Light, Liquids & Interfaces
Micro-390

Lecture 6

Sylvie Roke

Material to study:
JN Israelachvilli: Intermolecular and surface forces:
Chapter 7: 7.1-7.3
Chapter 8: 8.1; 8.2; 8.5-8.7 + Notes

Exercises 15-19

Key concepts Lecture 5

- Dipole-dipole interaction and its properties
- Angle-averaged potentials:

  When dipoles are free to move in solution, they will experience different orientations and thus different interaction potentials.

  Boltzmann weighting factor can give more weight to a specific orientation.

  Angle-average pair potentials are T-dependent

- Interactions of non-polar molecules
- Van der Waals forces group 3 forces with $1/r^6$ dependence
- Dipole moments can be induced in non-polar molecules
- Molecular polarizability vs. macroscopic polarizability

Interactions in liquids

$\frac{1}{r^2}$ or $\frac{1}{r^4}, \frac{1}{kT}$

Binding energies

Charge-dipole interactions

energy (J) 10^{-21} 10^{-20} 10^{-19} 10^{-18}

energy (k_BT) 1 10 200

Van-der-Waals Interactions

London
Keesom
Dispersion

H-bond

Ionic interactions (for an ion pair in vacuum)

100-300

Covalent bonds

$\frac{1}{r^3}$ or $\frac{1}{r^6}, \frac{1}{kT}$

$\frac{1}{r}$

Slide: E. Amstad; Soft Matter

Organizational comments

Upcoming Intermediate Test:

Oct. 24 - Week 6, lecture 6: (today) Water + Exercises 16-19

Oct. 31 - Week 7, lecture 7: Spectroscopy + no exercises (recap / prepare)

Nov. 8 - Week 8: Test (ELG 116)

Nov. 14 - Week 9, lecture 8: Spectroscopy & Interfaces (2D)
Nov. 21 – Week 10, lecture 9: Interfaces (2D & 3D)
…

Planned Lecture Material

Main Course book:
JN Israelachvili, Intermolecular and surface forces, Academic Press Third edition, 2009.; abbreviation JNI

Topics	**Material**
1. Introduction; Probability and thermodynamics	**Notes, Chapter 1** **Notes, Ben-Amotz, Chapter 1 + notes**
2. Driving forces and interactions	**Notes, Chapter 2: paragraphs: 2.1 - 2.4, 2.6, 2.7** **Notes, Chapter 3: paragraphs: 3.1 – 3.8** **Notes, Chapter 4: paragraphs: 4.1 – 4.7; 4.9-4.11** **Notes, Chapter 5: paragraphs: 5.1 - 5.4; 5.6;** **Notes, Chapter 6: paragraph: 6.1;** **Notes, Chapter 7: paragraph: 7.1-7.3;**
3. Water	Notes, Chapter 8: 8.1; 8.2; 8.5-8.7
4. Spectroscopy of liquids	Notes, Atkins 9.4,9.5 (Vibr. Motion); 13.1,13.2; 13.9; 13.13,13.14;13.15;13.16
5. Interfaces in 2D and 3D	Notes, Atkins Ch. 19.15; Ohshima, CH1:1-2;3.1.1-3.1.2.;
6. Techniques to probe interfaces	Notes
7. State of the art	Notes

Material so far covered

Planned Lecture Material

Main Course book:
JN Israelachvilli, Intermolecular and surface forces, Academic Press Third edition, 2009.; abbreviation JNI

Topics	Material
1. Introduction; Probability and thermodynamics	**Notes, Chapter 1** **Notes, Ben-Amotz, Chapter 1 + notes**
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3. Water	Notes, Chapter 8: 8.1; 8.2; 8.5-8.7
4. Spectroscopy of liquids	Notes, Atkins 9.4,9.5 (Vibr. Motion); 13.1,13.2; 13.9; 13.13,13.14;13.15;13.16
5. Interfaces in 2D and 3D	Notes, Atkins Ch. 19.15; Ohshima, CH1:1-2;3.1.1-3.1.2.;
6. Techniques to probe interfaces	Notes
7. State of the art	Notes

For the intermediate test: Lectures 1 - 5

Topic 3: Water

Material to study:
JN Israelachvilli: Intermolecular and surface forces:
Chapter 8: 8.1; 8.2; 8.5-8.7 + Notes

Water and Us

~~Planet earth ?~~

Planet water !

H_2O related Scientific Debates

“ Whiskey is for drinking, water is for fighting over “

The bulk structure of water: what is it?
Substructures? Rings, Cavities?
Single – two or multistate water?

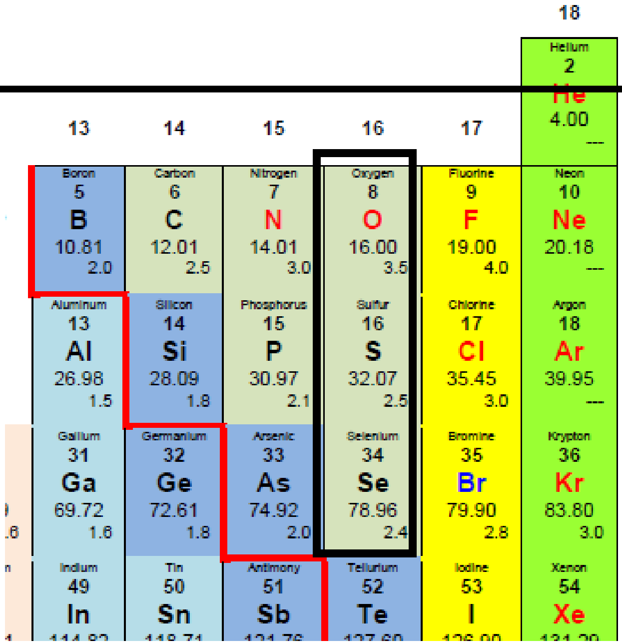
Water in biology
Membrane water?
Master or slave?
Confinement effects?

Hydrophobicity
Why are oil droplets in water stable?
What are the interactions between oil [hydrophobes] and water?
Water structure in contact with a hydrophobic interface?

Water in technology:
High humidity impacts devices: how to get around it?
Can we use osmosis to generate electricity?

What is special about water?

Boiling point



13	14	15	16	17	18
					Helium 2 He 4.00 ---
Boron 5 B 10.81 2.0	Carbon 6 C 12.01 2.5	Nitrogen 7 N 14.01 3.0	Oxygen 8 O 16.00 3.5	Fluorine 9 F 19.00 4.0	Neon 10 Ne 20.18 ---
Aluminum 13 Al 26.98 1.5	Silicon 14 Si 28.09 1.8	Phosphorus 15 P 30.97 2.1	Sulfur 16 S 32.07 2.5	Chlorine 17 Cl 35.45 3.0	Argon 18 Ar 39.95 ---
Gallium 31 Ga 69.72 1.6	Germanium 32 Ge 72.61 1.8	Arsenic 33 As 74.92 2.0	Selenium 34 Se 78.96 2.4	Bromine 35 Br 79.90 2.8	Krypton 36 Kr 83.80 3.0
Indium 49 In	Tin 50 Sn	Antimony 51 Sb	Tellurium 52 Te	Iodine 53 I	Xenon 54 Xe

Compare boiling point of small 3 atom molecules…

Compound	Boiling point (°C)	Dipole moment (D)
H_2Se	-60	0.63
H_2S	-41	0.97
H_2O	100	1.85

The boiling point of water is extremely high for a small molecule composed of 3 atoms…

Dielectric constant

The dielectric constant reflects the amount of charge that displaces due to the influence of an external electrostatic field

Compound	**ε (room temp)**
n-hexane (C_6H_{14})	1.89
Chloroform (CH_3Cl)	4.8
Octanol	10; frozen: 2
Methanol (CH_3OH)	32
H_2O	78: frozen (0 °C): ~82-110
TiO_2 (semiconductor)	~100

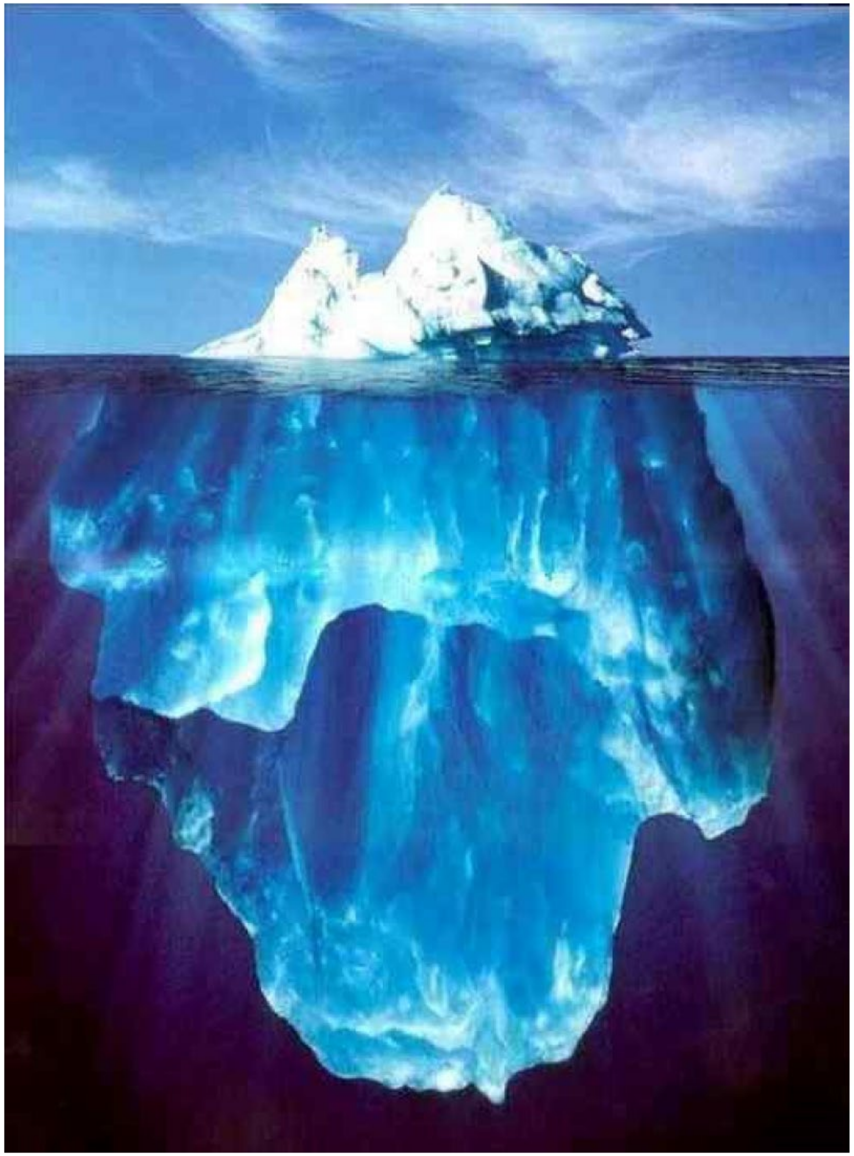
$$\varepsilon = 1 + \frac{N}{\varepsilon_0}\langle\alpha\rangle_{ij,orientations}$$

$$\alpha_{ij} = \alpha_{0,ij} + \frac{u_{ij}^2}{3kT}$$

The dielectric constant is unusually high for water – on the level of a semiconductor

The dielectric constant of water <u>increases</u> with decreasing temperature

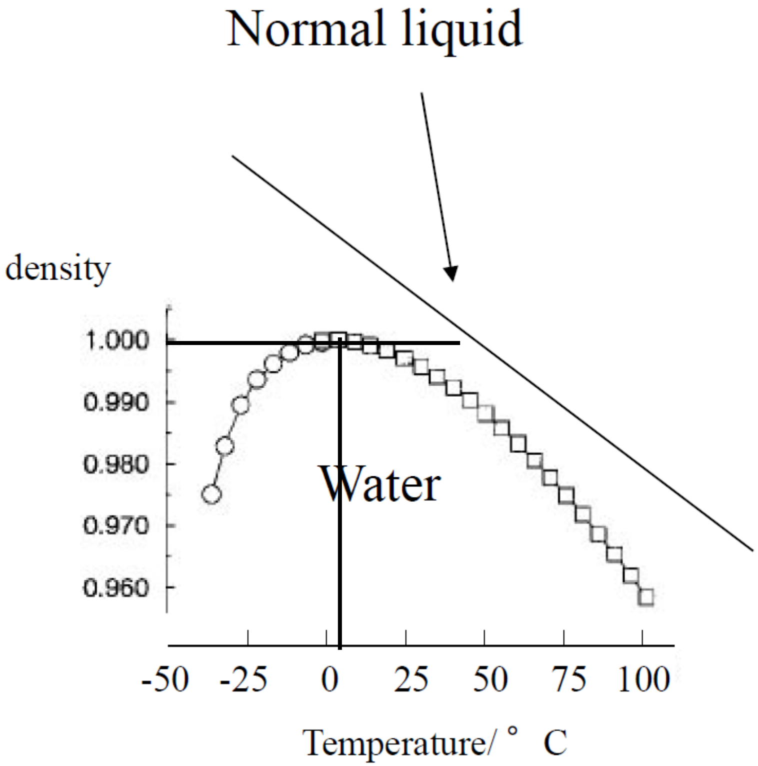
Liquid water is more dense than solid water



Solid is more dense than liquid for almost all liquids (ethanol, gasoline, etc)

