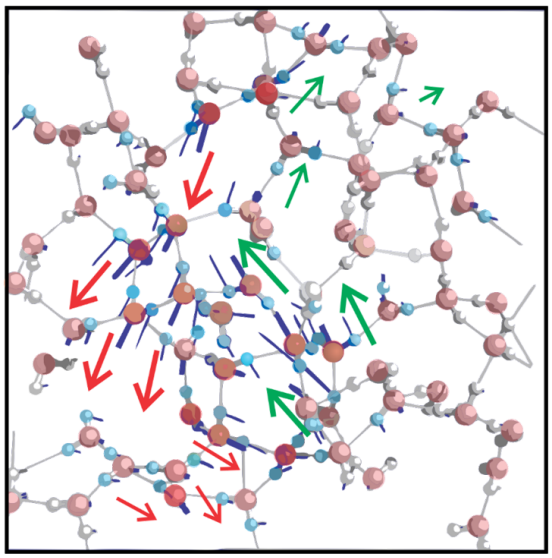
Water radial distribution functions



Water Dynamics

- Hydrogen bond distances and angles fluctuate with 200 and 60 femtosecond time scales, respectively.
- Hydrogen bonded structures reorganize in a collective manner on picosecond time scales (1–8 ps).





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The water HB energy is tough to measure:

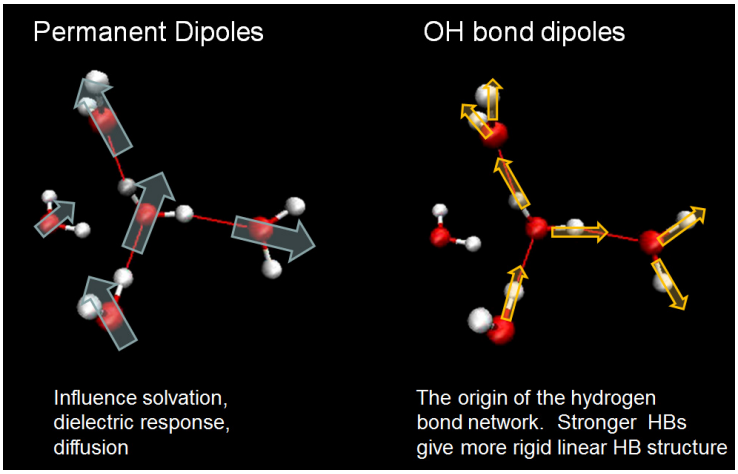
- 2–6 kcal mol^{-1} depending on the method used.
- These are ΔH for reorganization, but we do not know how many HB broken or formed in the process.

Electrical Properties of Pure Water

The motion of water's dipoles guide almost everything that happens in the liquid. Two important contributions:

1) Permanent dipole moment of molecule lies along symmetry axis.
2) Induced dipole moments (polarization) along the hydrogen bonds.

   Strengthening hydrogen bond increases $\mathbf{r}_{OH}$ and decreases R_{OO}, which increases the dipole moment. The dipole moment per molecule changes from 1.7 to 3.0 D going from gas phase to liquid.

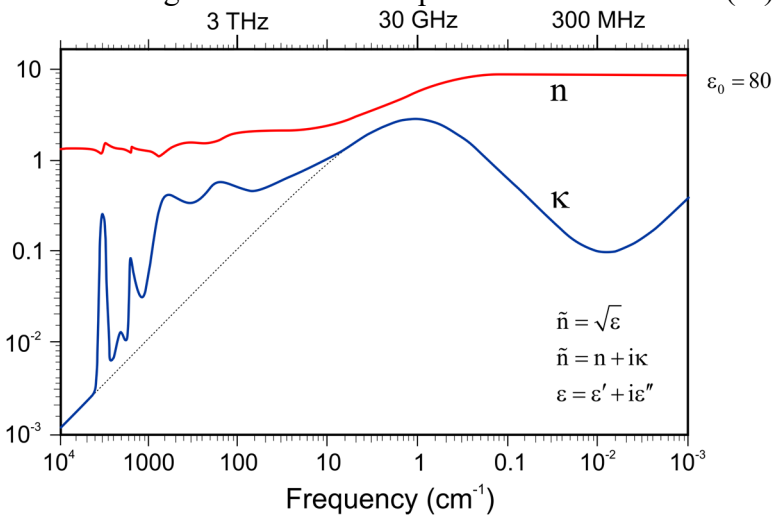


Water Dielectric Response

Pure water is a strong dielectric medium, meaning that long-range electrostatic forces acting between two charges in water are dramatically reduced. The static dielectric constant is $\varepsilon_r = 80$, also known as the relative permittivity $\varepsilon_r = \varepsilon/\varepsilon_0$. The dielectric response is strongly frequency and temperature dependent. Motion of water charges encoded in complex dielectric constant (ε) or index of refraction ($\tilde{n}$).

