Intermolecular Forces

One way or another, it's always Coulomb's Law:

$$V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

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Interactions between static charge distributions

I. Charge – charge interactions (for example – ion-ion interactions)

These just follow Coulomb's Law: $V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$

The strength of the interaction depends on how close the ions get to each other (R), and the magnitude of their charges (q_1 and q_2).

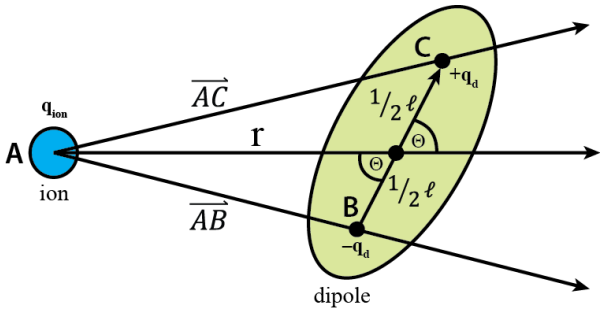
Crystal	Charges	r (in Å)	MP(K)
NaF	±1	2.31	1266
KCl	±1	3.14	1043
RbBr	±1	3.42	955
CsI	±1	3.95	894
MgO	±2	2.10	3125
CaS	±2	2.85	2798

MP is not strictly proportional to q_1q_2/r, because other effects come into play, including the polarizability of the ions. (More about polarizability later.)

Interactions between static charge distributions

II. Charge – dipole interactions

A dipole is a pair of charges ($\pm q_d$) separated by a distance, ℓ. This generates and electric field that can be modeled by letting ℓ go to zero while q_d increases so the product ($q_d\,\ell \equiv \mu$, the **dipole moment**) remains fixed. The interaction then depends on the orientation of the dipole moment relative to the charge, and on the distance.



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$$V(r,\theta) = -\frac{q_{ion}q_d}{4\pi\varepsilon_0}\left[\frac{1}{r+0.5\ell\cos\theta} - \frac{1}{r-0.5\ell\cos\theta}\right]$$

$$V(r,\theta) = -\frac{q_{ion}q_d}{4\pi\varepsilon_0}\left[\frac{r-0.5\ell\cos\theta}{r^2-0.25\ell^2\cos^2\theta} - \frac{r+0.5\ell\cos\theta}{r^2-0.25\ell^2\cos^2\theta}\right]$$

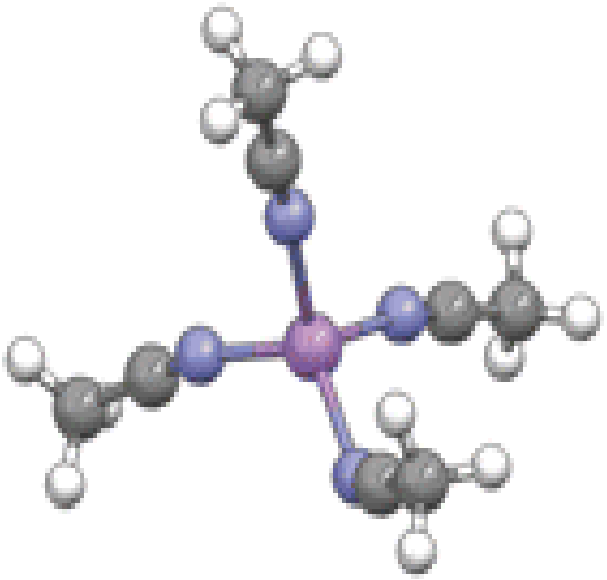
$$V(r,\theta) = -\frac{q_{ion}q_d}{4\pi\varepsilon_0}\left[\frac{\ell\cos\theta}{r^2-0.25\ell^2\cos^2\theta}\right]$$

$$\approx -\frac{q_{ion}q_d\ell}{4\pi\varepsilon_0}\left[\frac{\cos\theta}{r^2}\right] \quad \text{(assuming } r >> \ell/2\text{)}$$

$$V(r,\theta) = -\frac{q_{ion}\,\mu\cos\theta}{4\pi\varepsilon_0 r^2} \quad [\mu \equiv q_d\ell \text{ is the dipole moment}]$$

Note: This interaction can be positive or negative, depending on the alignment of the dipole ($\cos\theta$ ranges from +1 to -1). It also dies off more quickly than ion-ion interactions ($1/r$ dependence), due to the $1/r^2$ dependence.