But not for water:
Density of liquid water is higher than its solid

Liquid water is denser than solid water



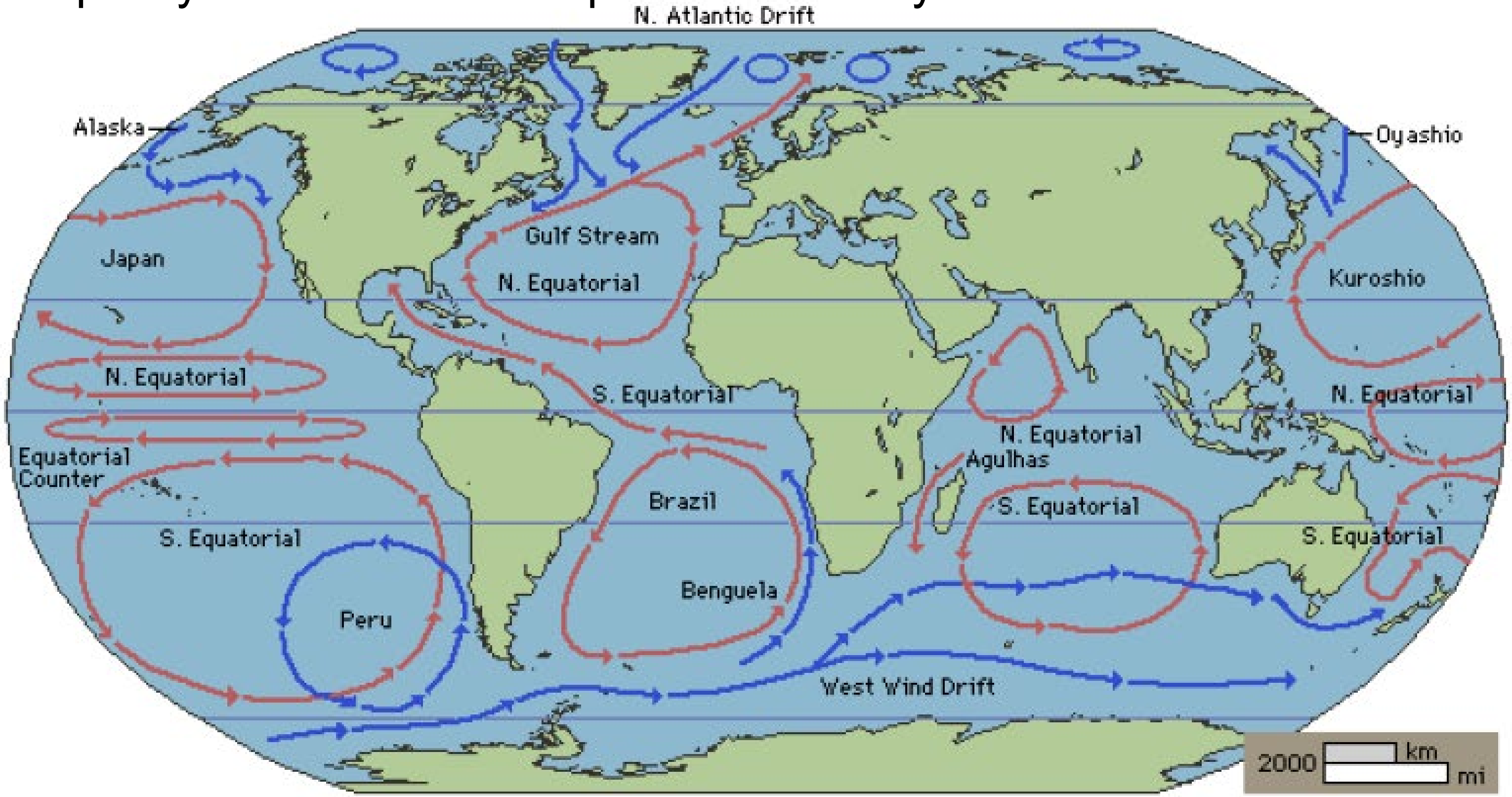
At the bottom of this glass with water and ice, water is 4°C

This allows for density driven convection: **Life in the artic regions**

High heat capacity (C_p)

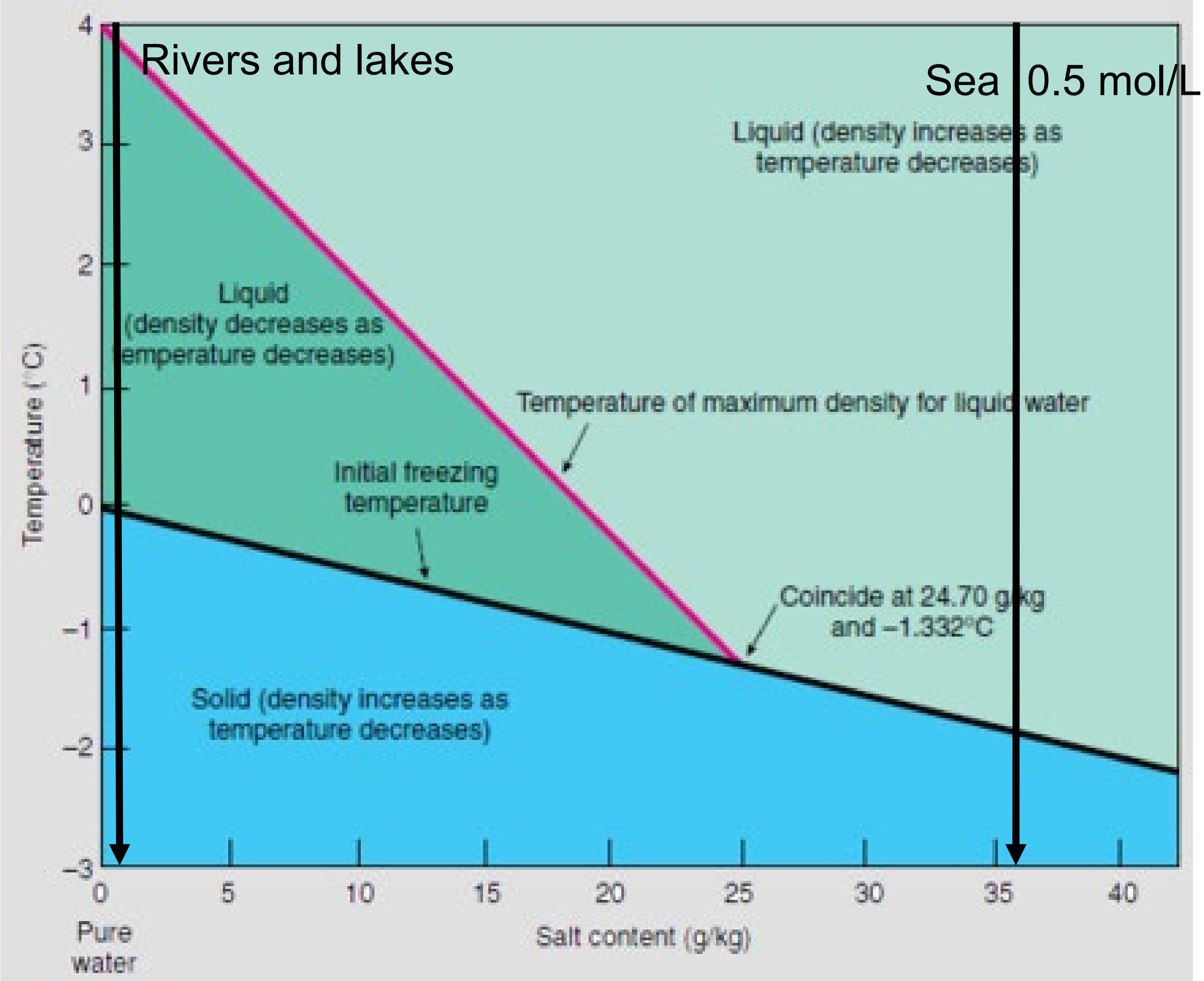
C_p = (dU/dT) The amount of heat needed for a 1°C temperature rise.
Water = 4.184 J/g K ; Methanol: 2.14 J/g K ; Cu = 0.386 J/g K

High heat capacity maintains the temperature stability in the oceans / lakes.



Because of the high heat capacity, ocean currents act as a stabilizer of the climate

Adding salt changes all this



In addition to density driven currents there are also currents due to concentration gradients

High surface tension (γ)

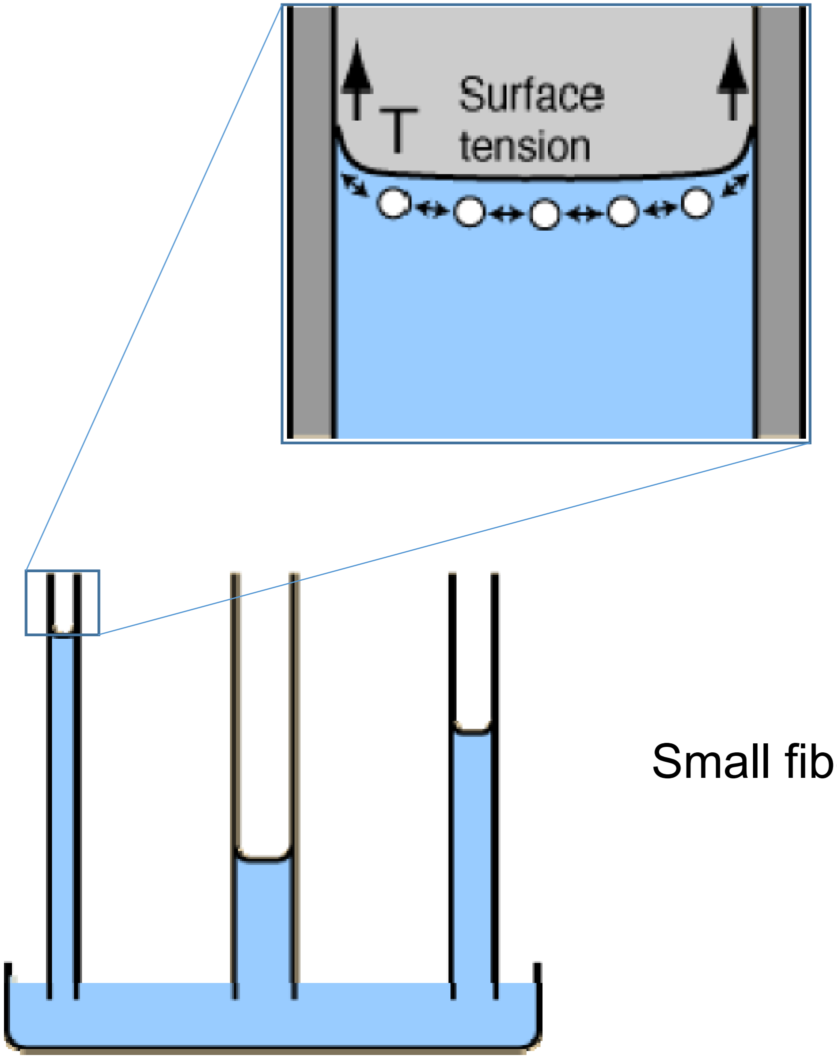
Water has an extremely high surface tension (γ_{aw} =72.8 mJ/m^2)
Methanol: 22.55 mJ/m^2

Formation of water drops

Insects can walk on water

Capillary forces

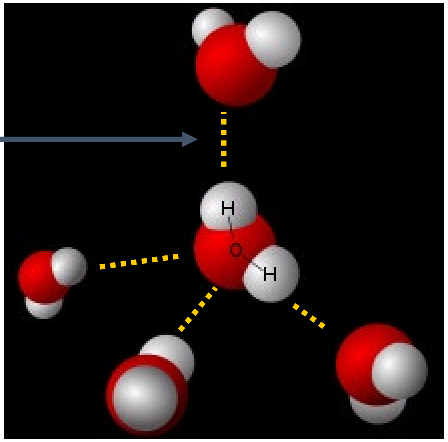
A high surface tension gives rise to a high capillary force



Small fibers in plants and trees:

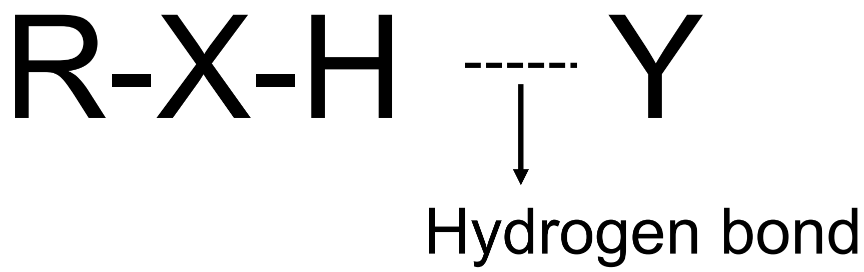
Hydrogen bonds

Hydrogen bond



What is a hydrogen bond?

IUPAC definition: “The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment R-X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule (Y), in which there is evidence of bond formation.”



R-X-H ------ Y

Hydrogen bond

X, Y: Electronegative

R-X-H: H bond donor
Y: H bond acceptor

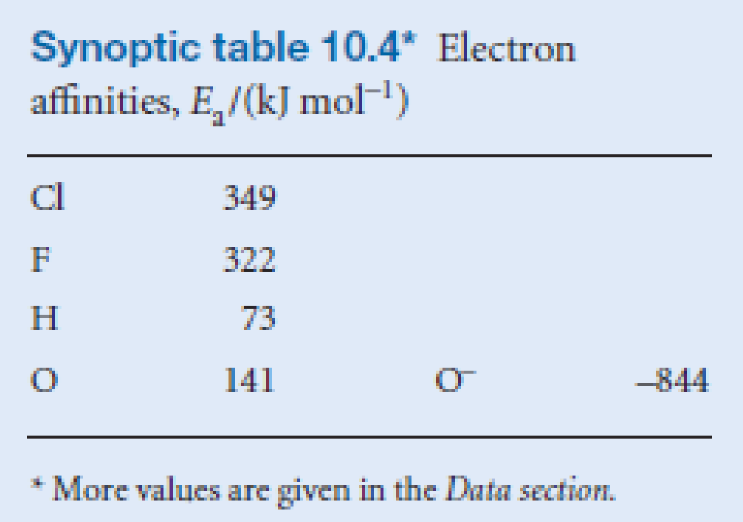
Note that the electrons move in the *other* direction

Reminder…electronegativity

Electronegativity (χ) = tendency of an atom to attract electrons.
There are several electronegativity scales. They are dimensionless and empirically derived from electron dissociation energies and electron affinities – relative to that of H.

Electron affinity (E_{ea}): is the energy released when an electron attaches to a gas phase atom

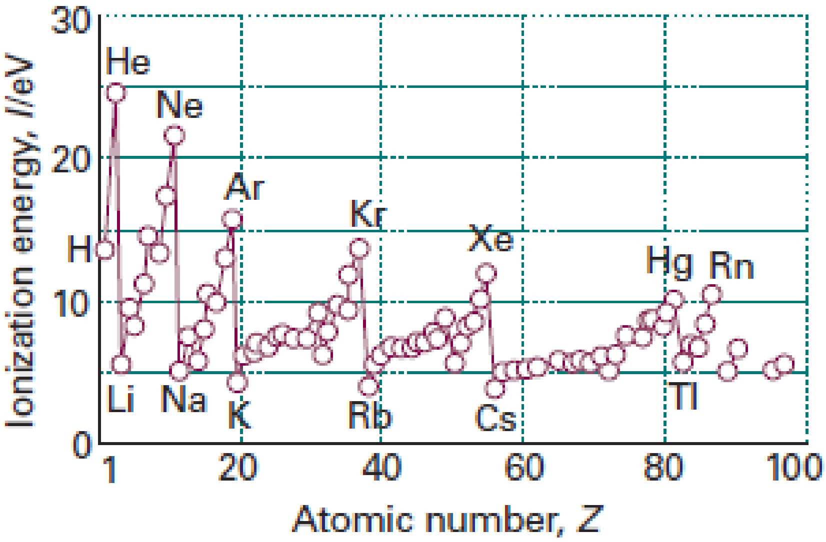
The (first) electron dissociation energy (I_1): Minimum energy necessary to remove an electron from a many-electron atom in the gas phase.



