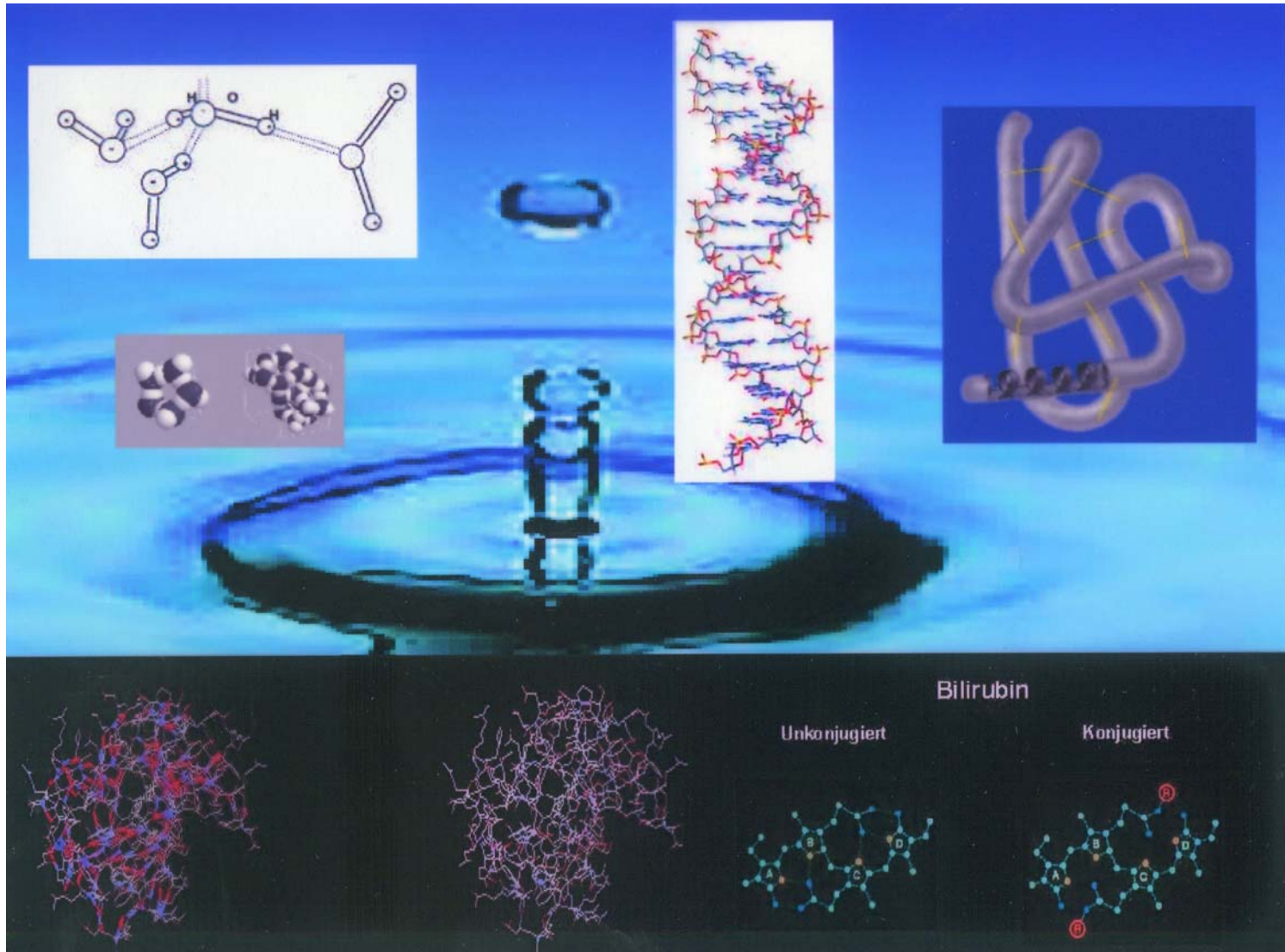


Hydrogen bonding



Where to find hydrogen bonds?

Hydrogen bonding

WHAT IS A HYDROGEN BOND?

A *hydrogen bond* exists when a hydrogen atom is bonded to two or more other atoms, a donor atom X and an acceptor atom Y. Since the hydrogen atom has only one orbital (1s) at sufficiently low energy, hydrogen bonds are mainly electrostatic in nature but covalent and repulsive orbital-orbital interactions are also present.

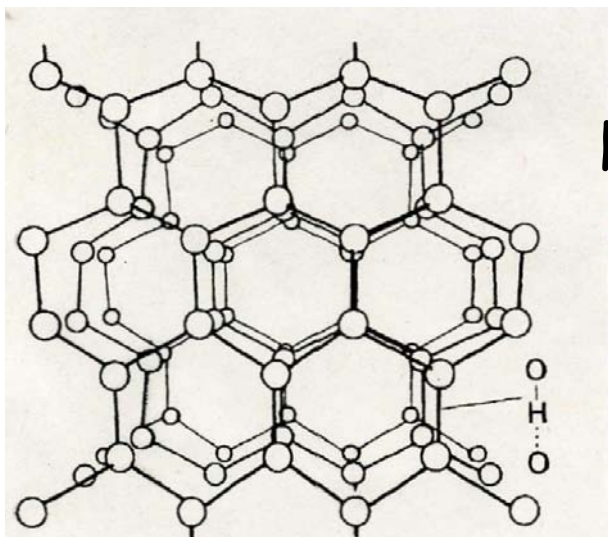
Depending on the type of X and Y, there are strong and weak hydrogen bonds.

In the case of *weak and very weak hydrogen bonds*, hydrogen bonding is mainly electrostatic in nature.

In the case of *strong and very strong hydrogen bonds*, covalent bonding phenomena are also of some importance.

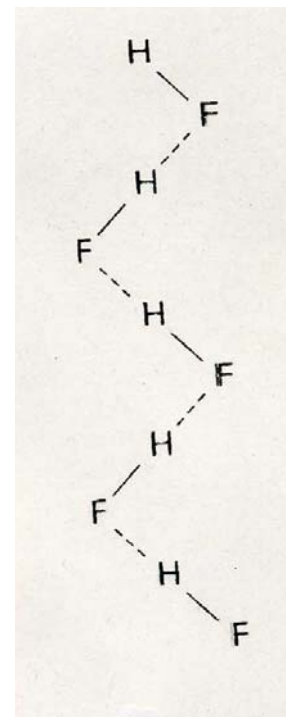
This means that hydrogen bonds are something special.

Hydrogen bonding

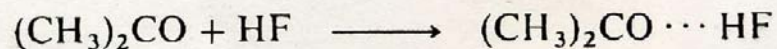


The structure of ice. The large spheres represent the O atoms; the H atoms lie on the lines joining O atoms.

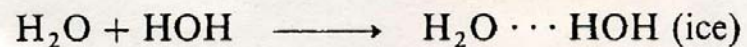
Hydrogen bonds
in
solid H_2O (weak)
and HF (strong)



$$\Delta H = -155^{18} \text{ kJ mol}^{-1}$$



$$\Delta H = -46 \text{ kJ mol}^{-1}$$



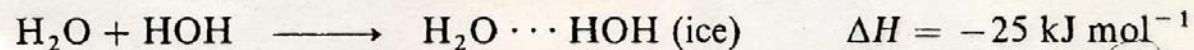
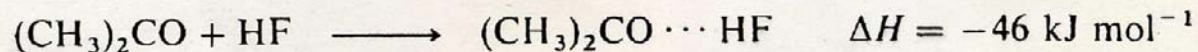
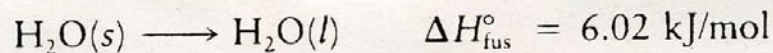
$$\Delta H = -25 \text{ kJ mol}^{-1}$$