Charge-dipole interactions are responsible for solvation of ions in solvents with large dipole moments

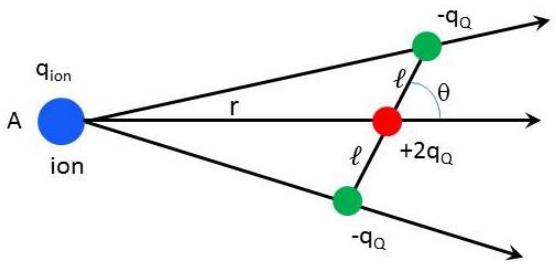


Li^+ solvated by four CH_3CN molecules, from a simulation of the structure of a solution. Acetonitrile (CH_3CN) cannot form hydrogen bonds, but has one of the largest dipole moments of common solvent molecules (3.92 D). For comparison, the dipole moment of an isolated H_2O molecule is 1.85 D; NH_3 is 1.47 D; free HCl is 1.03 D; free HF is 1.91 D.

Interactions between static charge distributions

III. Charge – quadrupole interactions

A quadrupole is a pair of dipoles arranged so their dipole moments cancel out. To represent it using equal point charges, four point charges are needed. A good example is CO_2. You can think of the partially charged atoms in CO_2 as the O atoms having a partial negative charge of $-q_Q$, while the C atom has a partial positive charge of $+2q_Q$



Working out the electrostatics as we did for the dipole, the interaction between an ion and a quadrupole distribution of charges (as in CO_2) works out to be:

$$V(r,\theta) = \frac{q_{ion}Q}{4\pi\epsilon_0 r^3}\cos^2\theta \qquad \text{(Only valid for r >> } \ell\text{)}$$

Here, Q is the quadrupole moment, defined by

$$Q = -2q_Q\ell^2$$

(units are charge times distance squared)

Because the end O atoms are negatively charged, CO_2 has a negative quadrupole moment.

Note: For both the charge-dipole and charge-quadrupole interactions, the forces can be much stronger at short distances ($r \sim \ell$) than these formulas would suggest.

Interactions between static charge distributions

IV. Dipole – dipole interactions

When two dipoles interact, the strength of the interaction depends on the separation (r), the orientation of the dipoles with respect to each other, and their orientation with respect to the axis connecting them. In all fixed orientations, the attraction (or repulsion) is proportional to $1/r^3$. Again, this assumes the dipoles are separated by a much greater distance than the distance separating the charges within the dipole. This isn't valid when the dipolar molecules get close to one another. For dipoles of magnitude μ_i and μ_j, separated by a distance r, the formulas are:

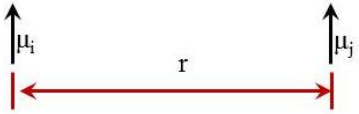
Optimal orientation:

$$V = -2\,\frac{|\mu_i||\mu_j|}{4\pi\epsilon_0 r^3}$$

Parallel, favorable orientation:

$$V = -\,\frac{|\mu_i||\mu_j|}{4\pi\epsilon_0 r^3}$$

Parallel, unfavorable orientation:



$$V = \frac{|\mu_i||\mu_j|}{4\pi\epsilon_0 r^3}$$

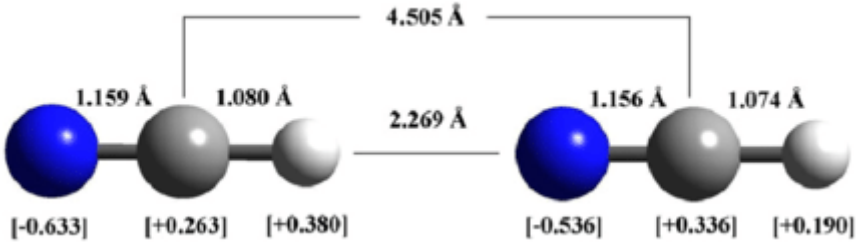
Worst orientation:

$$V = 2\,\frac{|\mu_i||\mu_j|}{4\pi\epsilon_0 r^3}$$

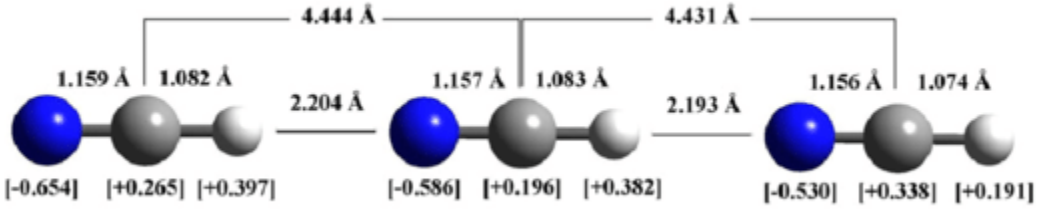
Again, only valid when r is much larger than the charge separations within the molecules.

Dipole-dipole interactions in real life

We now have lots of examples of complexes between two dipolar molecules that have been examined in the gas phase using spectroscopy to determine the actual molecular structure.



$N\equiv C\text{-}H\cdots N\equiv C\text{-}H$
or $(HCN)_2$



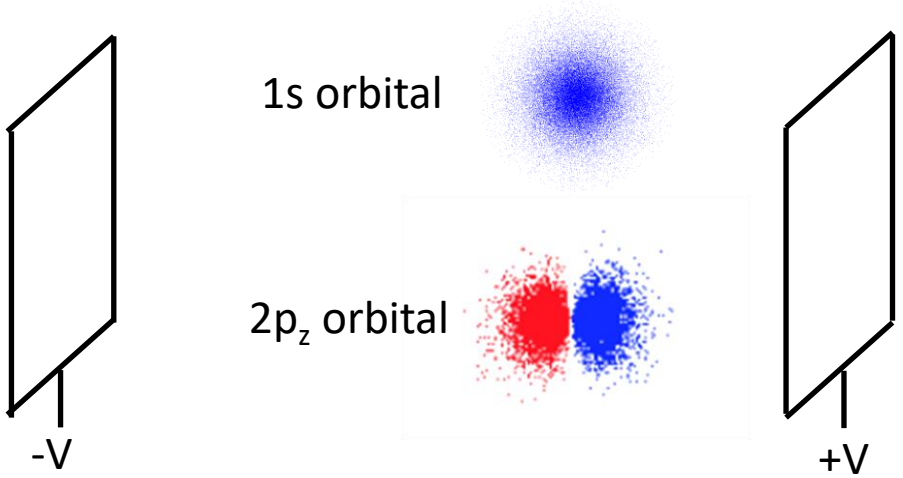
$N\equiv C\text{-}H\cdots N\equiv C\text{-}H\cdots N\equiv C\text{-}H$
or $(HCN)_3$

These species form when HCN is rapidly cooled in the gas phase, and only exist in appreciable concentration until the gas condenses.

Polarizability: A key property of atoms and molecules

In all of the previous examples, I've treated the distribution of charge within the molecule as if it is fixed and never changes in response to the environment. In fact, if an atom or molecule is placed in an electric field, the electrons move in response to that field. The molecular orbitals distort in response to the applied field, leading to an induced dipole moment. The molecule is polarizable.

For a simple atom like the H atom, this can be understood by adding a small amount of $2p_z$ character to the 1s orbital, which adds constructively on one side of the atom and destructively on the other side:



The wavefunction for the H atom actually distorts in the electric field by mixing a small fraction of the $2p_z$ orbital into the 1s orbital. Partial cancellation on the left reduces the electron density on that side; on the right side the two contributions are both positive and add in phase. The H atom distorts toward the +V plate.