Dielectric Constant

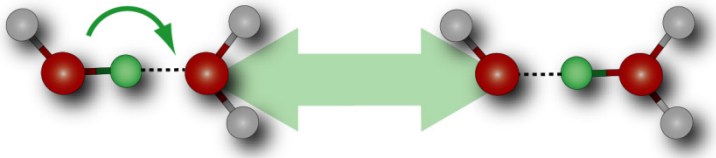
T(°C)	ε_r
0	88
20	80.1
100	55.3



P. S. Ray, Appl. Opt. **11**, 1836-1844 (1972).

Water Autoionization and pH

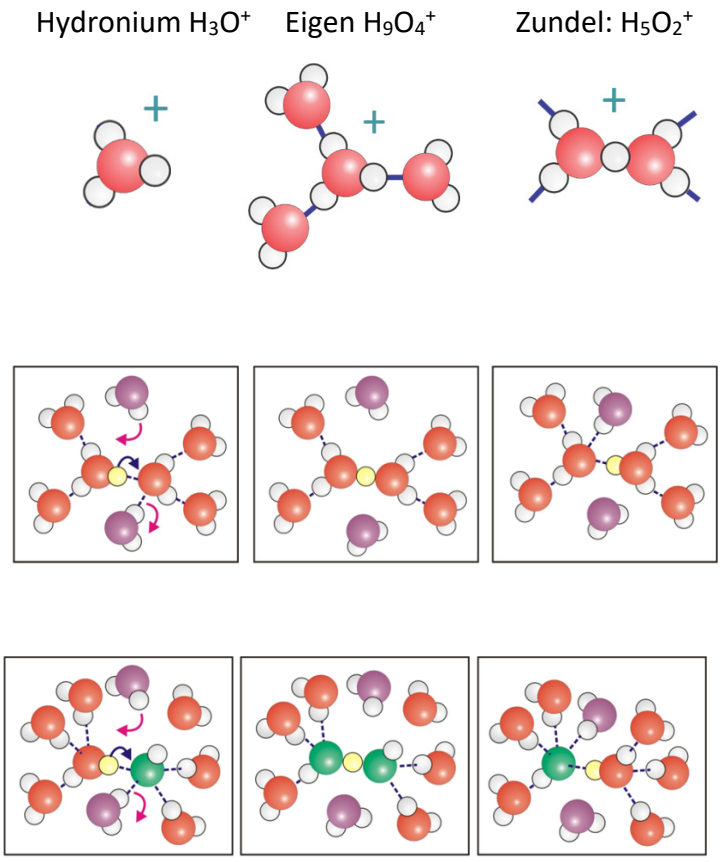
- Protons and hydroxide govern acid base chemistry.
- Any water molecule in the bulk lives about 10 hours before dissociating.
- In a liter, a water molecule dissociates every 30 microseconds.



$$K_W = [H_3O^+][OH^-] = 1.0\times10^{-14} \ (25^\circ\ C)$$

Protons in Water

- Structure of H^+ in water and the extent to which the excess charge is delocalized is still unresolved. It is associated strongly enough to describe as covalently interacting, but its time evolution is so rapid (<1 ps) that it is difficult to define a structure.
- Much higher mobility than expected by diffusion of a cation of similar size.
- Explained by Grotthus mechanism for transfer of proton to neighboring water molecules.
- OH^- is also very mobile and acts as a proton acceptor from water.



Water Physical Properties

Property		Units	T (°C)				
			0	25	37	50	100
Heat Capacity	C_P	J mol^{-1} K^{-1}	76.01	75.327		75.33	75.95
Density	ρ	kg m^{-3}	999.82	997.13	993.37	988.02	958.4
Dielectric Relaxation Time	τ	ps = 10^{-12} s	14.5	8.1	5.0	4.5	0
Surface Tension	γ	N m^{-1}	0.0756	0.07198			0.06
Self-Diffusion Constant	D	cm^2 s^{-1}	1.2E-05	2.1E-05	2.8E-05	4.0E-05	
Speed of Sound	c	m s^{-1}	1402	1494	1525	1543	1543
Dynamic Viscosity	η	mPa s (10^{-3} N s m^{-2})	1.792	0.893	0.692	0.547	0.283
Dielectric Constant	ϵ_r		87.7	78.3	73.9	69.88	55.3
Avg. dipole moment in liquid		D		2.95			

Protons and Hydroxide			25°C
H+ and OH- concentration	c	mol L^{-1}	1.004E-07
Proton mobililty	μ_+	cm^2 V^{-1} s^{-1}	0.00362
Hydroxide mobility	μ_-	cm^2 V^{-1} s^{-1}	0.00198
Proton diffusion constant		$Å^2$ ps^{-1}	0.931
Hydroxide diffusion constant		$Å^2$ ps^{-1}	0.503