The strongest hydrogen bonds are formed to the most electronegative elements

Hydrogen bonding

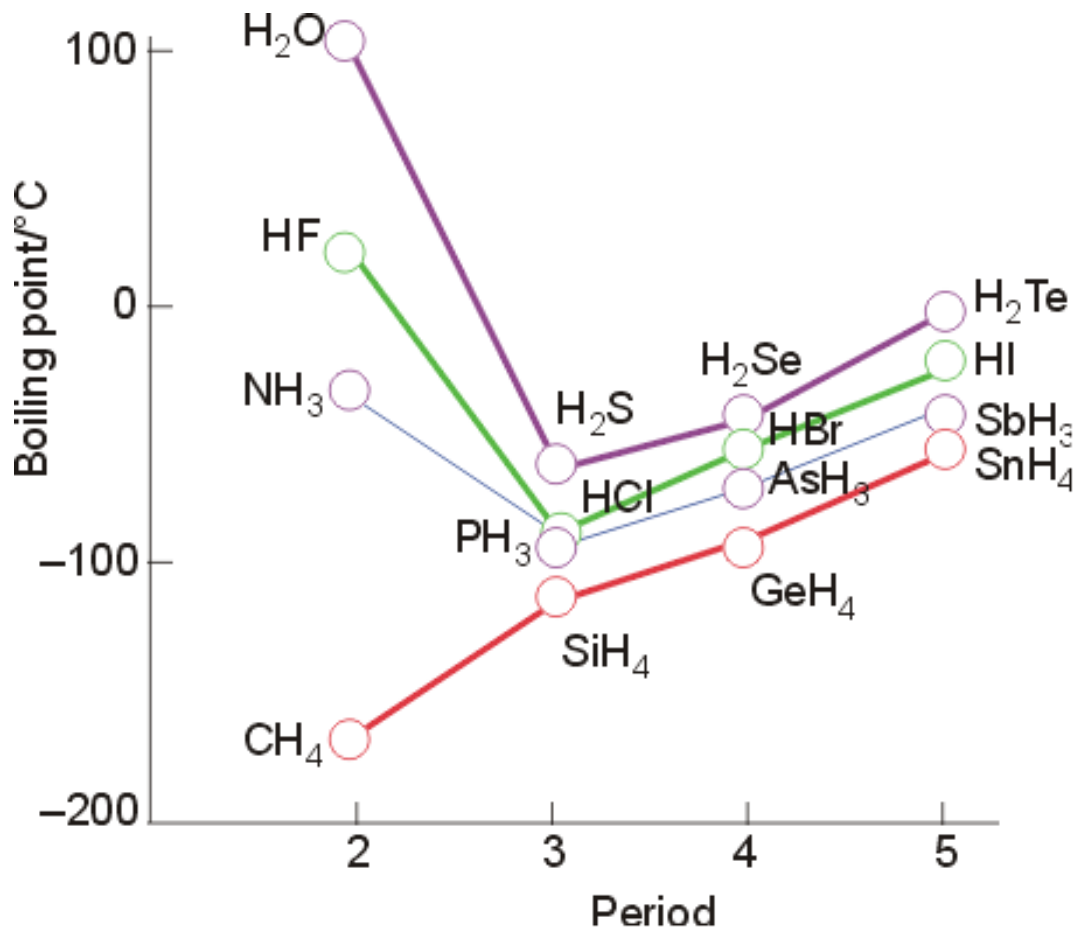
Table 4 Comparison of hydrogen bond enthalpies with the corresponding E—H covalent bond enthalpies (kJ mol⁻¹)

	Hydrogen bond (···)		Covalent bond (—)
HS—H···SH ₂	7	S—H	363
H ₂ N—H···NH ₃	17	N—H	386
HO—H···OH ₂	22	O—H	464
F—H···F—H	29	F—H	565
HO—H···Cl ⁻	55	Cl—H	428
F···H···F ⁻	165	F—H	565



Enthalpies of some hydrogen bonded systems and transitions

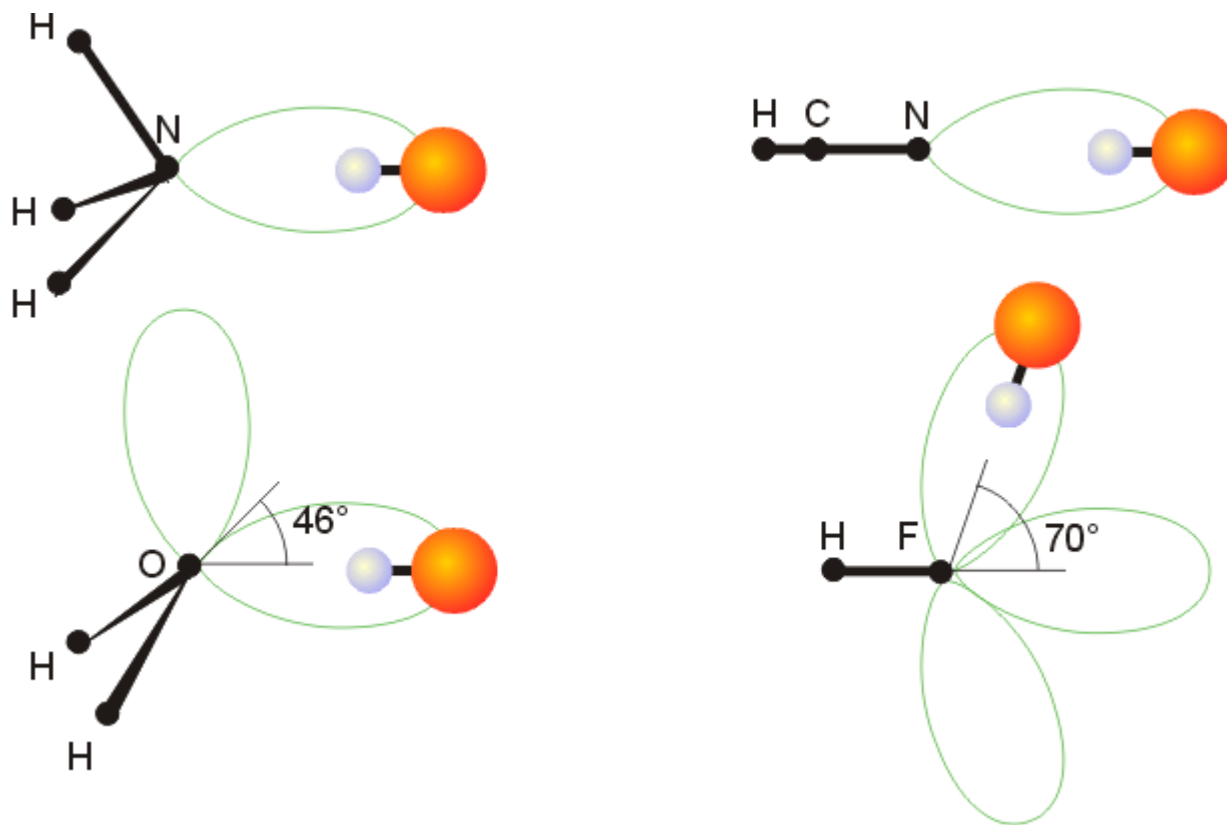
Hydrogen bonding



Normal boiling points of p-block binary hydrogen compounds

Hydrogen bonding

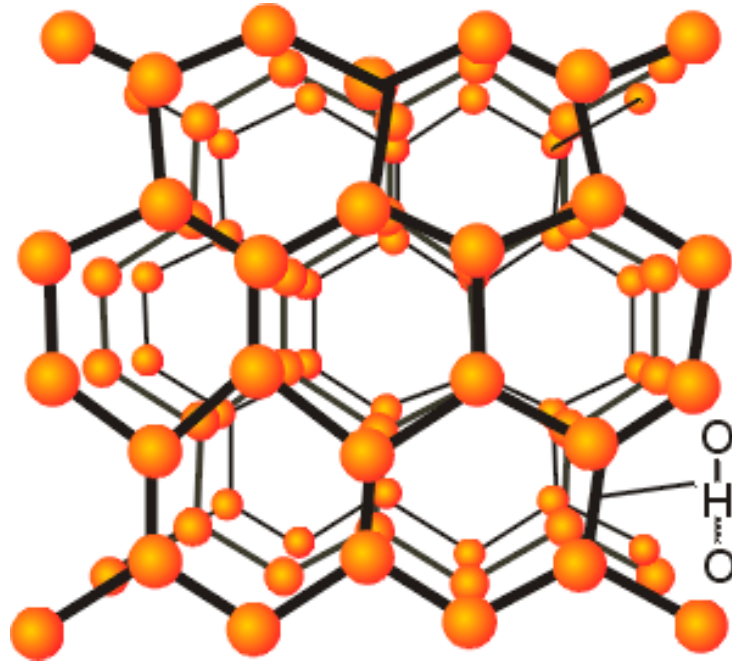
is directed by the lone pairs of the acceptor atom(s) Y



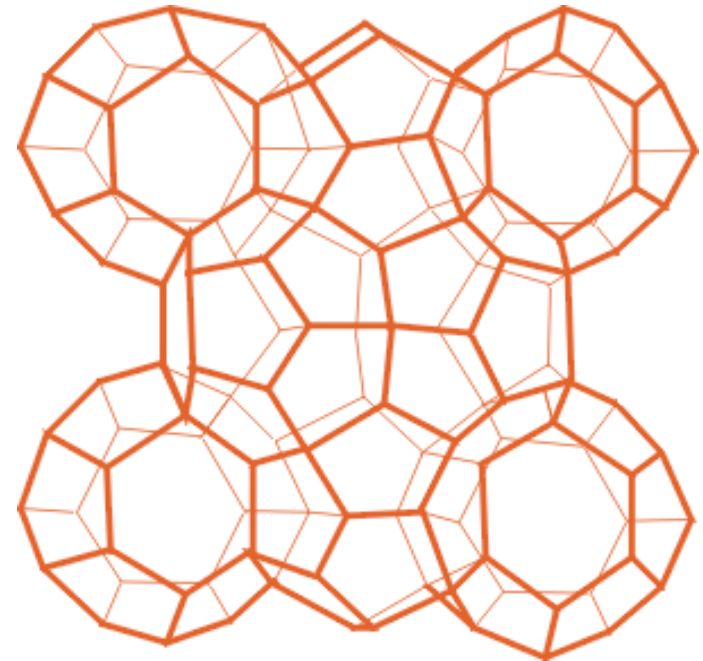
Gas-phase hydrogen-bonded complexes formed with HF and lone pair orientation as indicated by VSEPR theory