Polarizability: A key property of atoms and molecules

When describing the polarization induced in an atom (or molecule) by the applied electric field, we use the expression for the total dipole moment in the presence of the applied field:

$$\mu^{total} = \mu^{permanent} + \mu^{induced}$$

Here, $\mu^{induced}$ is proportional to the applied electric field:

$$\mu^{induced} = \alpha\, \mathcal{E}$$

Polarizability, α Applied electric field, $\mathcal{E}$

Of course, if you apply a greater electric field, the molecule develops a larger induced dipole moment!

The crudest model for the polarizability of an atom or molecule is to treat it like a conducting sphere with a certain volume. In this approximation, the polarizability is proportional to the volume of the sphere. This isn't exactly true for the atoms, but it is a useful fact that captures many of the trends.

Polarizabilities of the Neutral Atoms: (atomic units)

^{1}H 4.50								^{2}He 1.38
^{3}Li 164	^{4}Be 37.7		^{5}B 20.5	^{6}C 11.3	^{7}N 7.4	^{8}O 5.3	^{9}F 3.74	^{10}Ne 2.66
^{11}Na 163	^{12}Mg 71.2		^{13}Al 57.8	^{14}Si 37.3	^{15}P 25	^{16}S 19.4	^{17}Cl 14.6	^{18}Ar 11.1
^{19}K 290	^{20}Ca 161	…	^{31}Ga 50	^{32}Ge 40	^{33}As 30	^{34}Se 29	^{35}Br 21	^{36}Kr 16.8

Polarizability decreases going left to right across a period.

Polarizability increases going down a column.

Just like the atomic volume does!

Interactions with a polarizable charge distribution

I. Charge – induced dipole interactions

When an ion interacts with a polarizable molecule that has no permanent dipole moment, the interaction is given by

$$V = -\frac{q^2\alpha}{8\pi\epsilon_0 r^4}.$$

Here, q is the charge of the ion; α is the polarizability of the neutral molecule, and r is the distance between the two.

This falls off more quickly with distance than the charge-dipole interaction, because the charge has to induce the dipole. However, if the polarizability is large enough, this can become a stronger interaction overall.

Examples of gas phase ion-induced dipole complexes:

Complex	Bond energy	Complex	Bond energy
$V^+ \cdot Ar$	8.76 kcal/mol	$V^+ \cdot Kr$	11.3 kcal/mol
$Co^+ \cdot Ar$	11.75(2) kcal/mol	$Co^+ \cdot Kr$	15.4 kcal/mol
$Ni^+ \cdot Ar$	13.07(2) kcal/mol	$Nb^+ \cdot Xe$	8.73 kcal/mol

For comparison, the bond energy of H_2 is about 10 times stronger at 104 kcal/mol; the bond energy of I_2 is 36.46 kcal/mol. Are these charge-induced dipole interactions bonds? It depends on how you define a bond, which is a matter for endless debate.

Interactions with a polarizable charge distribution

II. London dispersion forces (LDF)

These may be understood by considering that a neutral atom or molecule that has no permanent dipole moment has an instantaneous dipole moment. The instantaneous dipole moment then causes the second molecule to polarize, leading to an induced dipole moment. The result is a net attraction between the two molecules.

A better way of understanding LDFs is to note that the electronic positions in the two interacting molecules are correlated. To understand this in more detail, let's look at H_2. The actual ground state wavefunction for an H_2 molecule in the valence bond theory includes the standard covalent wavefunction (symbolized by $\Psi(H_A\text{-}H_B)$, where A and B designate the nuclei) along with a contribution from ionic resonance structures, where both electrons are on the same atom (symbolized by $\Psi(H_A^+ H_B^-)$ and $\Psi(H_A^- H_B^+)$). The true ground state wavefunction is approximated as a sum of these:

$$\Psi = 0.97\,\Psi(H_A\text{-}H_B) + 0.18\,\Psi(H_A^+ H_B^-) + 0.18\,\Psi(H_A^- H_B^+)$$

The contribution of covalent character to Ψ is given by $(0.97)^2 = 0.94 = 94\%$
The contribution of the ionic structure $H_A^+ H_B^-$ is $(0.18)^2 = 0.03 = 3\%$
The contribution of the ionic structure $H_A^- H_B^+$ is $(0.18)^2 = 0.03 = 3\%$
The ionic resonances don't make a very big contribution to the wavefunction.