Synoptic table 10.4* Electron affinities, $E_a/(\mathrm{kJ\ mol^{-1}})$

Cl	349		
F	322		
H	73		
O	141	O^-	–844

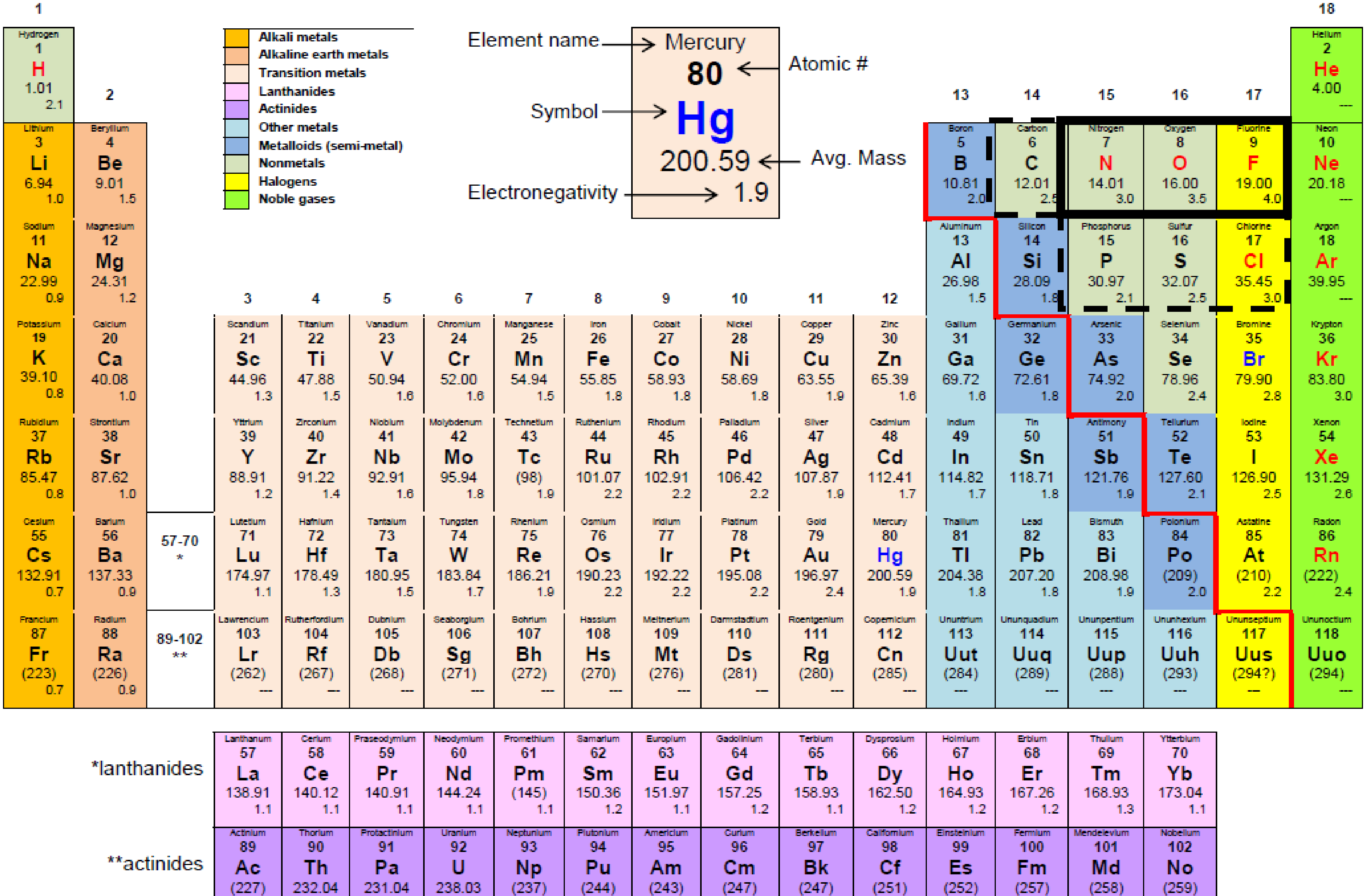
* More values are given in the *Data section.*



Mulliken electronegativity*: $\chi_M = 1/2(I_1 + E_{ea})$

*Values are taken in eV; PW Atkins, Physical Chemistry

Reminder…electronegativity



The Periodic Table of the Elements (with Electronegativities)

- ■ Alkali metals
- ■ Alkaline earth metals
- ■ Transition metals
- ■ Lanthanides
- ■ Actinides
- ■ Other metals
- ■ Metalloids (semi-metal)
- ■ Nonmetals
- ■ Halogens
- ■ Noble gases

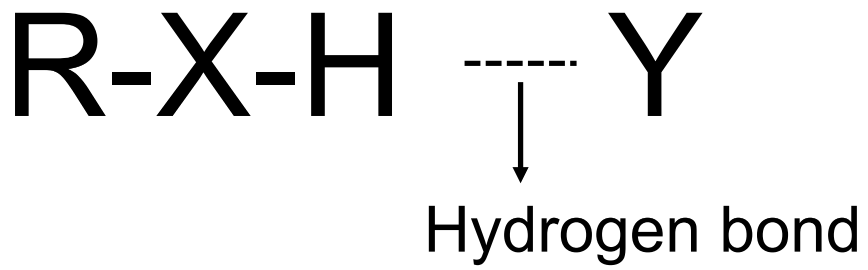
Element name → Mercury
80 ← Atomic #
Symbol → Hg
200.59 ← Avg. Mass
Electronegativity → 1.9

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Hydrogen 1 H 1.01 2.1																		Helium 2 He 4.00 ---
Lithium 3 Li 6.94 1.0	Beryllium 4 Be 9.01 1.5												Boron 5 B 10.81 2.0	Carbon 6 C 12.01 2.5	Nitrogen 7 N 14.01 3.0	Oxygen 8 O 16.00 3.5	Fluorine 9 F 19.00 4.0	Neon 10 Ne 20.18 ---
Sodium 11 Na 22.99 0.9	Magnesium 12 Mg 24.31 1.2												Aluminum 13 Al 26.98 1.5	Silicon 14 Si 28.09 1.8	Phosphorus 15 P 30.97 2.1	Sulfur 16 S 32.07 2.5	Chlorine 17 Cl 35.45 3.0	Argon 18 Ar 39.95 ---
Potassium 19 K 39.10 0.8	Calcium 20 Ca 40.08 1.0		Scandium 21 Sc 44.96 1.3	Titanium 22 Ti 47.88 1.5	Vanadium 23 V 50.94 1.6	Chromium 24 Cr 52.00 1.6	Manganese 25 Mn 54.94 1.5	Iron 26 Fe 55.85 1.8	Cobalt 27 Co 58.93 1.8	Nickel 28 Ni 58.69 1.8	Copper 29 Cu 63.55 1.9	Zinc 30 Zn 65.39 1.6	Gallium 31 Ga 69.72 1.6	Germanium 32 Ge 72.61 1.8	Arsenic 33 As 74.92 2.0	Selenium 34 Se 78.96 2.4	Bromine 35 Br 79.90 2.8	Krypton 36 Kr 83.80 3.0
Rubidium 37 Rb 85.47 0.8	Strontium 38 Sr 87.62 1.0		Yttrium 39 Y 88.91 1.2	Zirconium 40 Zr 91.22 1.4	Niobium 41 Nb 92.91 1.6	Molybdenum 42 Mo 95.94 1.8	Technetium 43 Tc (98) 1.9	Ruthenium 44 Ru 101.07 2.2	Rhodium 45 Rh 102.91 2.2	Palladium 46 Pd 106.42 2.2	Silver 47 Ag 107.87 1.9	Cadmium 48 Cd 112.41 1.7	Indium 49 In 114.82 1.7	Tin 50 Sn 118.71 1.8	Antimony 51 Sb 121.76 1.9	Tellurium 52 Te 127.60 2.1	Iodine 53 I 126.90 2.5	Xenon 54 Xe 131.29 2.6
Cesium 55 Cs 132.91 0.7	Barium 56 Ba 137.33 0.9	57-70 *	Lutetium 71 Lu 174.97 1.1	Hafnium 72 Hf 178.49 1.3	Tantalum 73 Ta 180.95 1.5	Tungsten 74 W 183.84 1.7	Rhenium 75 Re 186.21 1.9	Osmium 76 Os 190.23 2.2	Iridium 77 Ir 192.22 2.2	Platinum 78 Pt 195.08 2.2	Gold 79 Au 196.97 2.4	Mercury 80 Hg 200.59 1.9	Thallium 81 Tl 204.38 1.8	Lead 82 Pb 207.20 1.8	Bismuth 83 Bi 208.98 1.9	Polonium 84 Po (209) 2.0	Astatine 85 At (210) 2.2	Radon 86 Rn (222) 2.4
Francium 87 Fr (223) 0.7	Radium 88 Ra (226) 0.9	89-102 **	Lawrencium 103 Lr (262) ---	Rutherfordium 104 Rf (267) ---	Dubnium 105 Db (268) ---	Seaborgium 106 Sg (271) ---	Bohrium 107 Bh (272) ---	Hassium 108 Hs (270) ---	Meitnerium 109 Mt (276) ---	Darmstadtium 110 Ds (281) ---	Roentgenium 111 Rg (280) ---	Copernicium 112 Cn (285) ---	Ununtrium 113 Uut (284) ---	Ununquadium 114 Uuq (289) ---	Ununpentium 115 Uup (288) ---	Ununhexium 116 Uuh (293) ---	Ununseptium 117 Uus (294?) ---	Ununoctium 118 Uuo (294) ---

*lanthanides	Lanthanum 57 La 138.91 1.1	Cerium 58 Ce 140.12 1.1	Praseodymium 59 Pr 140.91 1.1	Neodymium 60 Nd 144.24 1.1	Promethium 61 Pm (145) 1.1	Samarium 62 Sm 150.36 1.2	Europium 63 Eu 151.97 1.1	Gadolinium 64 Gd 157.25 1.2	Terbium 65 Tb 158.93 1.1	Dysprosium 66 Dy 162.50 1.2	Holmium 67 Ho 164.93 1.2	Erbium 68 Er 167.26 1.2	Thulium 69 Tm 168.93 1.3	Ytterbium 70 Yb 173.04 1.1
**actinides	Actinium 89 Ac (227)	Thorium 90 Th 232.04	Protactinium 91 Pa 231.04	Uranium 92 U 238.03	Neptunium 93 Np (237)	Plutonium 94 Pu (244)	Americium 95 Am (243)	Curium 96 Cm (247)	Berkelium 97 Bk (247)	Californium 98 Cf (251)	Einsteinium 99 Es (252)	Fermium 100 Fm (257)	Mendelevium 101 Md (258)	Nobelium 102 No (259)

What is a hydrogen bond?

IUPAC definition: “The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.”

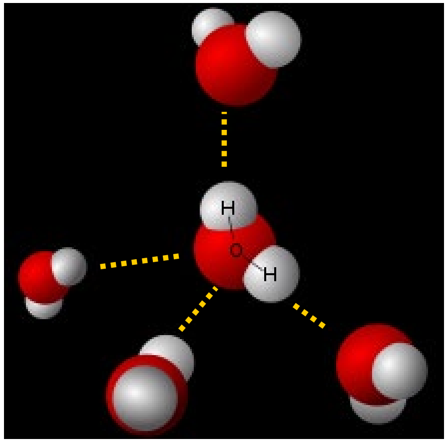


There are proper and improper H-bonds:

Proper H-bonds lead to a lengthening of the X-H bond and a spectroscopic red shift (=to lower energy/frequency) of the X-H vibration.
Improper H-bonds lead to shortening of the X-H bond and a spectroscopic blue shift (=to higher energy/frequency) of the X-H vibration.

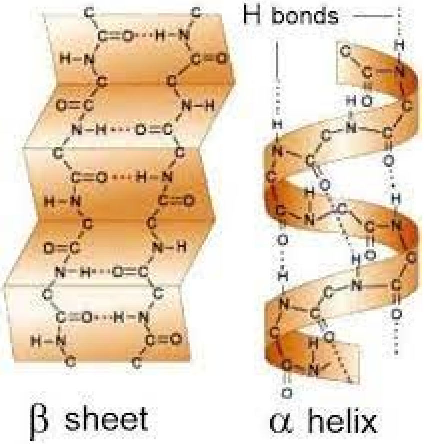
Hydrogen bonds

H – bonds can be inter- or intra-molecular and can lead to 1-D, 2-D and 3-D structures

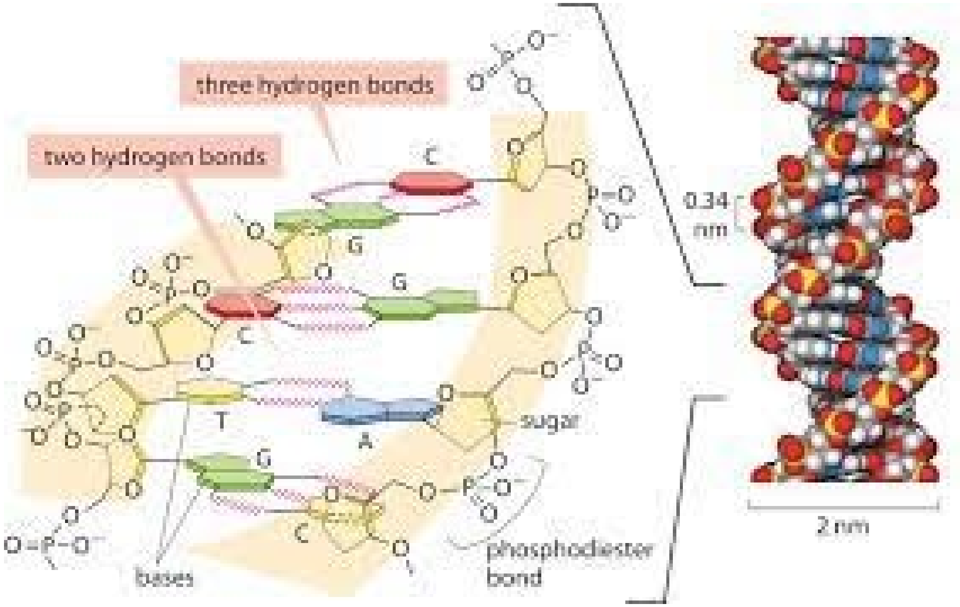


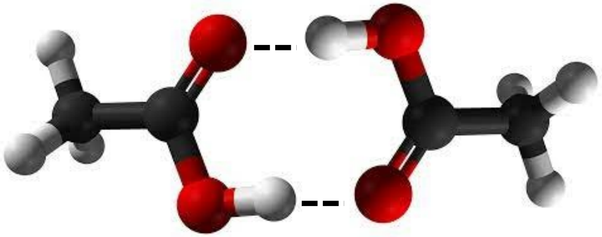
3D structure in water; ideal as a solvent