Hydrogen bonding

for $Y = O$ this leads to



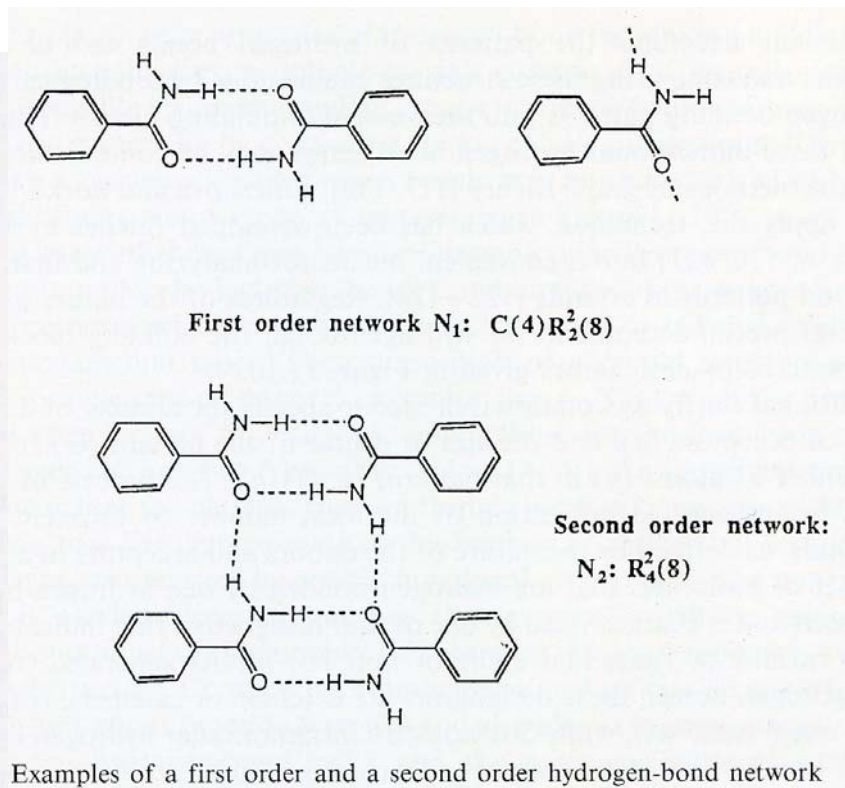
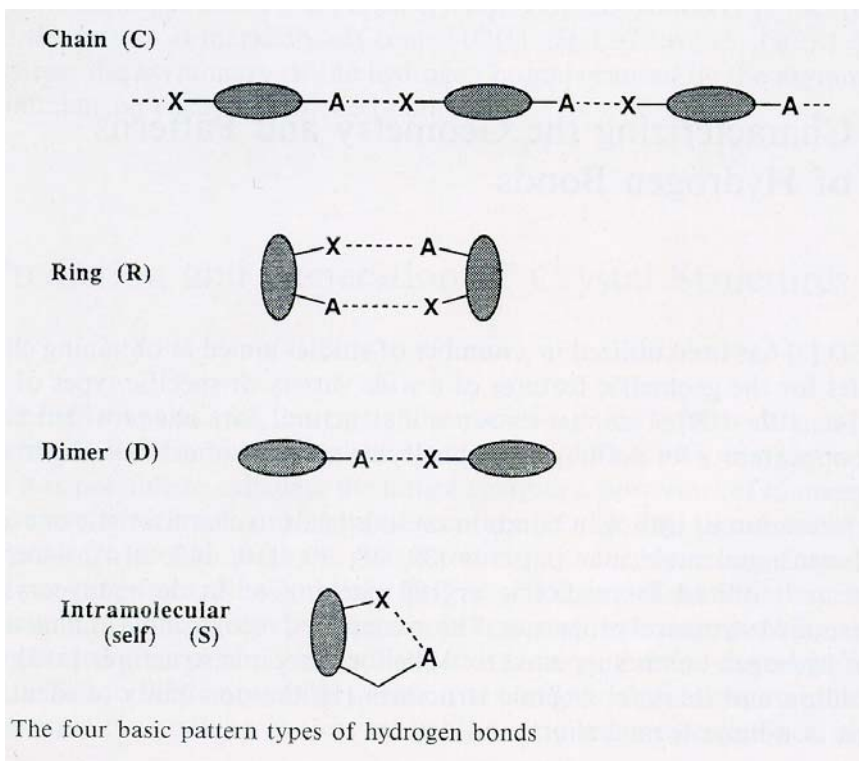
The crystal structure of ice. The large cycles represent O atoms. The H atoms are placed between the O atoms.



H_2O cages in the clathrate hydrate $Cl_2 \cdot (H_2O)_{7.25}$. O atoms occupy intersections H atoms the lines.

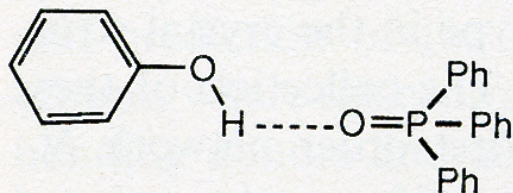
Structure building of hydrogen bonds

Hydrogen bonding

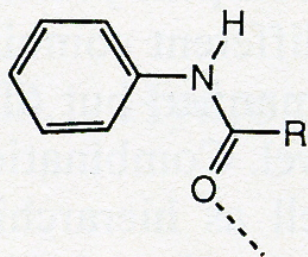


Types and structure building of hydrogen bonds

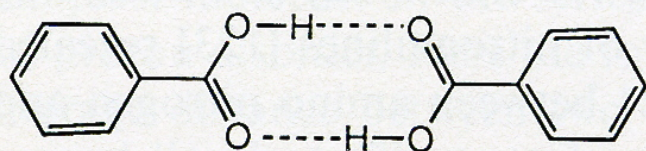
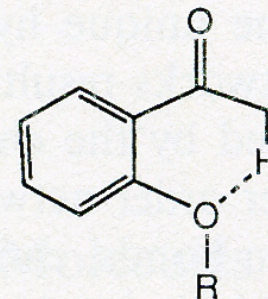
Hydrogen bonding



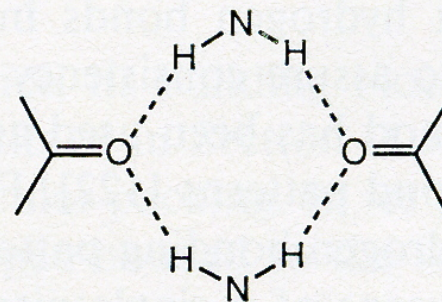
D



C(4)



R₂(8)



Types and structure building of hydrogen bonds
(intra and intermolecular hydrogen bonds)