Interactions with a polarizable charge distribution

II. London dispersion forces (LDF) (continued)

Now suppose we have two H_2 molecules arranged in a line:

$$H_A\text{-}H_B \cdots\cdots H_C\text{-}H_D$$

Why do these molecules attract?

The full wavefunction for the system is the product of two wavefunctions, one for each molecule. This should be:

$$\Psi = [0.97\,\Psi(H_A\text{-}H_B) + 0.18\,\Psi(H_A^+ H_B^-) + 0.18\,\Psi(H_A^- H_B^+)]\,[0.97\,\Psi(H_C\text{-}H_D) + 0.18\,\Psi(H_C^+ H_D^-) + 0.18\,\Psi(H_C^- H_D^+)]$$

Molecule AB — Molecule CD

This gives equal probabilities of an $(H_A^+ H_B^-)(H_C^+ H_D^-)$ configuration (which is good) and an $(H_A^+ H_B^-)(H_C^- H_D^+)$ configuration (which is bad). Both get a coefficient of $(0.18)(0.18) = (0.18)^2$.

What really happens is that the wavefunction responds to the nearby molecule so that the term in the product wavefunction with the $(H_A^+ H_B^-)(H_C^+ H_D^-)$ configuration is enhanced [its coefficient is greater than $(0.18)^2$] while the term with the unfavorable $(H_A^+ H_B^-)(H_C^- H_D^+)$ configuration is diminished [its coefficient is less than $(0.18)^2$]

Interactions with a polarizable charge distribution

II. London dispersion forces (LDF) (continued)

An approximate formula for the potential energy for London dispersion forces between molecules A and B:

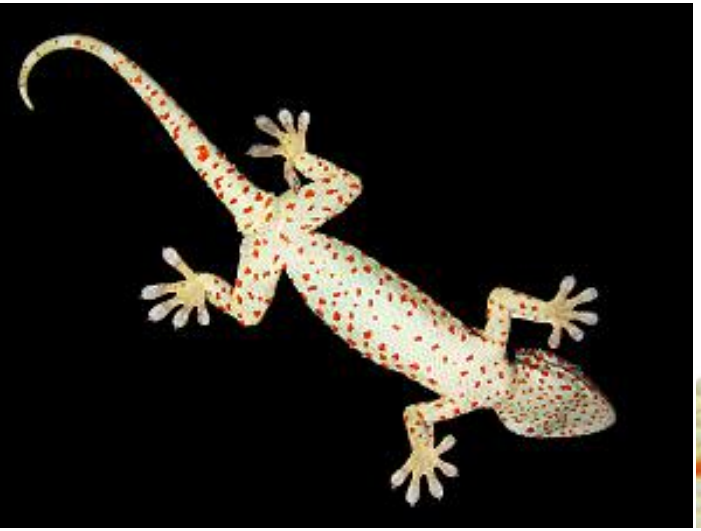
$$V(R) = -\frac{3}{2}\frac{I_A I_B}{I_A + I_B}\frac{\alpha_A \alpha_B}{R^6}$$

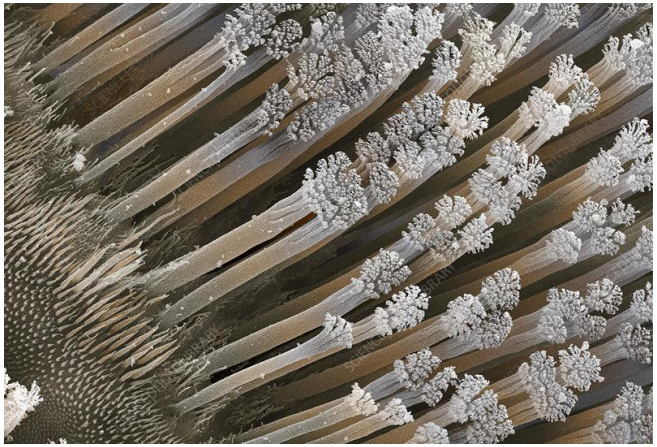
Here, I_A and I_B are the ionization energies of molecules A and B
And α_A and α_B are the polarizabilities of the molecules.