Secondary structure of peptides



3D structure of double helix of DNA

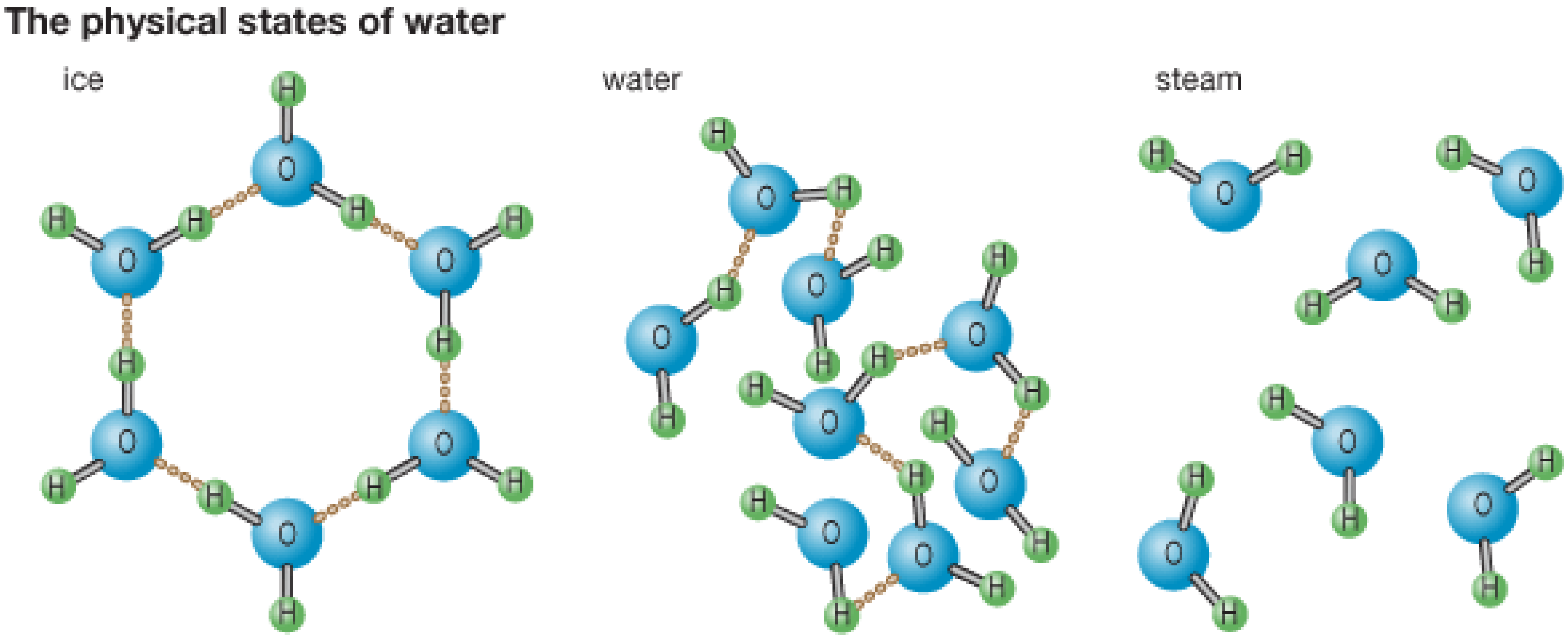




Acetic acid dimer

Hydrogen bonds in water

H-bonds in water and ice


The physical states of water

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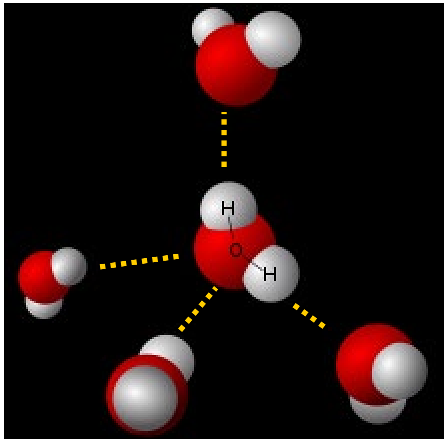
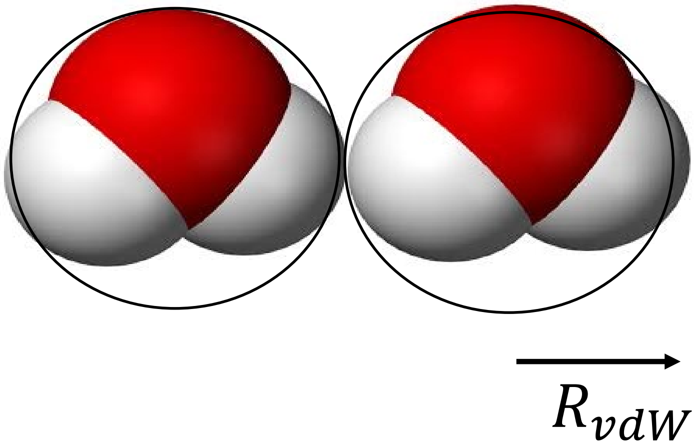


- Ice has 4 H bonds per molecule
- Liquid water has ~ 3.6* H bonds per molecule
- (Almost) no H-bonds in gas phase
- Directional interaction – often seen as part chemical and part electrostatic interaction

* At room temperature; latest current insights

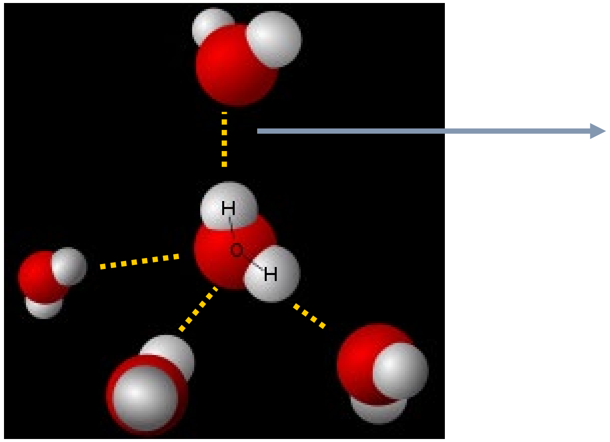
H-bonds in water

Hydrogen bonds reduce the distance between water molecules



$2R_{vdW}$ = 0.26 nm

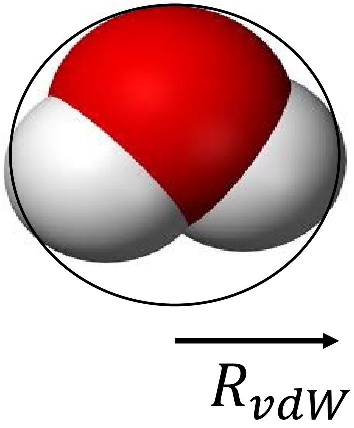
Van der Waals radius (R_{vdW}): radius if we approximate the molecule as a hard sphere



Average H-bond length in water: 0.18 nm

Reminder: The size of a molecule

How do we know and define the size of a molecule / atom ?



Van der Waals radius (R_{vdW}): the radius of an imaginary hard sphere representing the distance of closest approach for another hard sphere.
Is obtained from P-V isotherms using the van der Waals equation of state for a gas.

Ideal gas law (per mole) $P = \frac{RT}{V_m}$

Van der Waals gas (per mole)

$$P = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$$

Now we also know where the term "Van der Waals interaction" comes from…

Volume reduced by gas volume, b relates to the radius, $b = N_{av}\frac{4}{3}\pi R_{vdW}^3$

Pressure reduced by short range attraction a, that scales with $\frac{1}{V_m^2} = \frac{1}{r^6}$

H-bonds in water

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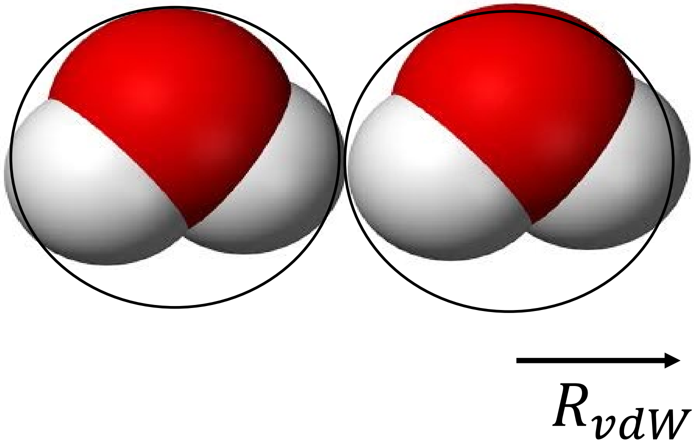

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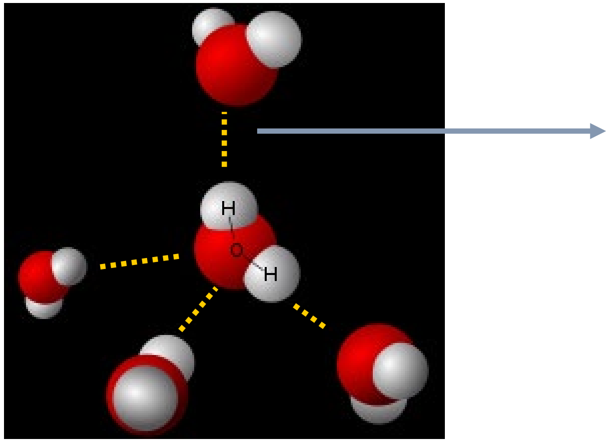

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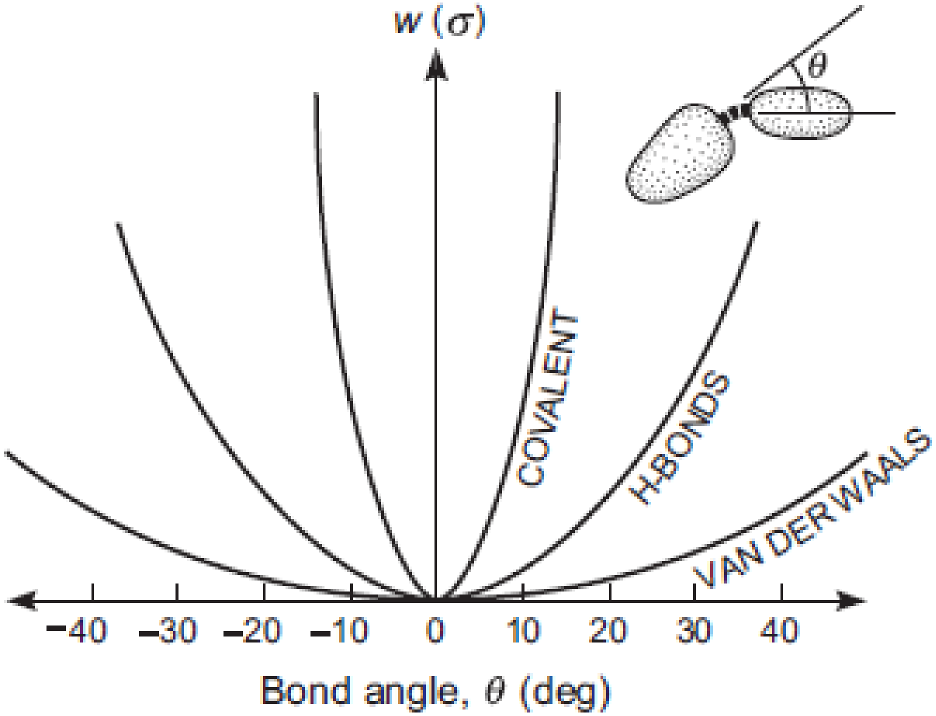
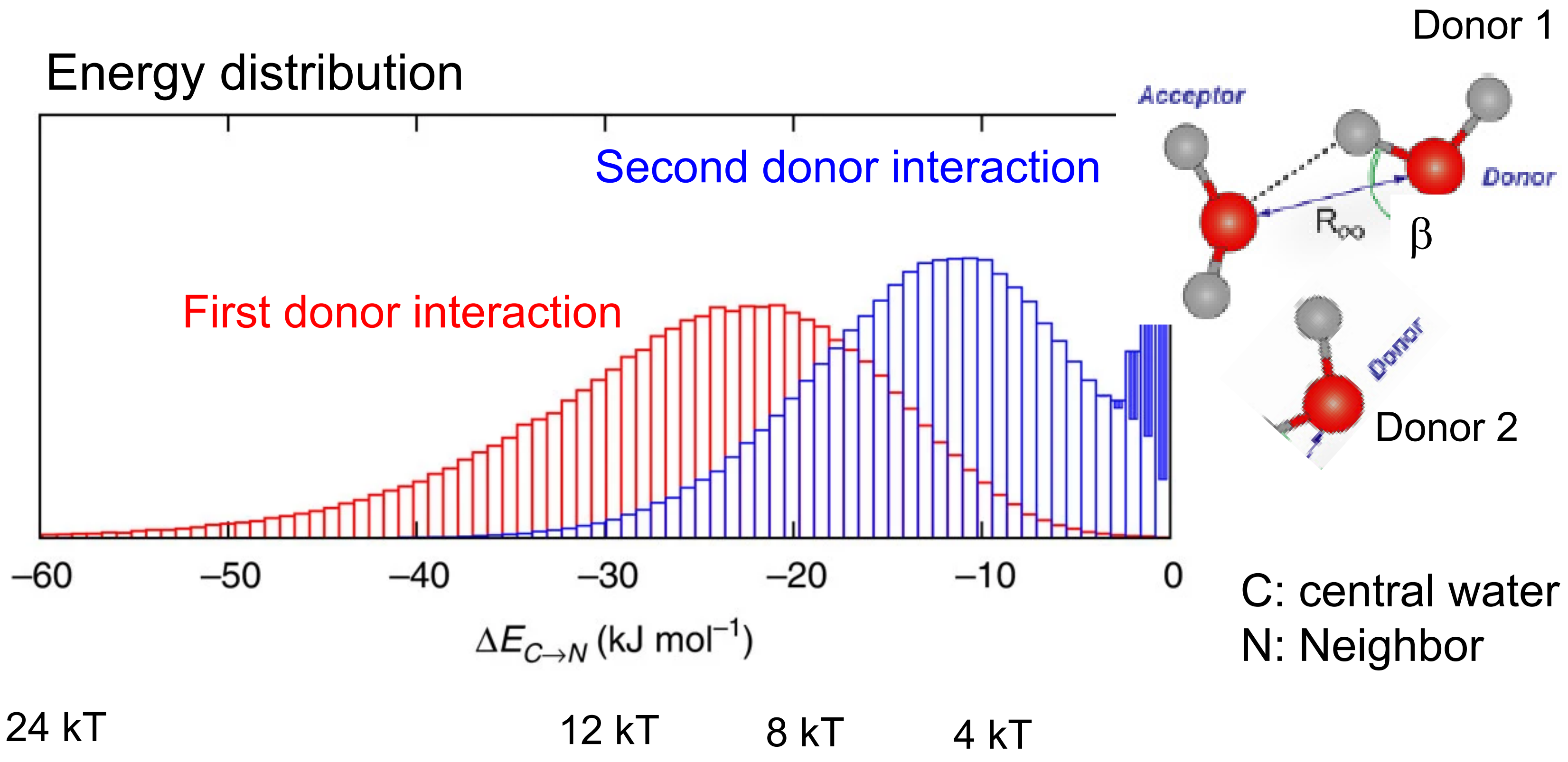
H-bond directionality



H-bonds in water have an orientational dependence that is more directional than interactions between non-polar / dipolar and charged molecules but less directional than a covalent bond

H-bonds

H-bonds vary in energy, length and angle;
Neigboring H-bonds influence energy / length / angle of given H-bond
they are also dynamic – time constant of forming H-bonds is ~ <1-10 ps.