Hydrogen bonding

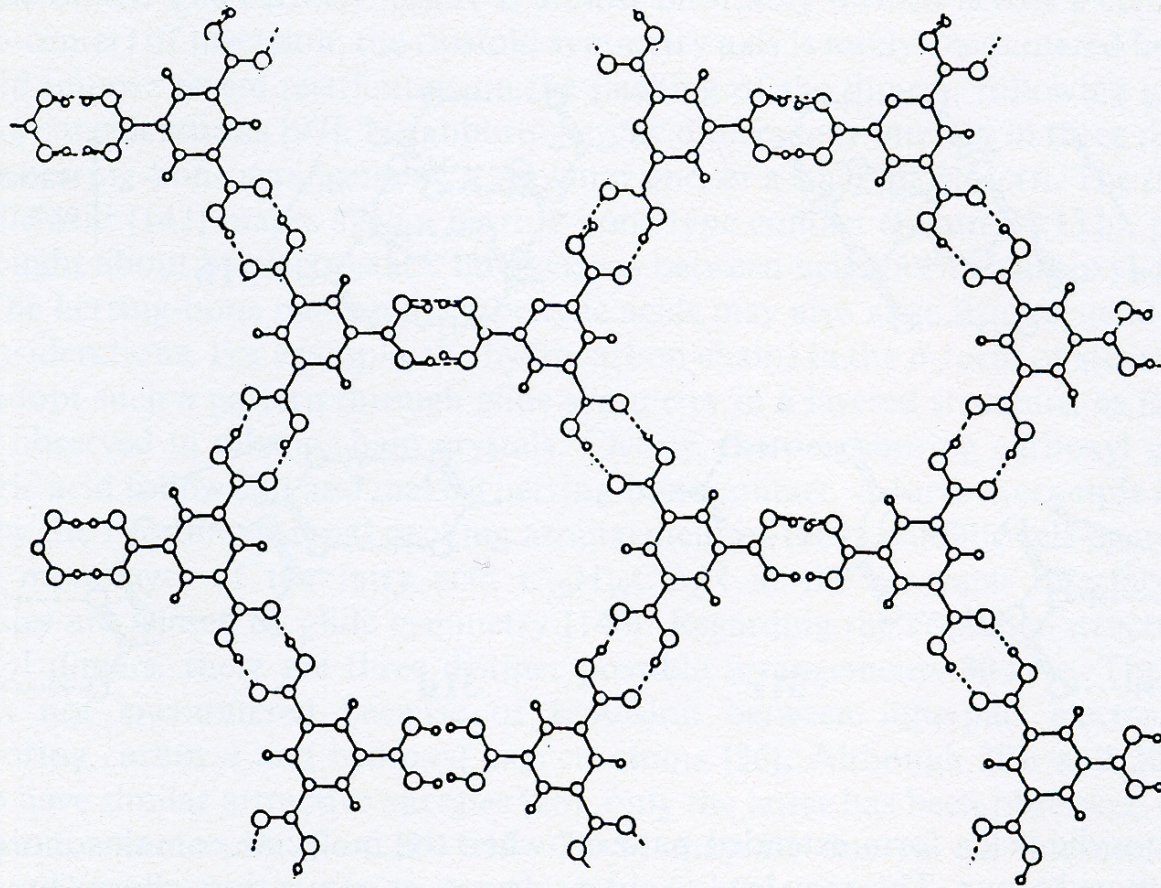
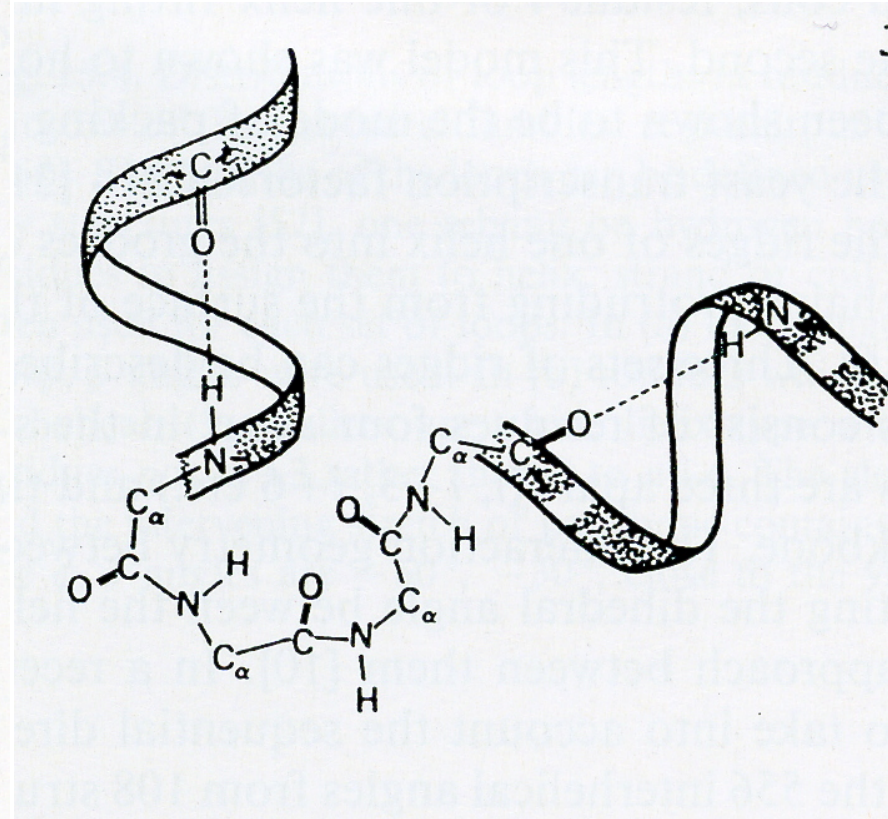
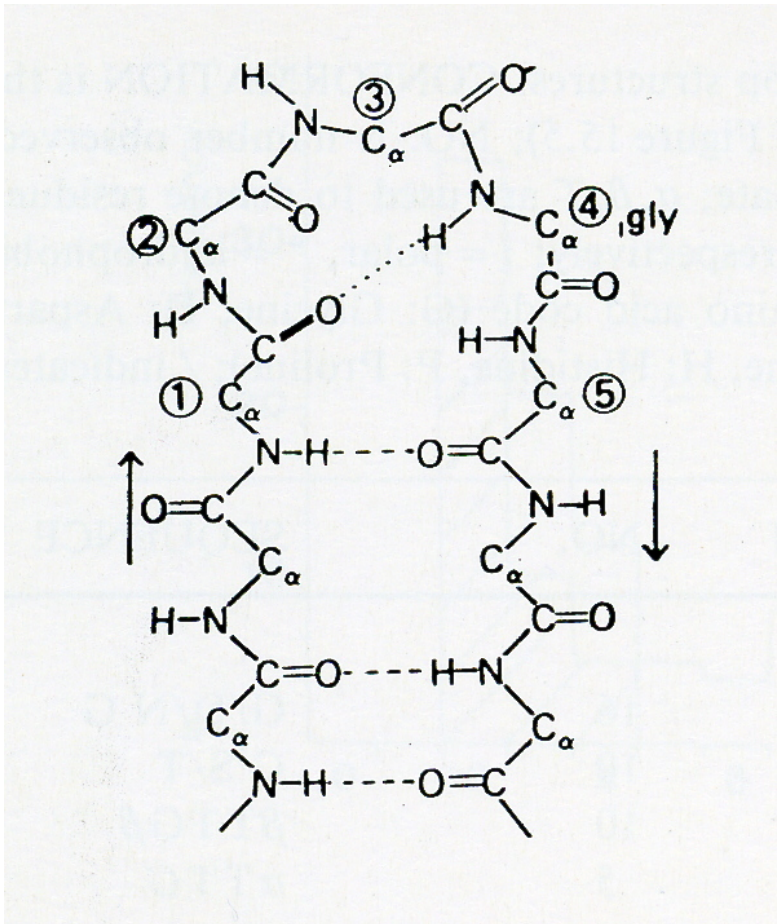


Fig. 11.17. 1,3,5-Trimesic acid. The “chicken-wire” motif

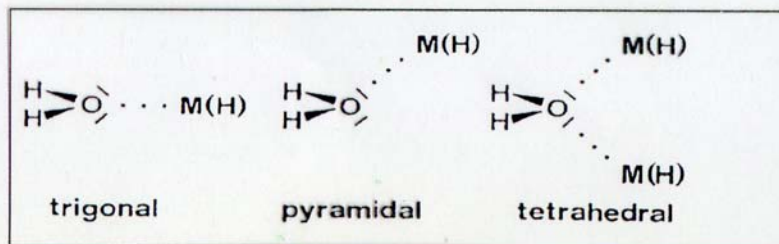
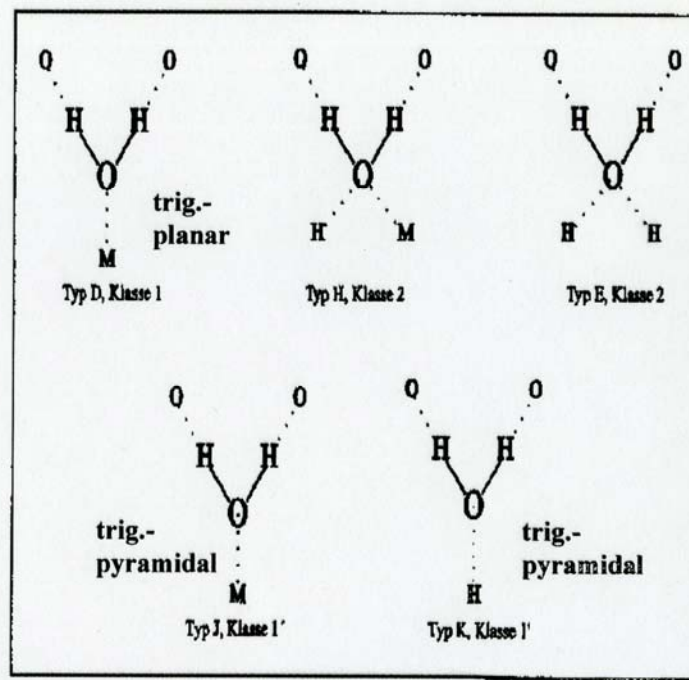
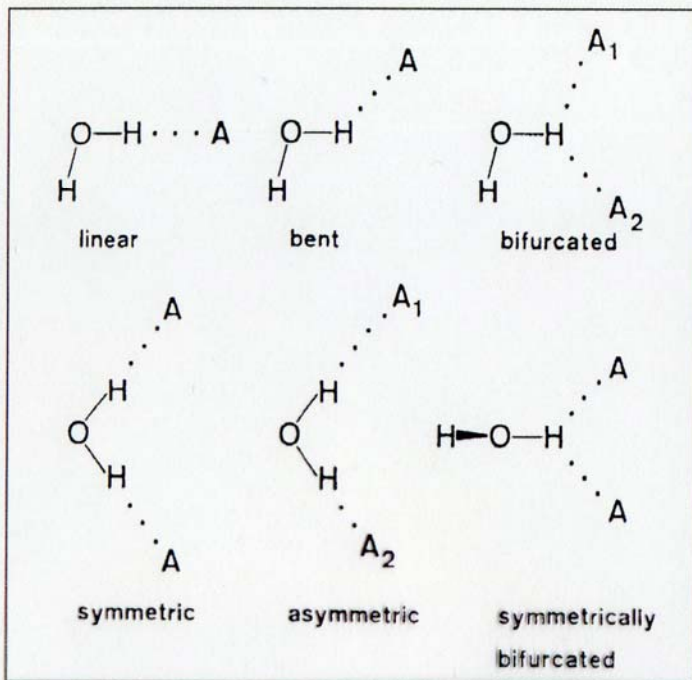
Structure building of hydrogen bonds