The ionization energy portion of this expression isn't too important, since these don't vary by more than about a factor of 2 for most molecules. Polarizabilities vary enormously, however! If we remember that polarizability is in the simplest model proportional to the molecular volume, the LDF potential is (roughly) proportional to the product of the volumes of the interacting molecules.

This is why LDF forces are weak in $H_2 \cdots H_2$ interactions, but get stronger as you go to $CH_4 \cdots CH_4$, and much stronger when you get to $C_8H_{18} \cdots C_8H_{18}$! For C_{60}, the LDF force is so strong that even at 900K (1160º F), the vapor pressure is only 0.1 Torr!

A Macroscopic Example of LDFs: The Gecko's Foot



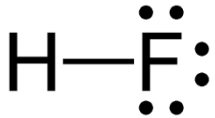


~ 3μm

The tiny hairs on the gecko's foot allow a large surface area of the foot to be in contact (small R) with the wall, allowing the gecko to climb on glass or other smooth surfaces.

Hydrogen Bonds

Think about a molecule like HF, for which the Lewis structure is



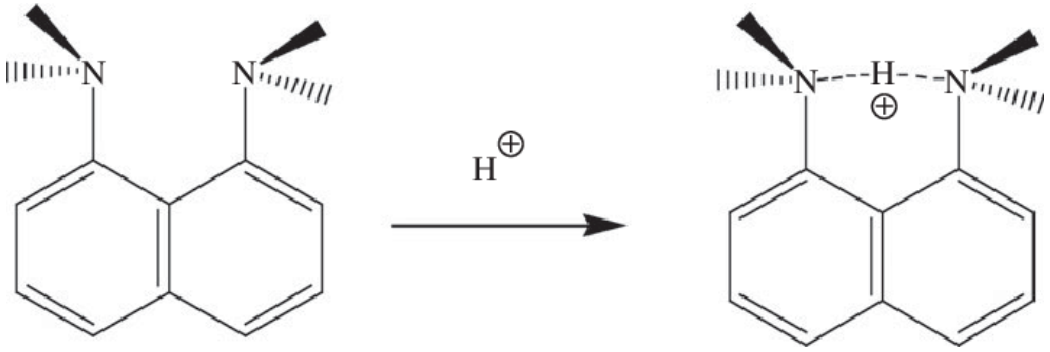
The poor H atom only has one electron to begin with, and now it's being pulled toward the far more electronegative F atom. This leaves an empty spot on the backside of the H atom where the electron density is severely depleted. The net result in not a naked proton, but it's approaching that. This is a unique situation because hydrogen has only one electron to begin with, and now it's losing it. There is a strong electrostatic force that attracts anything with accessible electrons (lone pairs or π bonds, for example; even σ bonds in some cases).

The strongest hydrogen bonds are symmetrical, where the proton is shared equally between two anions:

$[F\cdots H\cdots F]^-$ Bifluoride anion, formed by passing HF gas over NaF
Here the bond energy is 38.6 kcal/mol – stronger than the I_2 bond! This is the strongest known hydrogen bond.

Hydrogen Bonds

Another symmetrical hydrogen bonded molecule is protonated 1,8-bis(dimethylamino)naphthalene:



The parent molecule absorbs protons so readily (the pKa of the conjugate acid is 12.34!) that it is used in organic synthesis as a "proton sponge". The proton is equally shared between the two amine groups, giving a bond order of 0.5 between the proton and each nitrogen.

Symmetric sharing of the proton in hydrogen bonds is also observed in hydrogen-bonding systems under high pressure, including high-pressure ice and high-pressure formic acid.

Hydrogen Bonds

Because the “backside” of the hydrogen atom is only exposed when highly electronegative atoms are attached, normally we think of hydrogen bonding only occurring when the H is bonded to highly electronegative F, O, or N atoms.