Kuehne, et al. Nature Commun, 4, 1450 (2013)

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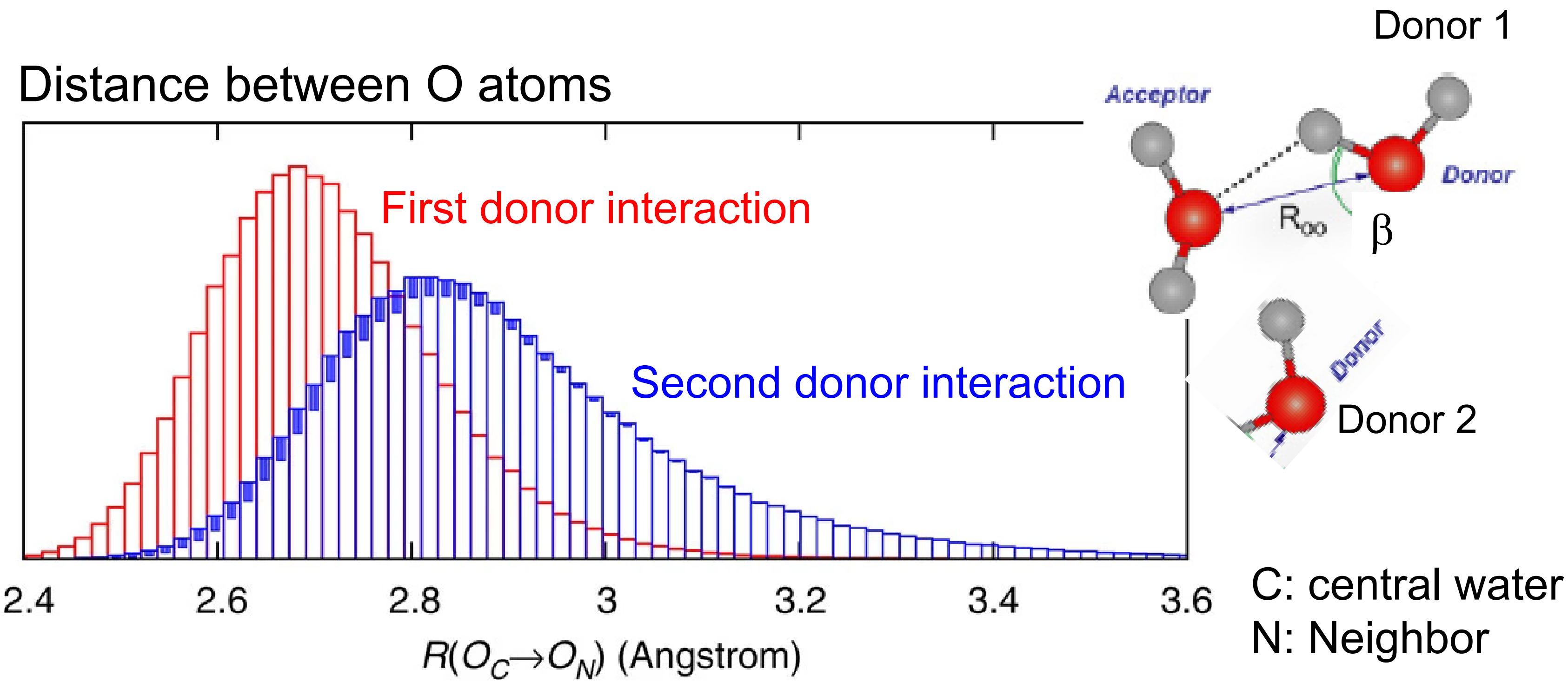

C: central water
N: Neighbor

Nature Commun, 4, 1450 (2013)

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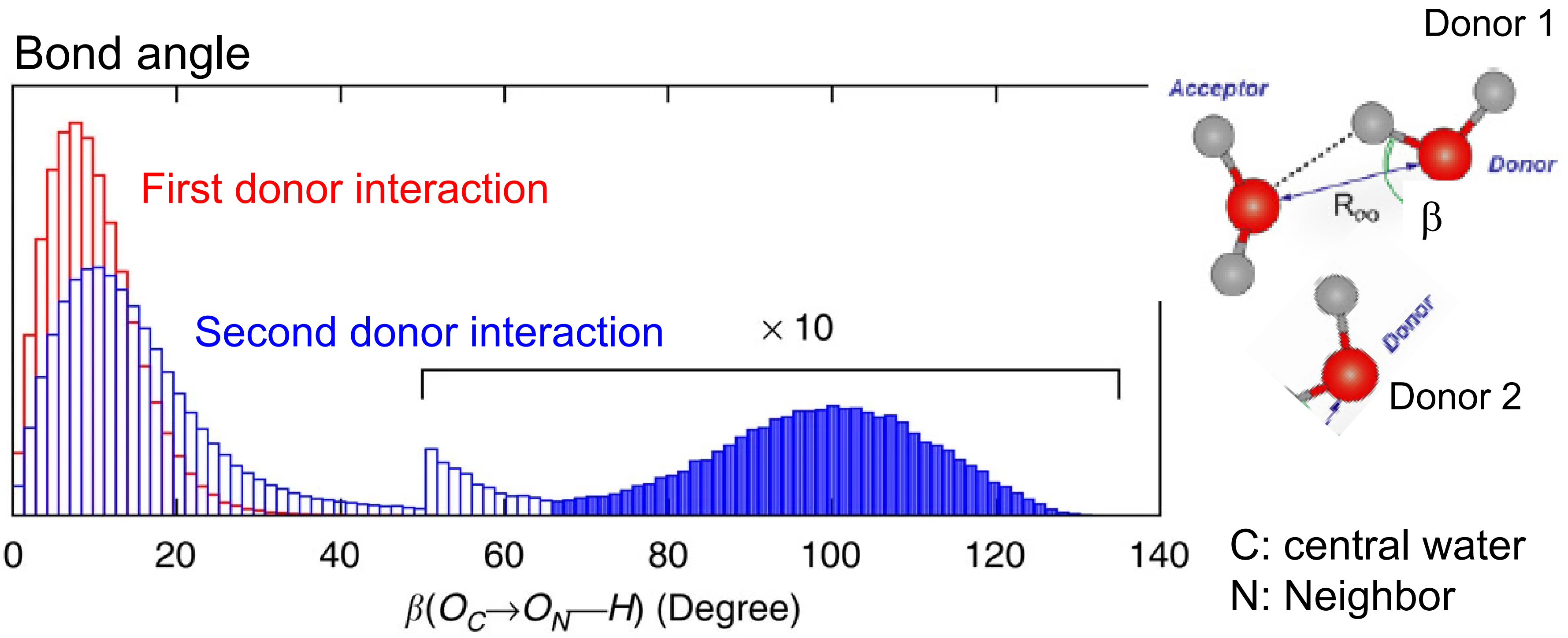
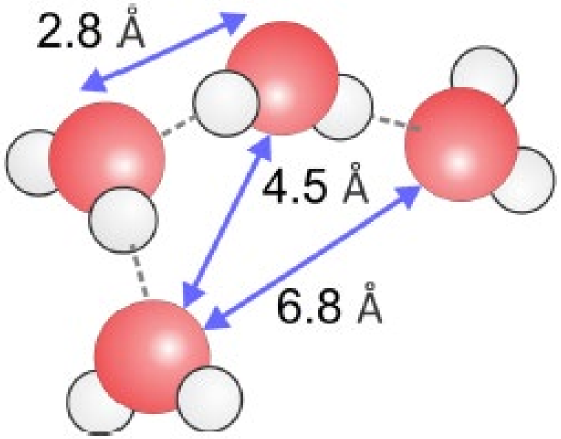
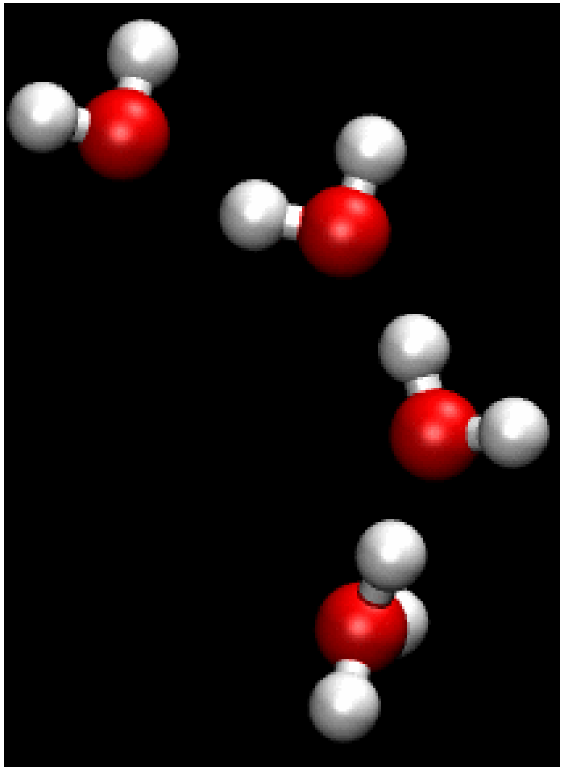


C: central water
N: Neighbor

Nature Commun, 4, 1450 (2013)

H-bonds and their motion

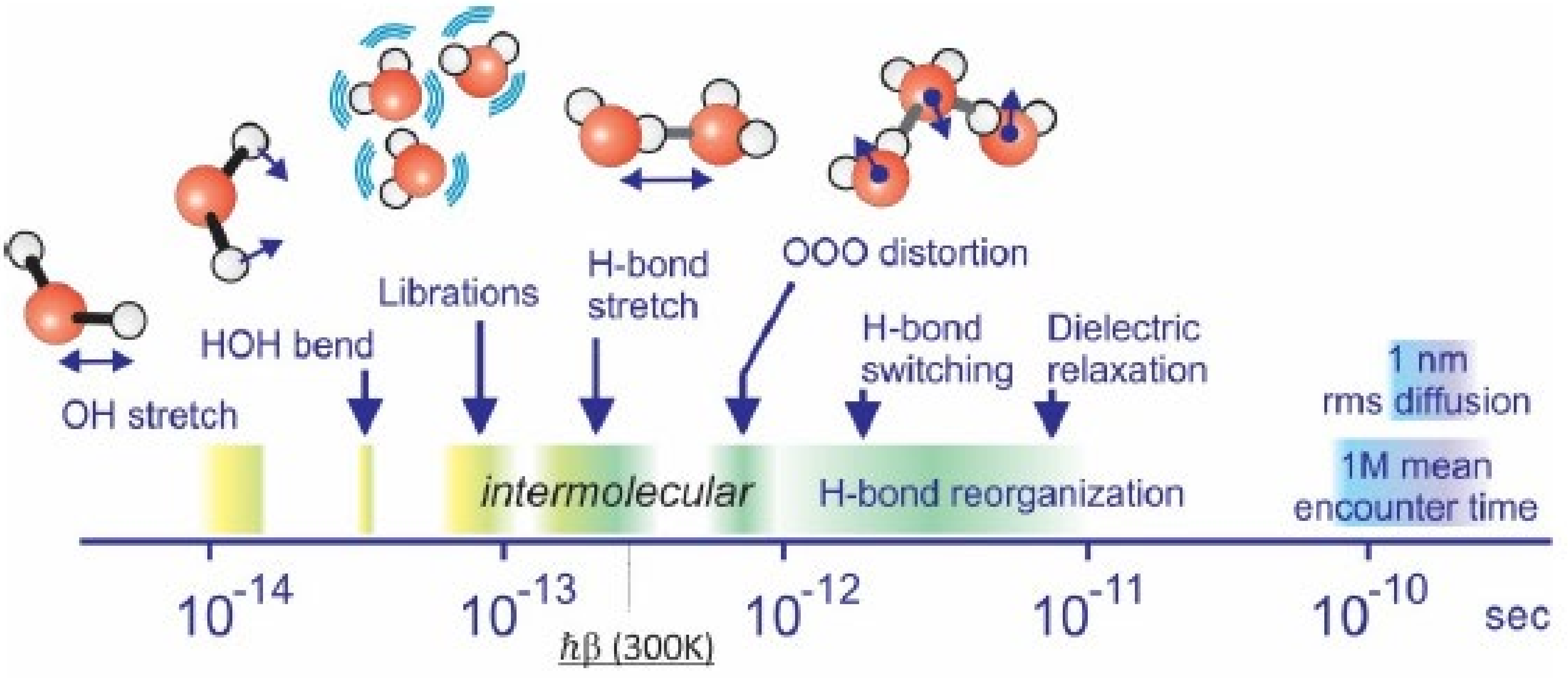




H-bonds are dynamic: transport of H is achieved via the Grotthuss mechanism: Correlated positions and orientations of water molecules allow H hopping

Link to video

H-bonds and the motion of water in water



The complex motion of water can be decomposed into various motions – the time constants of these motions vary from the fs time scale (~ 60 fs O-H stretch – 200 ps for 1 nm diffusion). H-bond formation: ~ 1-10 ps (8 ps average)
These motions can be measured spectroscopically

What are the interactions responsible for H-bonding?

What is a hydrogen bond?

Insights from energy decomposition analysis of density functional theory computations on pairs of molecules:

H-bonds are the result of several interactions:

- Charge transfer interactions: Electron density is transferred between orbitals
- Pauli repulsion: Repulsion between filled overlapping orbitals
- Coulombic interactions: Interactions between molecular charge densities
- Dispersion interactions: Interactions due to correlated electron fluctuations
- Polarizability: Charge density induced charge density fluctuations

H-bonds are shorter / longer based on the balance of these interactions, which leads to different H-bond binding constants and spectroscopic frequency shifts to higher / lower vibrational energies

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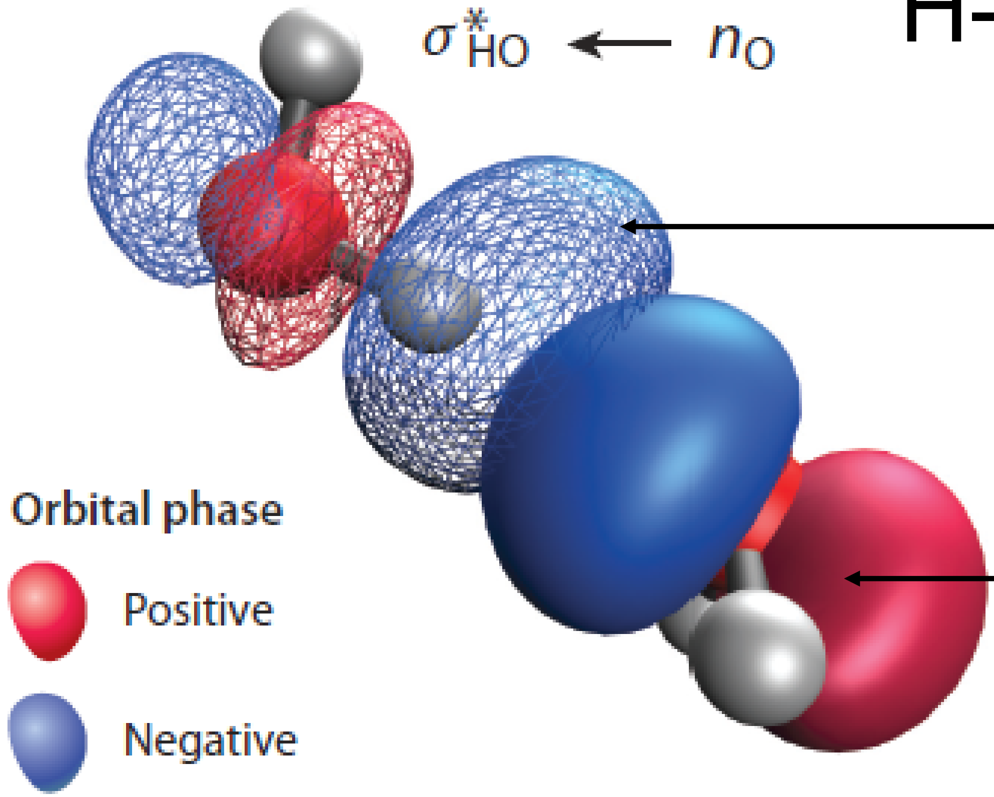
Charge Transfer