Hydrogen bonding



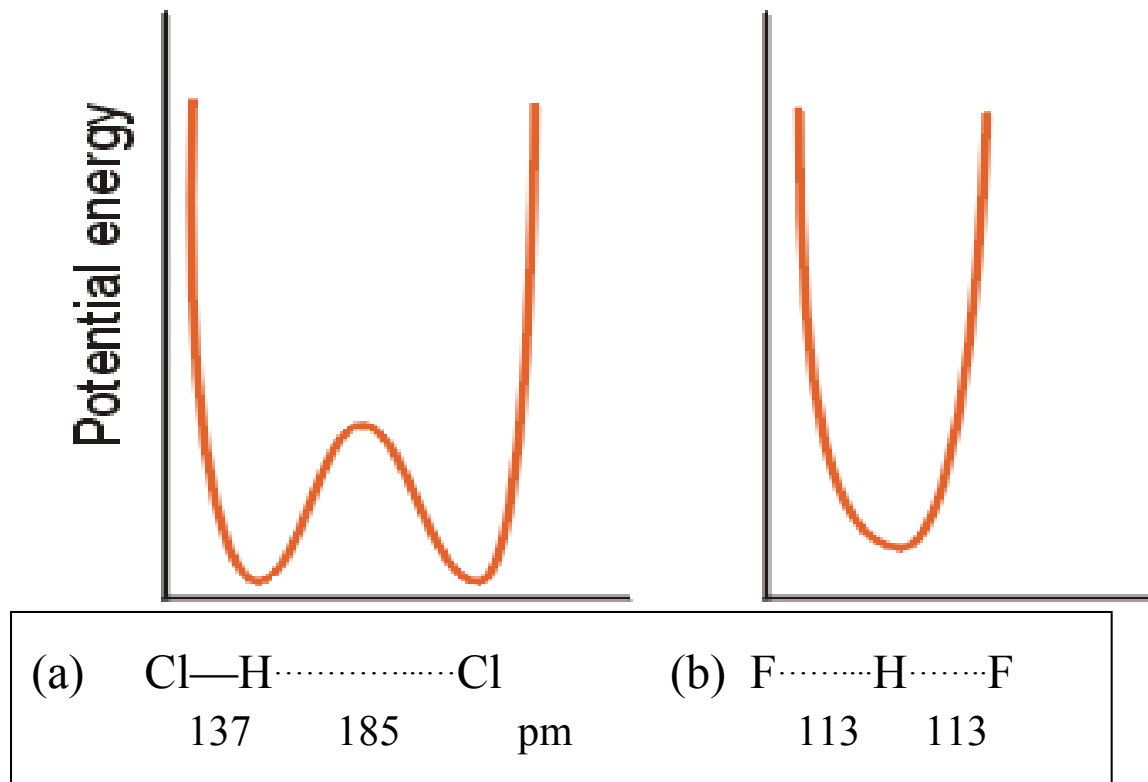
Structure building of hydrogen bonds

Hydrogen bonding



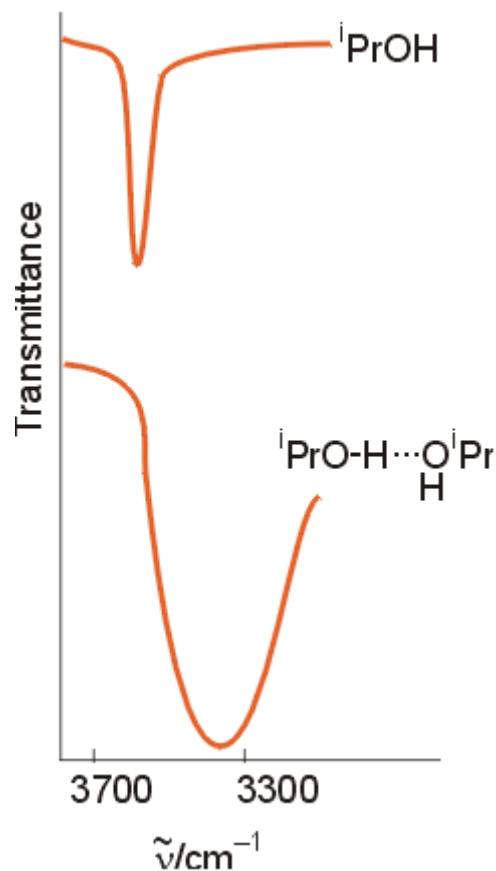
Configuration/coordination of water molecules of crystallization

Hydrogen bonding



Potential energy curves for X-H...X bonds with
(a) double-minimum for weak and (b) single-minimum for strong H-bonds

Hydrogen bonding

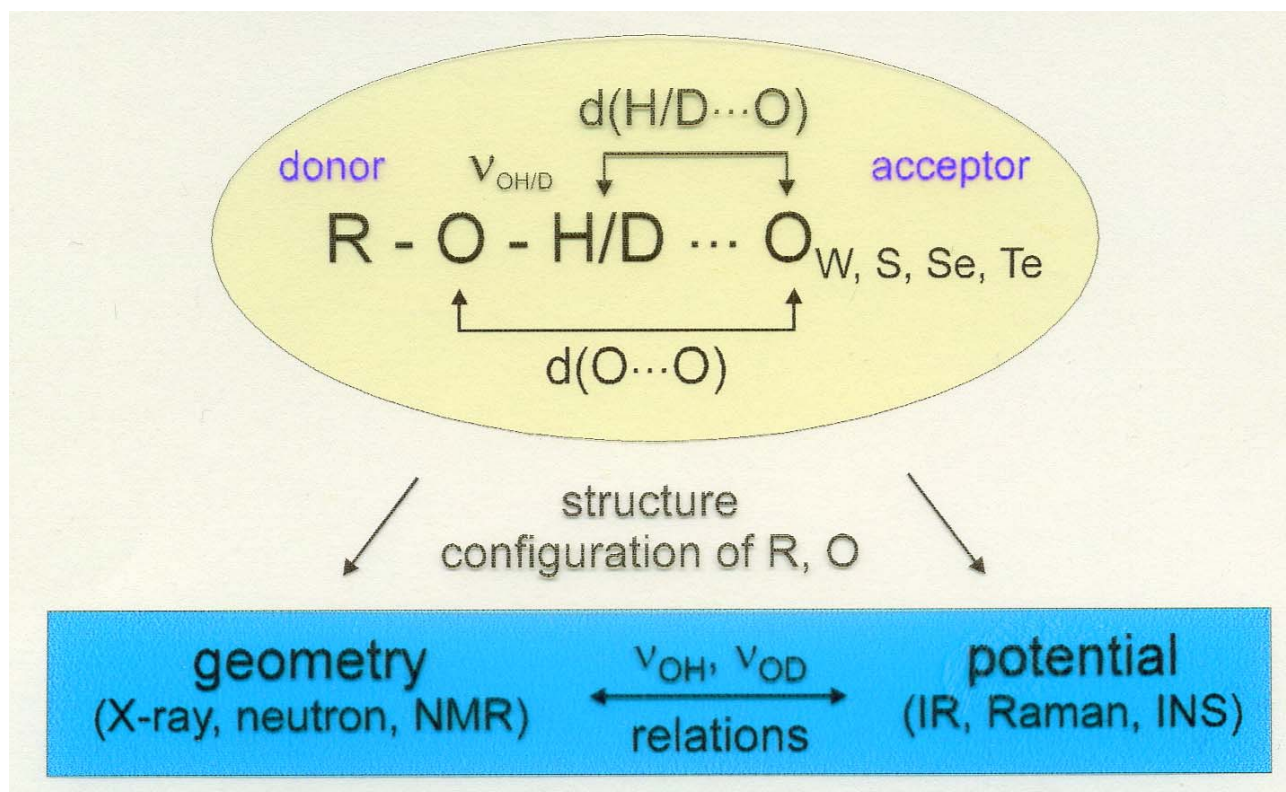


Infrared spectra of pure (bottom) and diluted (top) Isopropanol showing the shift and the broadening of the O-H stretching band by hydrogen bonding