Table of gas phase hydrogen bond energies:

Molecule	Bond energy (kcal/mol)
$[F\cdots H\cdots F]^-$	38.6 (the proton-bound fluoride dimer)
$[H_2O\cdots H\cdots OH_2]^+$	33 (the proton-bound water dimer)
$[H_3N\cdots H\cdots NH_3]^+$	24 (the proton-bound ammonia dimer)
$HOH\cdots OH^-$	23 (water-hydroxide)
$NH_4^+\cdots OH_2$	19 (the proton-bound ammonia-water dimer)
$HOH\cdots NH_3$	6.9 (water-ammonia)
$HOH\cdots OH_2$	5.0 (water dimer)
$HOH\cdots OH_3^+$	4.3 (water-hydronium)
$N\equiv C\text{-}H\cdots OH_2$	3.8 (weak acid – water)
$H_2N\text{-}H\cdots NH_3$	3.1 (ammonia dimer)
$HSH\cdots SH_2$	1.1 (not normally considered hydrogen bonded)

Multiple Donors and Acceptors

In sp^3 hybridized systems, the central atom can have 0 to 4 hydrogens that can be donated and 4 to 0 lone pairs that can serve as hydrogen bond acceptors.

Thus, in principle:
CH_4 could donate 4 hydrogens (in principle)*, but cannot accept any hydrogen bonds
NH_3 can donate 3 hydrogens, but can only accept 1 hydrogen bond
H_2O can donate 2 hydrogens, and can accept 2 hydrogen bonds
HF can donate 1 hydrogen and can accept 3 hydrogen bonds
Ne cannot donate any hydrogens, and can (in principle)* accept 4 hydrogen bonds

Water is perfectly set up to make a hydrogen bonded network where each molecule simultaneously donates two hydrogens to form hydrogen bonds and accepts two hydrogens to form two more hydrogen bonds. Thus, each molecule participates in 4 hydrogen bonds.

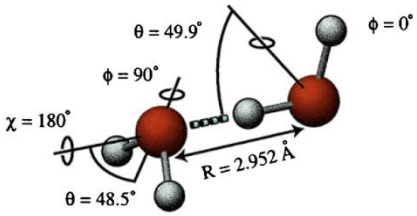
In HF and NH_3, each molecule can only participate in two hydrogen bonds.

This is why H_2O is a liquid at room temperature, but HF and NH_3 are gases.

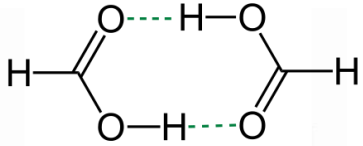
*from the French, “En principe”, meaning “no”.

Hydrogen bonded dimers:

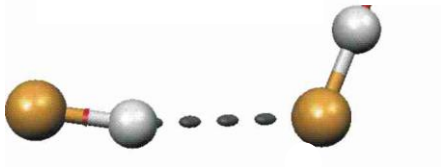
Many have been spectroscopically studied in the gas phase



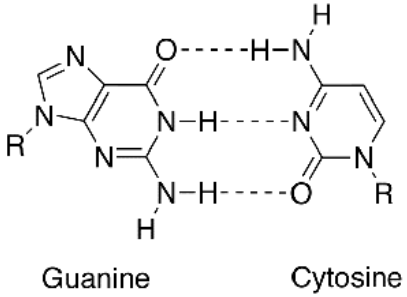
Water dimer – larger water cluster geometries are also known from gas phase spectroscopic work



Formic acid dimer – present in the gas phase over liquid formic acid (similar structures occur for acetic acid dimer and other carboxylic acids, especially when dissolved in non-hydrogen bonding solvents)



HF dimer (a **very** floppy structure)



Cytosine-guanine (a triply hydrogen bonded system): crucial for the stabilization of the DNA double helix
This structure is bound by about 21 kcal/mol!
Adenine-thymine is bound by about 12 kcal/mol.

Thanks for listening!

Anytime you'd like to ask me a question:

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