H-O-H ---- O



Empty electron density accepting H orbital

Filled electron density donating orbital

Charge transfer from filled O lone pair to anti bonding H orbital; electron density is shared between neighboring molecules; O-H bond length increases (red shift in frequency)

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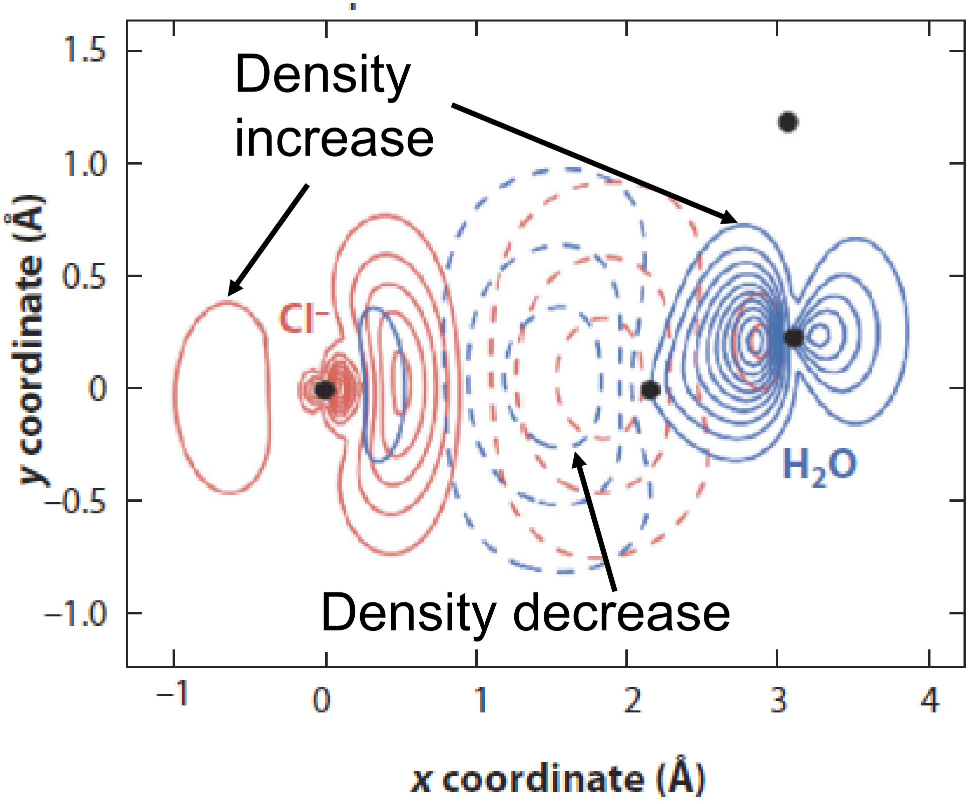
Pauli repulsion

Pauli repulsion between a Cl^- ion and a water molecule

Cl^- ---- H-O-H



Density increase

Density decrease

Electron density distortions resulting from orbital overlap.
The O-H bond length decreases

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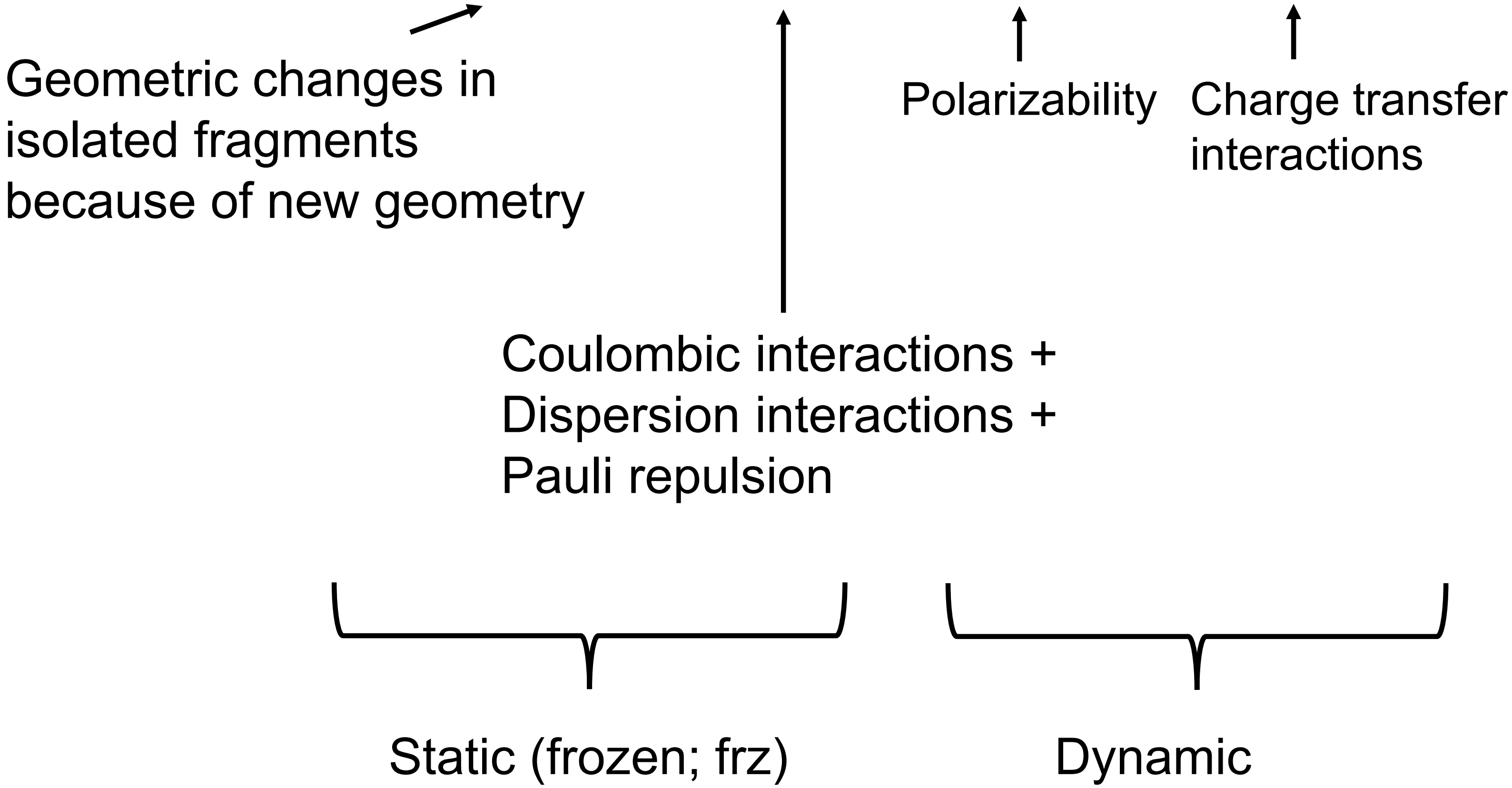
Energy Decomposition Analysis

Interaction energy is decomposed in different parts that are accessible via different computational steps.

$$\Delta E_{\mathrm{INT}} = \Delta E_{\mathrm{GD}} + \Delta E_{\mathrm{FRZ}} + \Delta E_{\mathrm{POL}} + \Delta E_{\mathrm{CT}}.$$



Geometric changes in isolated fragments because of new geometry

Polarizability

Charge transfer interactions

Coulombic interactions +
Dispersion interactions +
Pauli repulsion

Static (frozen; frz)

Dynamic

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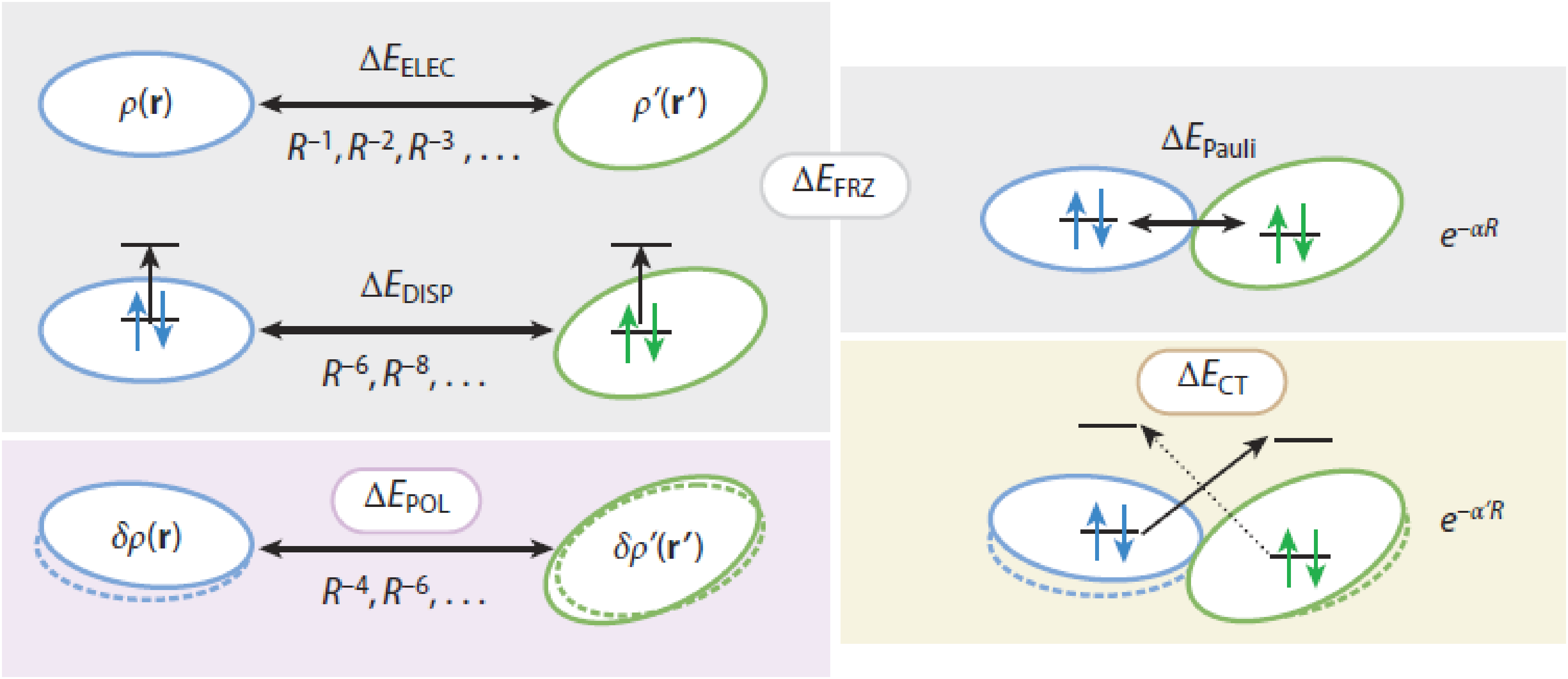
Energy Decomposition Analysis

$$\Delta E_{\mathrm{INT}} = \boxed{\Delta E_{\mathrm{GD}} + \Delta E_{\mathrm{FRZ}}} + \boxed{\Delta E_{\mathrm{POL}}} + \boxed{\Delta E_{\mathrm{CT}}}.$$



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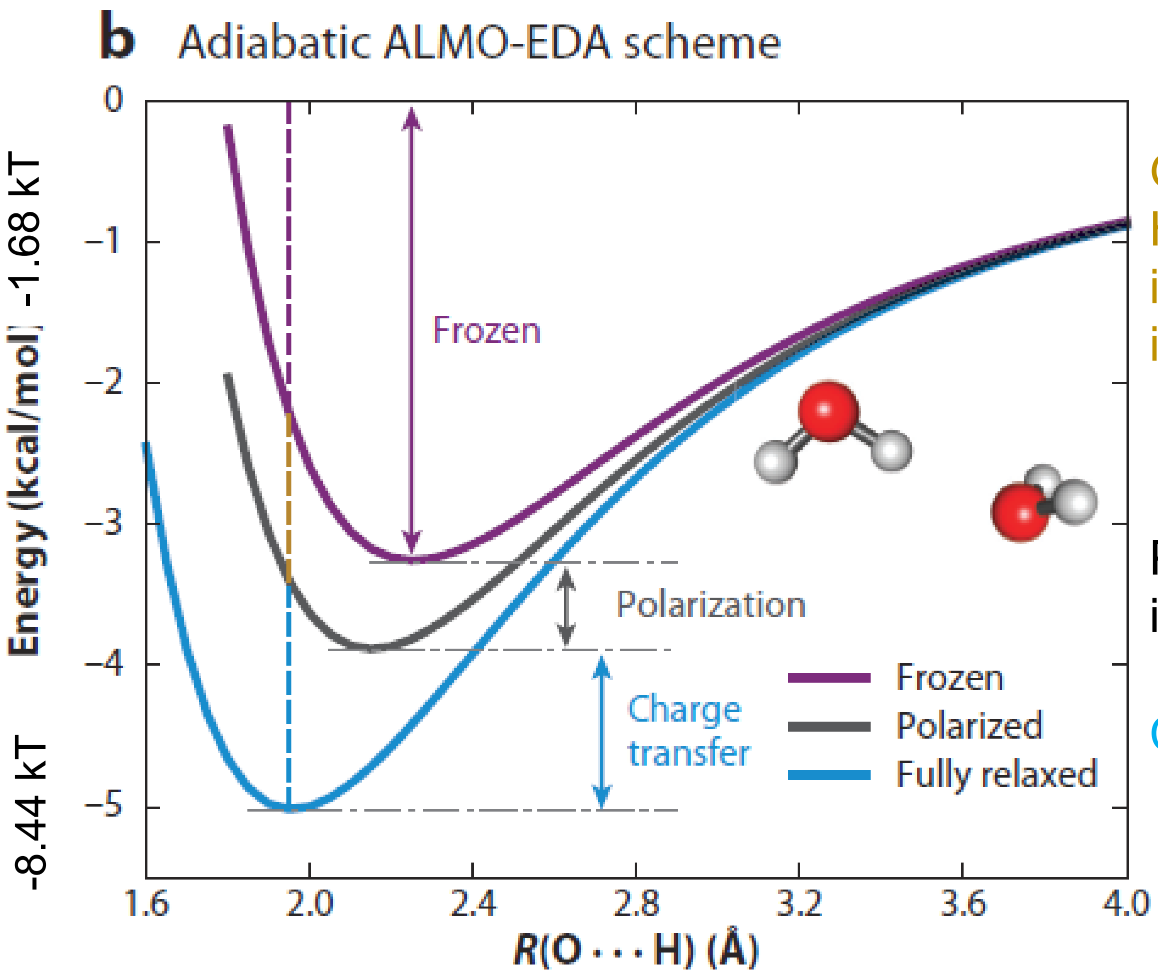
Decomposition analysis for water dimer