Hydrogen bonding

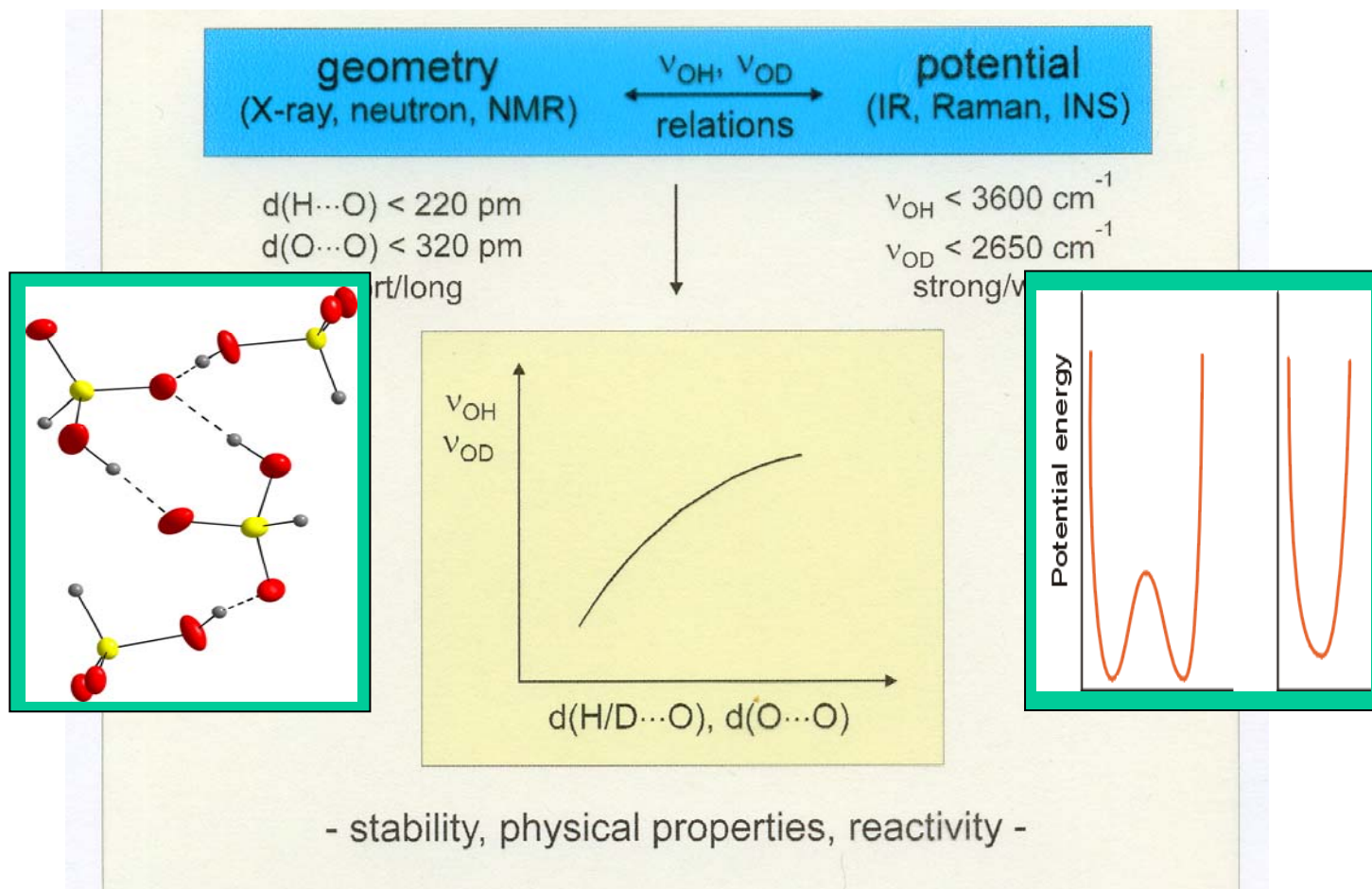
How to investigate/characterize hydrogen bonds?

By systematic investigation of isotopic compounds (e.g. Oxohydrates $\text{MXO}_3 \cdot n\text{H}_2\text{O}$ ($X = \text{S}, \text{Se}, \text{Te}$), $\text{M}(\text{HSeO}_3)_2 \cdot n\text{H}_2\text{O}$) with X-ray and neutron diffraction, NMR, IR, Raman, INS



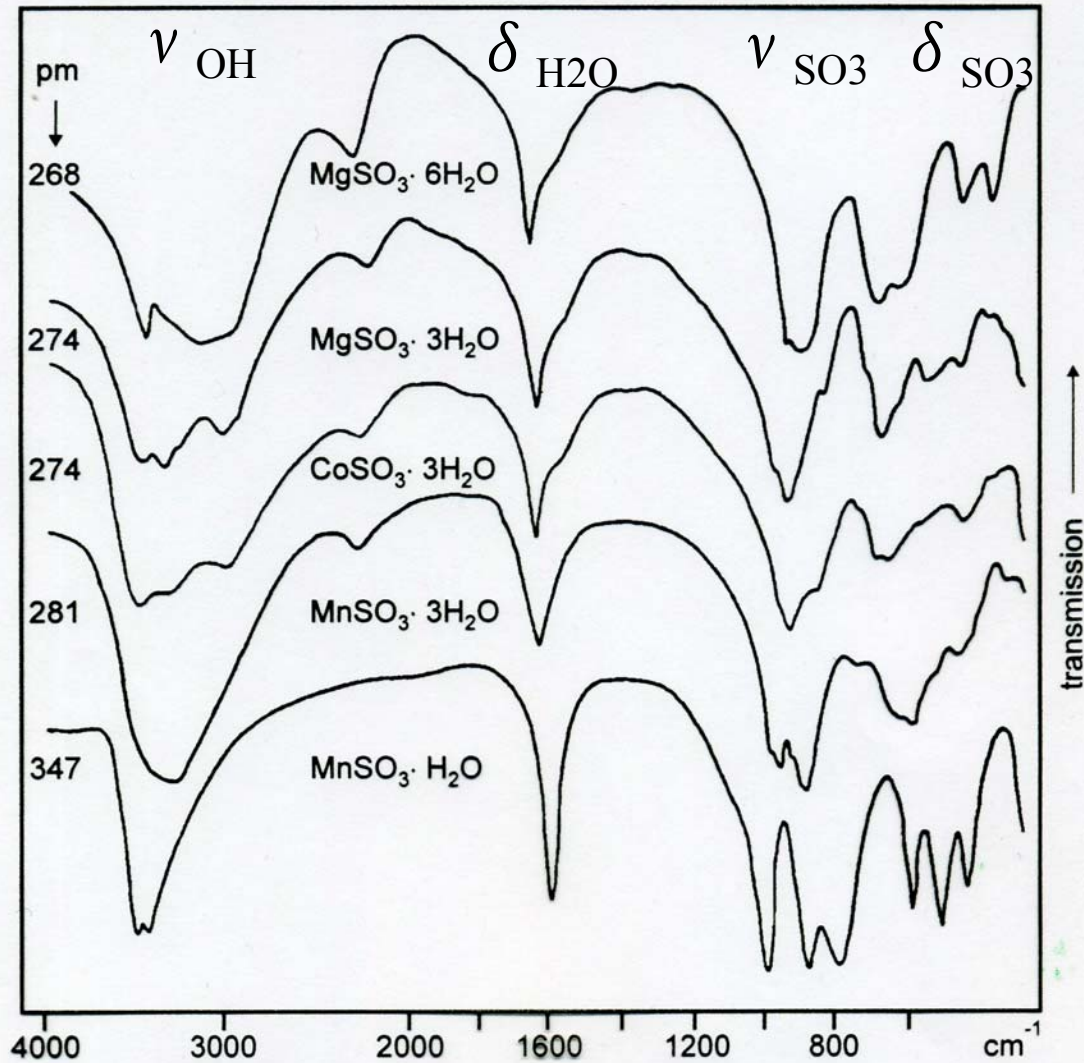
Hydrogen bonding

How to investigate/characterize hydrogen bonds?



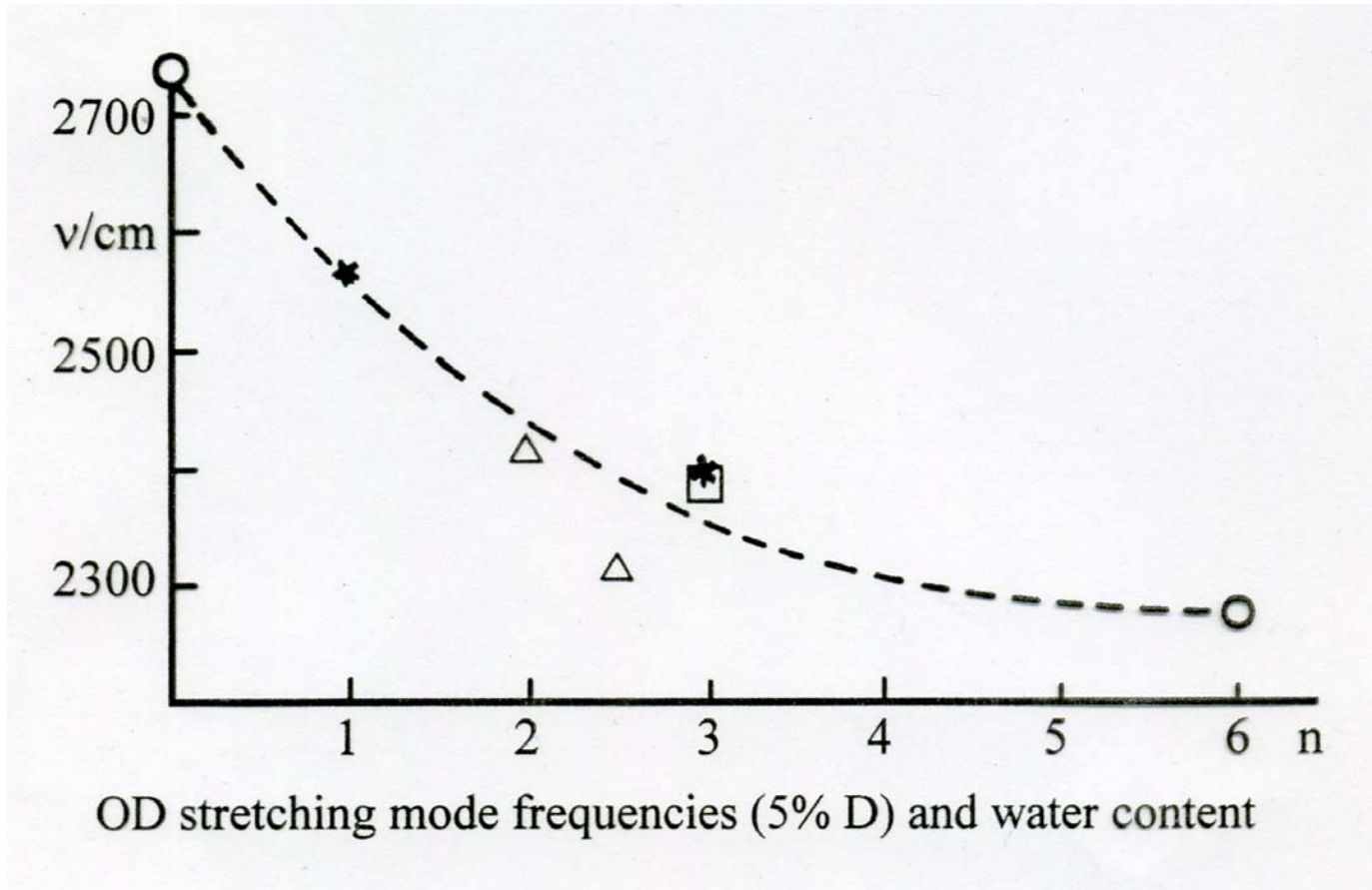
By systematic investigation of isotopic compounds and correlation of the structural, spectroscopic and theoretical data

Hydrogen bonding

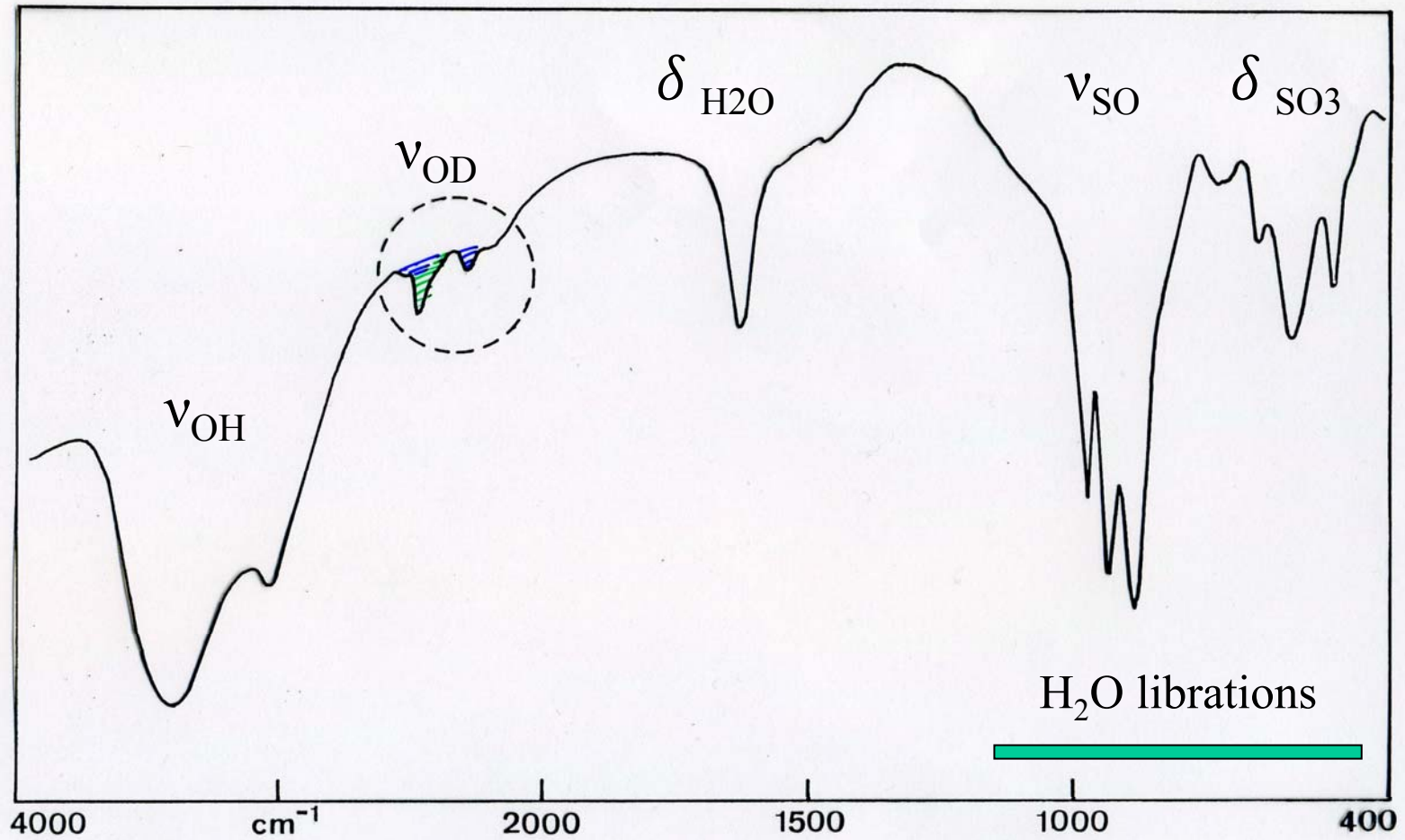


IR spectra and H-bond distances of several sulphite hydrates
(Lutz et al. 1977, Engelen, 1983)