Geometric deformation of H_2O units + Coulombic interaction + Dispersive interaction + Pauli repulsion

Polarizability (dipole-dipole interactions + higher order)

Charge transfer between orbitals

Each interaction influences the H-bond energy and bond length of a pair of water molecules

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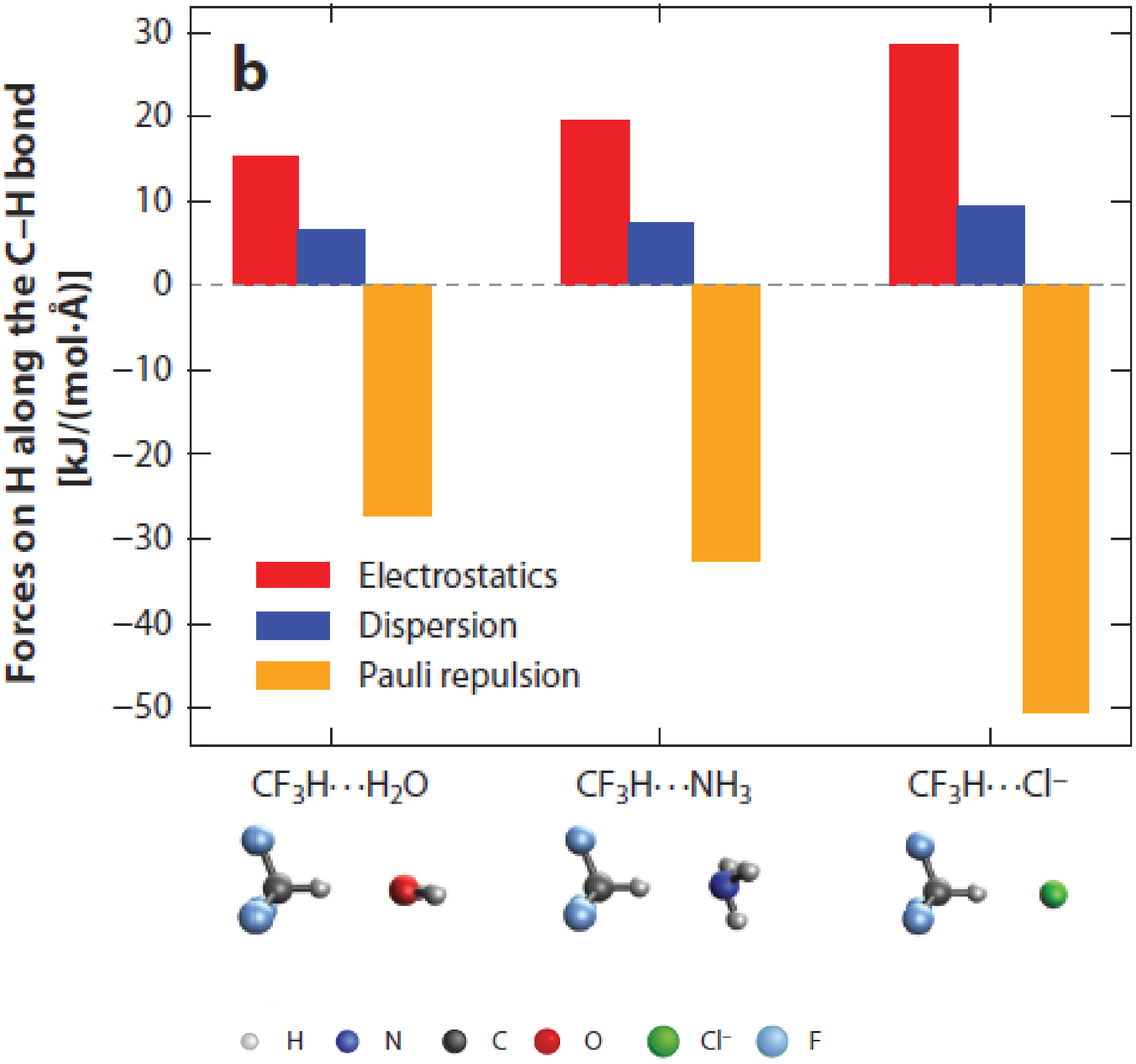
Static contribution for other H-bonds



Bond lengthening
(C-H)

Bond shortening
(C-H)

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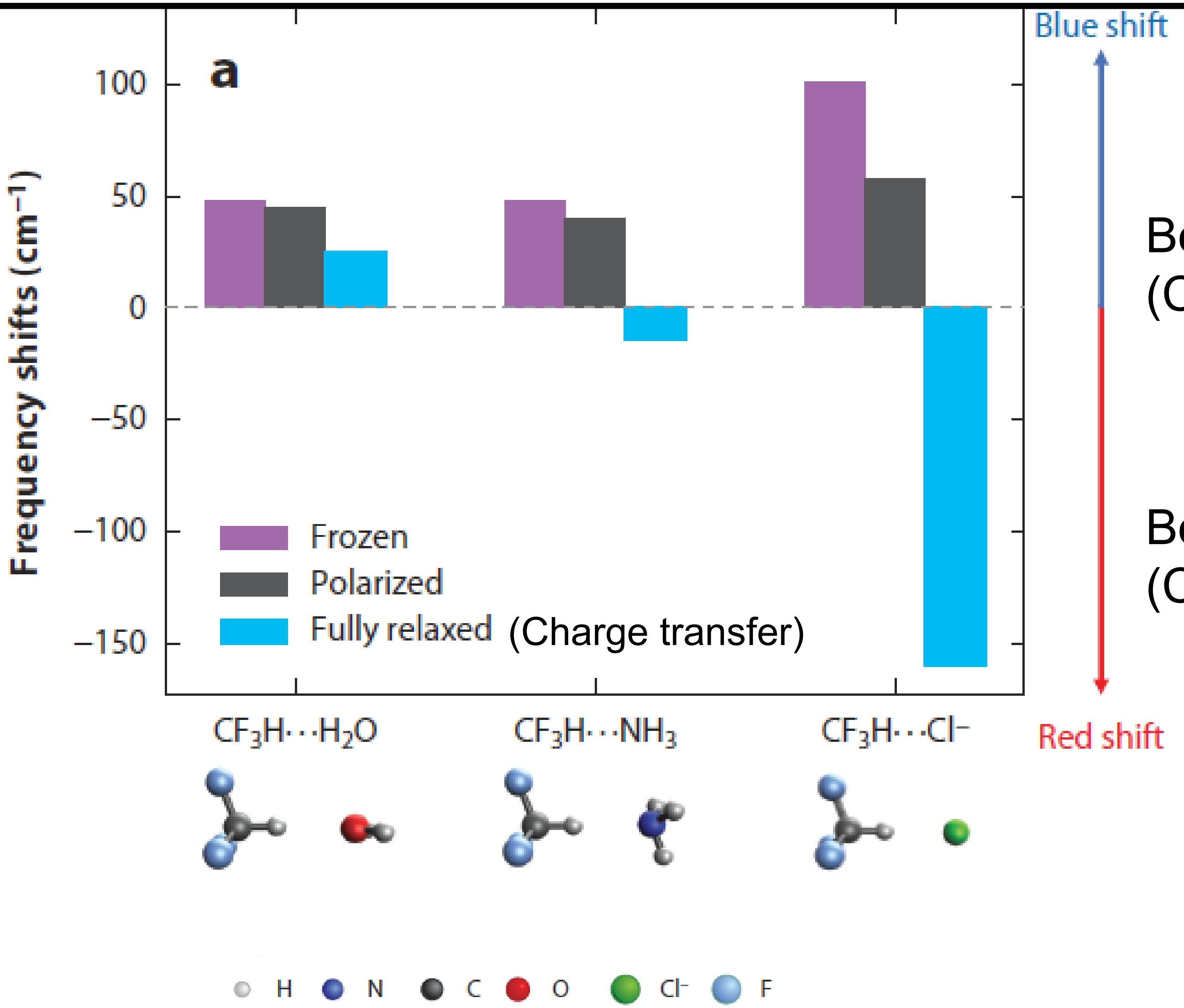
Other H-bonds: static & dynamic contributions



(Charge transfer)

Bond shortening
(C-H)

Bond lengthening
(C-H)

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What is a hydrogen bond?

Insights from energy decomposition analysis from density functional theory:

H-bonds are the result of several interactions:

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- Coulombic interactions: Interactions between molecular charge densities
- Dispersion interactions: Interactions due to correlated electron fluctuation
- Polarizability: Charge density induced density fluctuations

The relative value of each of these interactions depends on the local structure and leads to very weak or very strong hydrogen bonds.

Compare again molecular interactions

Strength of H-bonds

Average H bonding strengths based on vaporization enthalpies

F−H···:F (161.5 kJ/mol, 65 kT), illustrated uniquely by HF_2^-, bifluoride

O−H···:N (29 kJ/mol, 12 kT), illustrated by water-ammonia

O−H···:O (21 kJ/mol, 8.5 kT), illustrated by water-water, alcohol-alcohol

N−H···:N (13 kJ/mol, 5 kT), illustrated by ammonia-ammonia

N−H···:O (8 kJ/mol, 3 kT), for example, water-amide

C−H···:O (~2 kJ/mol, <1 kT), for example, methane - water

wikipedia

Boiling point

Compound	Boiling point (°C)	Dipole moment (D)
H_2Se	-60	0.63
H_2S	-41	0.97
H_2O	100	1.85
Methanol (CH_3OH)	66	1.7
Ethanol (CH_3CH_2OH)	78	1.7
Propanol ($CH_3(CH_2)_2OH$)	97	1.7

H-bonds increase the boiling point but also does the size of molecules (dispersive – van der Waals interactions)

Strength of H-bonds

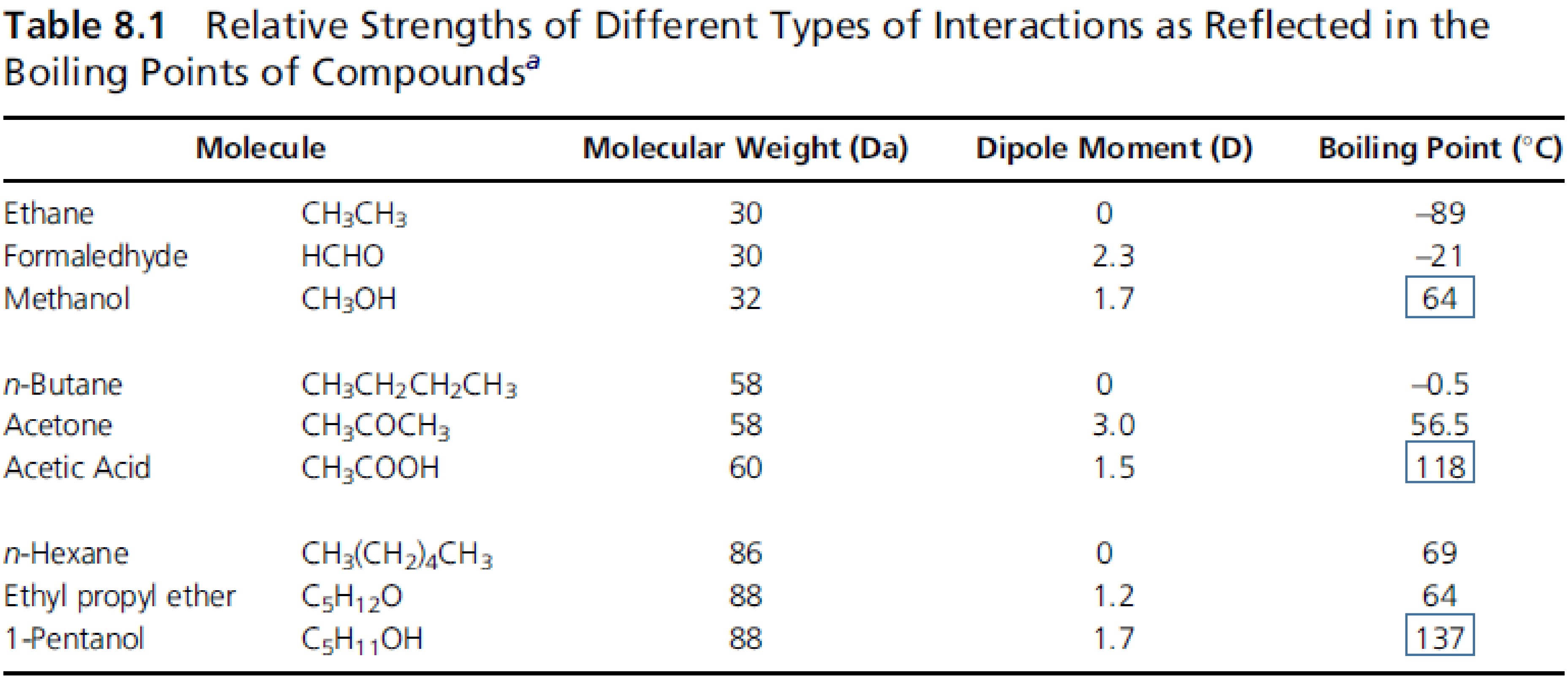


Table 8.1 Relative Strengths of Different Types of Interactions as Reflected in the Boiling Points of Compounds[a]

Molecule		Molecular Weight (Da)	Dipole Moment (D)	Boiling Point (°C)
Ethane	CH_3CH_3	30	0	–89
Formaledhyde	$HCHO$	30	2.3	–21
Methanol	CH_3OH	32	1.7	$\boxed{64}$
n-Butane	$CH_3CH_2CH_2CH_3$	58	0	–0.5
Acetone	CH_3COCH_3	58	3.0	56.5
Acetic Acid	CH_3COOH	60	1.5	$\boxed{118}$
n-Hexane	$CH_3(CH_2)_4CH_3$	86	0	69
Ethyl propyl ether	$C_5H_{12}O$	88	1.2	64
1-Pentanol	$C_5H_{11}OH$	88	1.7	$\boxed{137}$

Effect of H-bonds

Strength of H-bonds

Compound	**ε (room temp)**	
n-hexane (C_6H_{14})	1.89	Non-polar
Chloroform (CH_3Cl)	4.8	Dipolar
Octanol	10; frozen: 2	H-bonds + dipole
Methanol (CH_3OH)	32	
H_2O	78: frozen: ~82-110	3D H-bonds + dipole
TiO_2 (semiconductor)	~100	Semiconductor

Dielectric constant reflects the amount of charges that can relocate;
strong enhancement from H-bonding;
Dielectric constant of water increases with decreasing temperature:
4 H bonds in ice; form a good way to redistribute charge

H-bonds Properties

IUPAC definition: “The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.”

Properties:

A mixture of various interactions that combine

Not pairwise additive

H-bonds are cooperative

H-bonds are dynamic

1-D, 2-D and 3-D structures are possible (life…)

Magnitude in water: 5-10 kT (but smaller and larger also possible)

Light vs Heavy water

H_2O and D_2O are very similar in their properties:

Property	**D_2O**	**H_2O**
Freezing point	3.82 °C	0.0 °C
Boiling point	101.4 °C	100.0 °C
Density at STP (g/mL)	1.1056	0.9982
Temp. of maximum density	11.6 °C	3.98 °C[11]
Dynamic viscosity (at 20 °C, mPa·s)	1.2467	1.0016
Surface tension (at 25 °C, N/m)	0.07187	0.07198
Dipole moment*	1.8558	1.8546
Dielectric constant (298 K)	78.06	78.39

But … we cannot live from D_2O….

*J. Chem. Phys. 59, 2254 (1973)

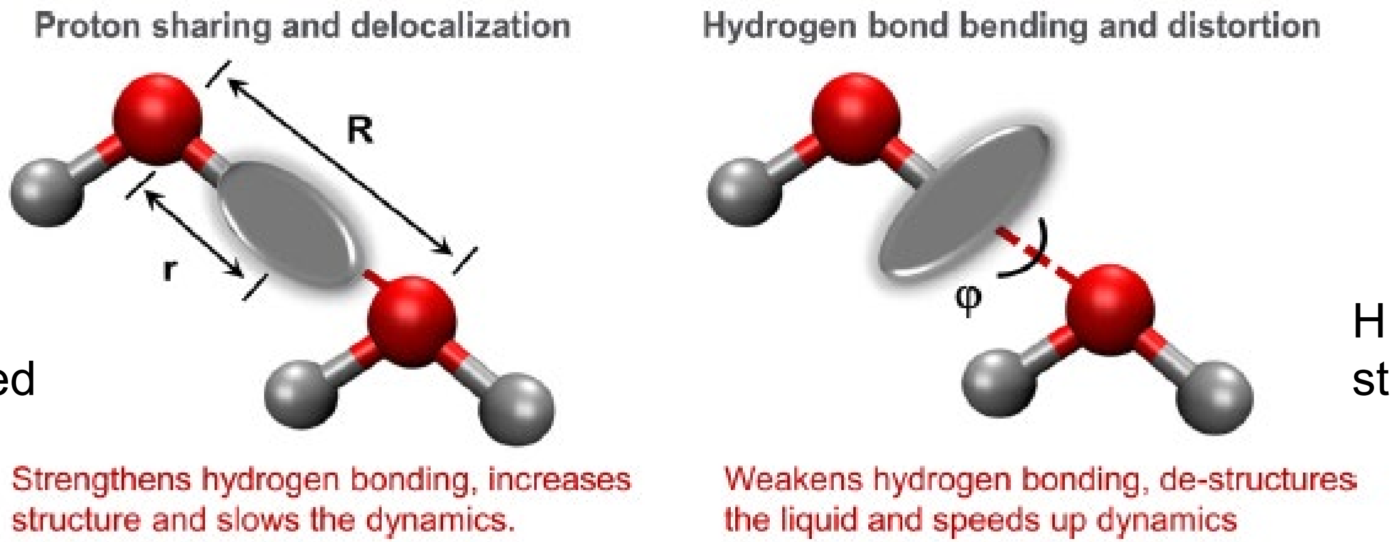
** J. Phys. Chem, 71, (1967), 656 - 662

Nuclear Quantum Effects

The H atom is so light that it cannot be treated fully classically, and its position is a probability density rather than a fixed position

H-bonding and Nuclear Quantum Effects (NQEs)

Computations: NQEs manifest themselves via 2 competing effects:



Proton sharing and delocalization

Strengthens hydrogen bonding, increases structure and slows the dynamics.

Hydrogen bond bending and distortion

Weakens hydrogen bonding, de-structures the liquid and speeds up dynamics

HB stretch
is weakened

HB bend is
strengthened

$H_2O > D_2O$;

$D_2O > H_2O$

Computational Prediction:
The H-bond bending mode is stronger, for D_2O compared to H_2O, whereas the H-bond stretching mode is weaker for D_2O compared to H_2O.

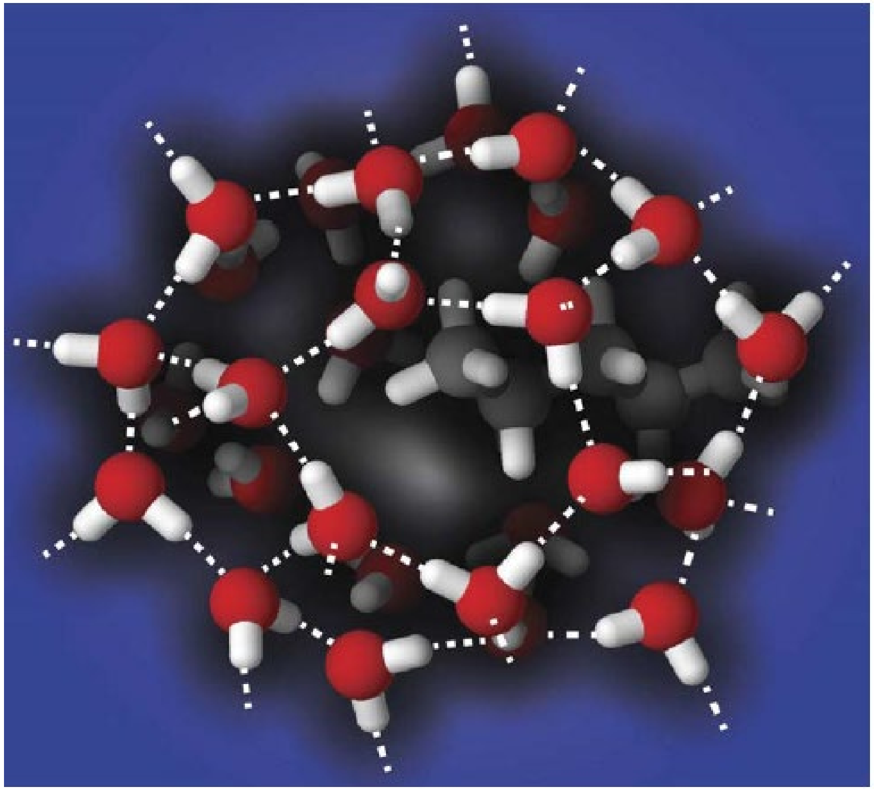
H-bond interactions thus vary subtly for H_2O and D_2O, which impacts correlated interactions such as enzymatic reactions

Chem. Rev. 2016, 116, 7529−7550

Hydrophobicity

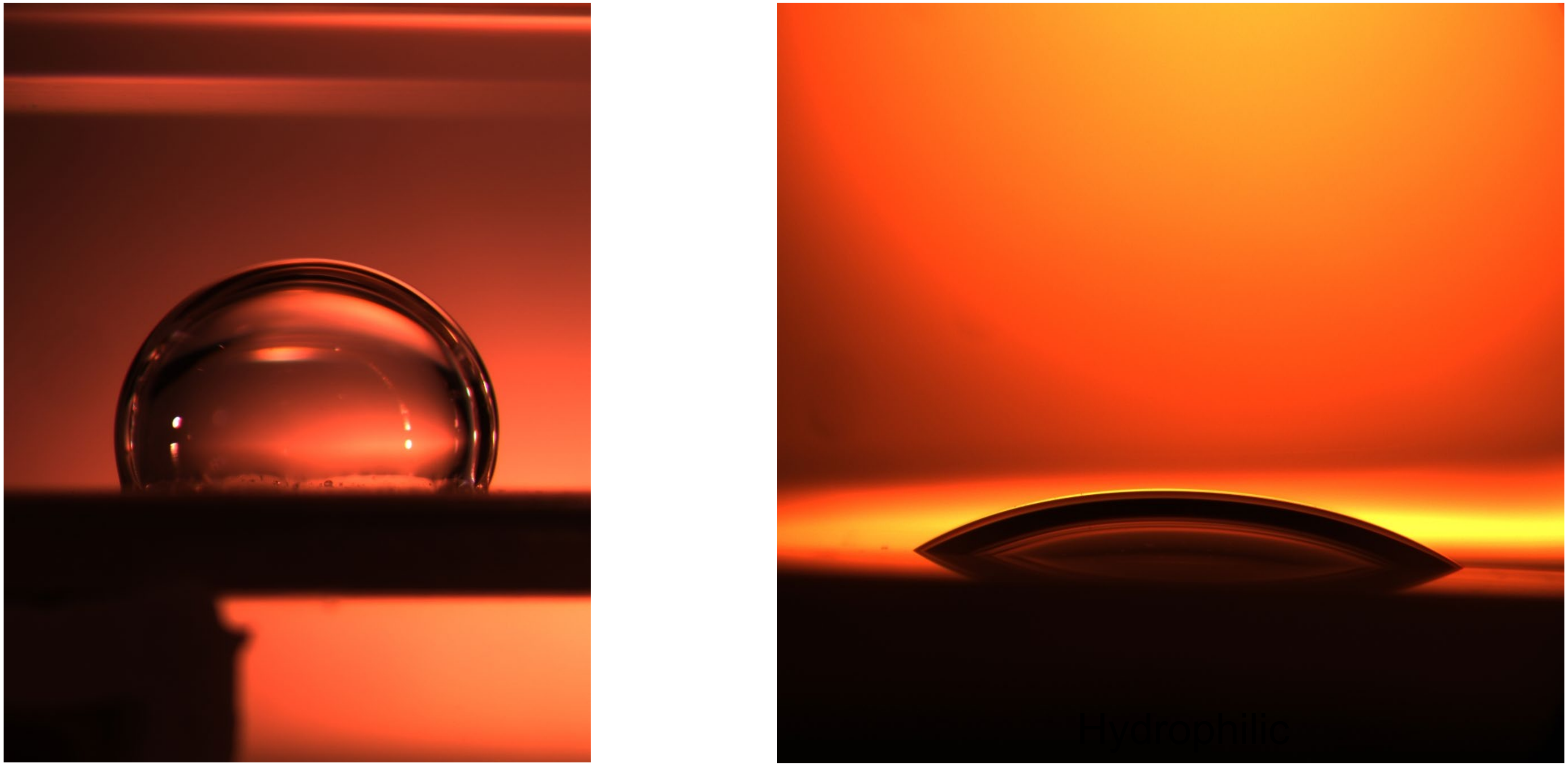
Hydrophobicity

IUPAC definition: “Hydrophobicity is the association of non-polar groups or molecules in an aqueous environment which arises from the tendency of water to exclude non-polar molecules.”



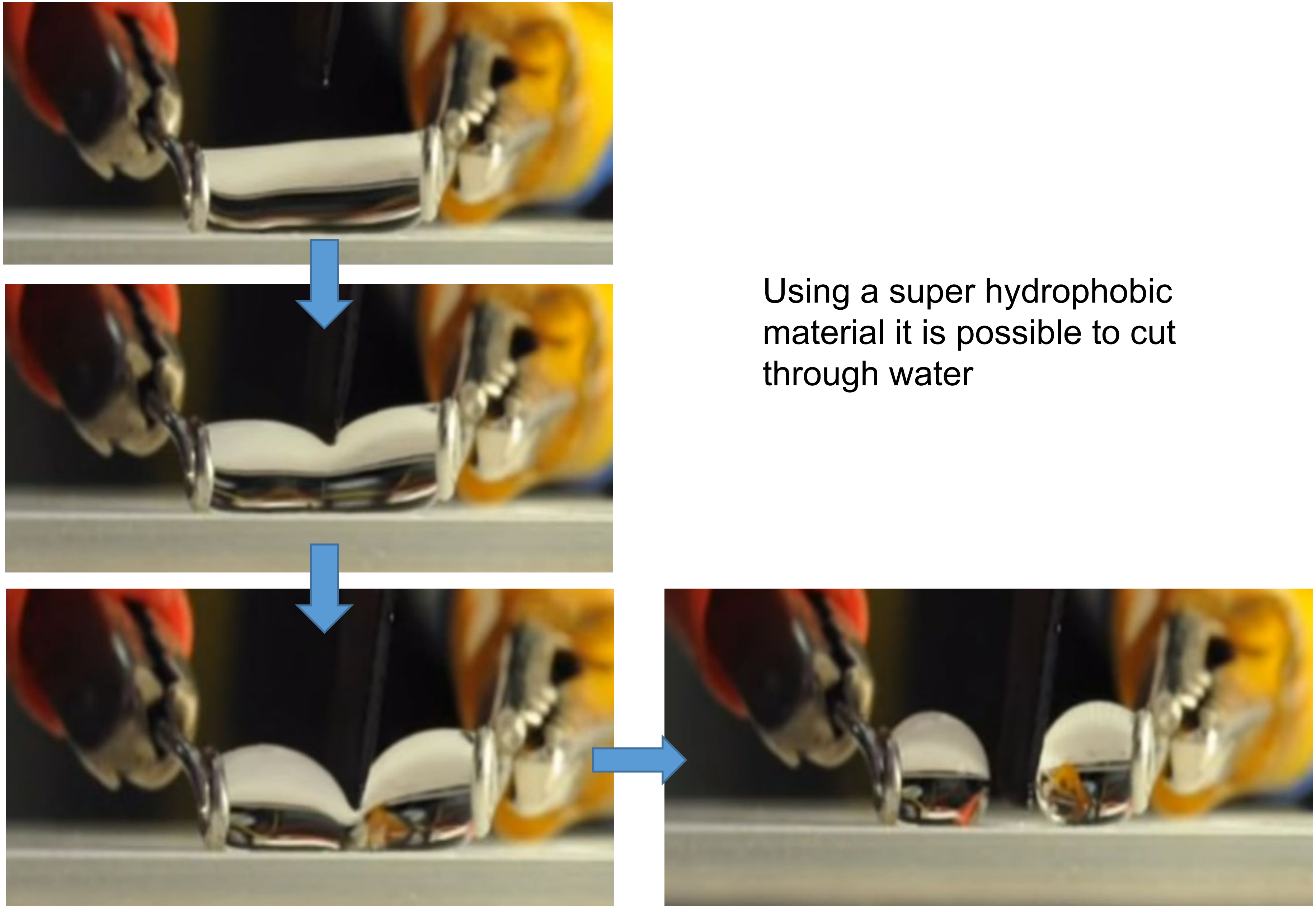
The H-bond network is restricted in its degrees of freedom by the presence of the non-H-bond forming solute

Hydrophobicity



Hydrophobic surfaces display poor adhesion of water

Hydrophobicity



Using a super hydrophobic material it is possible to cut through water

Estimating hydrophobic solvation

Key concepts Lecture 6

- Water has unique properties that are intimately connected with all aspects of life & our planet

- H-bonding is a dynamic interaction that occurs between H atoms and electronegative atoms / groups

- H-bonding comprises a complex interplay of several interactions – it is cooperative, not pair-wise additive and for water in the range of 5-10 kT

- Hydrophobicity is a consequence of the response of the solvent (water) to the solute that is based on the loss of entropy in the solvent

NEXT: probing liquid structure (Topic 4)