Hydrogen bonding

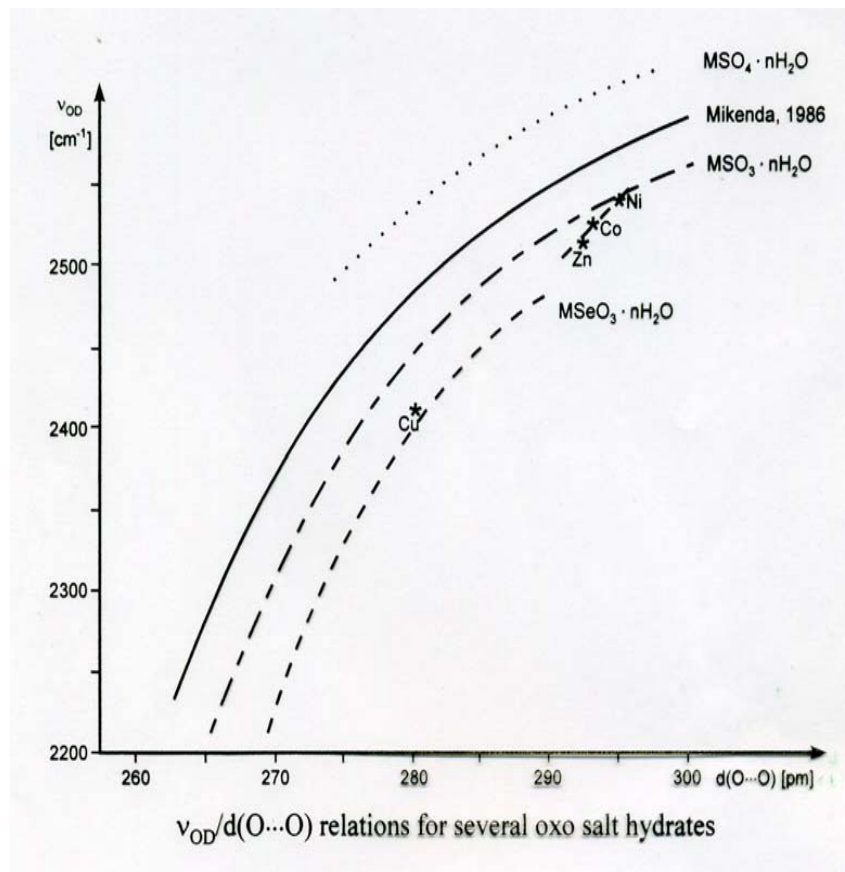
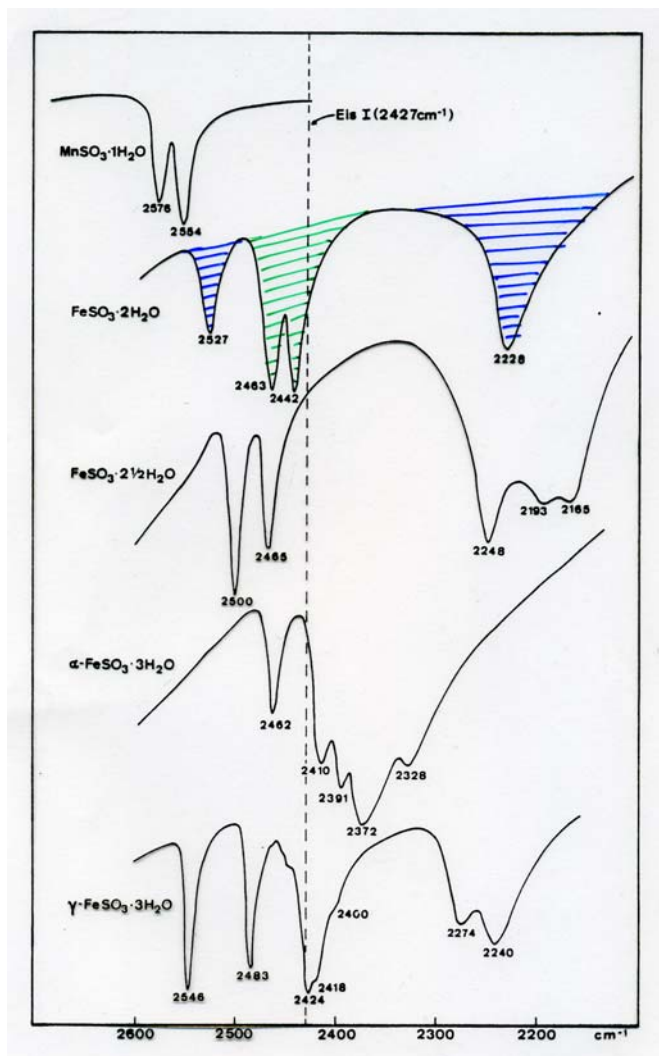


Hydrogen bonding



IR spectrum of $\text{MnSO}_3 \cdot 2\text{H}_2\text{O}$ (isotopic diluted samples, 5% D_2O , KBr-disk, 295K)

Hydrogen bonding



IR spectra and $\nu_{\text{OD}}/d(\text{O}\cdots\text{O})$ relations of some salt hydrates 21

Hydrogen bonding

WHAT IS A HYDROGEN BOND?

A *hydrogen bond* exists when a hydrogen atom is bonded to two or more other atoms. Since the hydrogen atom has only one orbital (1s) at sufficiently low energy, hydrogen bonds are mainly electrostatic in nature but covalent and repulsive orbital-orbital interactions are also present.

The *strength of hydrogen bonds* is governed by

- (i) the inherent hydrogen bond donor strength (acidity) of the hydrogen atom and the acceptor capability of the respective acceptor group,
- (ii) collective effects, as cooperative, competitive, and synergetic effects, which increase or decrease the inherent donor strengths and acceptor capabilities,
- (iii) structural features, as the number of acceptor groups, e. g. two-center, three-center (bifurcated), etc. hydrogen bonds, and the hydrogen bond angles $X-H\cdots Y$ and $H\cdots Y-Z$ built by the donor (X), acceptor (Y), and H atoms (linear or bent), and
- (iv) packing effects and constraints of the respective crystal structure.

Hydrogen bonding

STRENGTH OF HYDROGEN BONDS

In the case of *weak and very weak hydrogen bonds*, the respective bonding is mainly electrostatic in nature with attractive and repulsive charge-charge, charge-dipole, charge-induced dipole, and charge-multipole interactions between the partially positive charged hydrogen atom and the negative charged areas of the acceptor atom *Y*.

In the case of *strong and very strong hydrogen bonds*, in addition to the Coulomb forces, covalent bonding phenomena via orbital-orbital overlap attractive and closed-shell repulsive forces are of some importance.

Hydrogen bonding

STRENGTH OF HYDROGEN BONDS

The *strength of hydrogen bonds in inorganic solids* is governed by both the hydrogen-bond donor strength of the hydrogen-bond donor X and the hydrogen-bond acceptor capability of the hydrogen-bond acceptor Y .

For the formation of hydrogen bonds two rules have been established:

- (i) All hydrogen-bond acceptors available in a molecule will be engaged in hydrogen bonds as far there are available donors.
- (ii) The hydrogen-bond acceptors will be saturated in order of decreasing strength of the hydrogen bonds formed.

Both the hydrogen-bond donor strengths and the hydrogen-bond acceptor capabilities, are modified by additional phenomena like the synergetic, the cooperative, and the anti-cooperative or competitive effects. The various effects are highly non-additive.

Hydrogen bonding

Hydrogen-bond donor strength and acceptor capability

The *synergetic effect* describes the increase of the strength of a hydrogen bond through metal ions coordinated to the donor atom *X*.

The *cooperative effect* means the increase of the donor strength of a hydrogen-bond donor if the donor concurrently acts also as acceptor for a second hydrogen bond.

The *anti-cooperative* or *competitive effect* means the decrease of the strength of hydrogen bonds due to the decrease of

- (i) the donor strength e.g. through coordination (*donor competitive effect*) or
- (ii) the acceptor capability (*acceptor competitive effect*) of the entities involved in the respective hydrogen bonds.

Both may be caused by the different coordination of the donor and acceptor atoms *X* and *Y*.

Hydrogen bonding

Hydrogen-bond donor strength and acceptor capability

The *acceptor capability* primarily depends on the gas-phase basicity of the hydrogen-bond acceptor groups to hydrogen atoms. It is modified by the *acceptor competitive effect* due to the coordination and bond strength of the acceptor atom Y , e.g. by

- (i) the receipt of more than one hydrogen bonds,
- (ii) the total number of atoms coordinated to the acceptor atom,
- (iii) the strength of the $Y-Z$ bonds of the hydrogen-bond acceptor group, and
- (iv) the deviation from the most favorable hydrogen-bond acceptor angle $H \cdots Y-Z$.

In the case of $O-H \cdots Y$ hydrogen bonds, the relative acceptor capability range as $ClO_4^- < NO_3^- < BrO_3^- < IO_3^- < I^- < Br^- < H_2O < Cl^- < SO_4^{2-} < SeO_4^{2-} < SO_3^{2-} < SeO_3^{2-} < PO_4^{3-} < F^- < OH^-$ (*hydrogen-bond acceptor series*).

The *donor strengths* of common hydrogen-bond donors range as $OH^- < SH^- < NH_2^- < NH_3 < H_2O < HSeO_3^- < H_{5-n}IO_6^{n-} < H_3O^+$. It is governed by both the positive partial charge at the acid hydrogen atom, and the strength and hybridization of the $X-H$ bond of the donor molecule. The donor strength is increased due to the cooperative and the synergetic effects and decreased due to the anti-cooperative/donor competitive effect.

Hydrogen bonding

Hydrogen-bond donor strength and acceptor capability

In the case of the *synergetic effect*, i. e., bonding of the donor atom X to metal atoms, the $X-H$ bonds of the donor are both weakened and polarized with increasing strength of the respective $M-X$ bonds and, hence, the acidity of the respective hydrogen atom and the donor strength are increased.

The synergetic effect increases with increasing charge and decreasing size of the respective metal ions as well as with increasing covalence of the $M-X$ bonds. The latter is particularly strong in the case of Cu^{2+} , Zn^{2+} , and Pb^{2+} ions.

In the case of the *cooperative effect*, the $X-H$ bond of the hydrogen-bond donor is weakened because the donor atom X acts concurrently as hydrogen-bond acceptor and hydrogen-bond donor, and, hence, acidity and donor strength of the respective hydrogen atom are increased.

