Weak Chemical Force SEM-II : CC-4

Date: 27/03/2020

Hydrogen bonding

There are different kind of bonding and force of interaction:

Covalent/ionic bonding	Hydrogen bonding	Vander Waal force of attraction
Energy: (200 - 450 kJ/mol)	(8-42 kJ/mol) (ion-dipole or dipole-dipole interaction)	(< 8 kJ/mol)

Hydrogen bonding represented as, A—H··· D denotes the interaction between the donor atom D and the acceptor species A—H through hydrogen bond. By defination, H atom should remain between the atom (i.e A and D) of more electro-negative nonmetallic elements. Thus B-H-B (in BH_3) and W-H-B link (in $(CO)_5WHW(CO)_5$] are not considered as H-bonds because W and B are less electronegative than H.

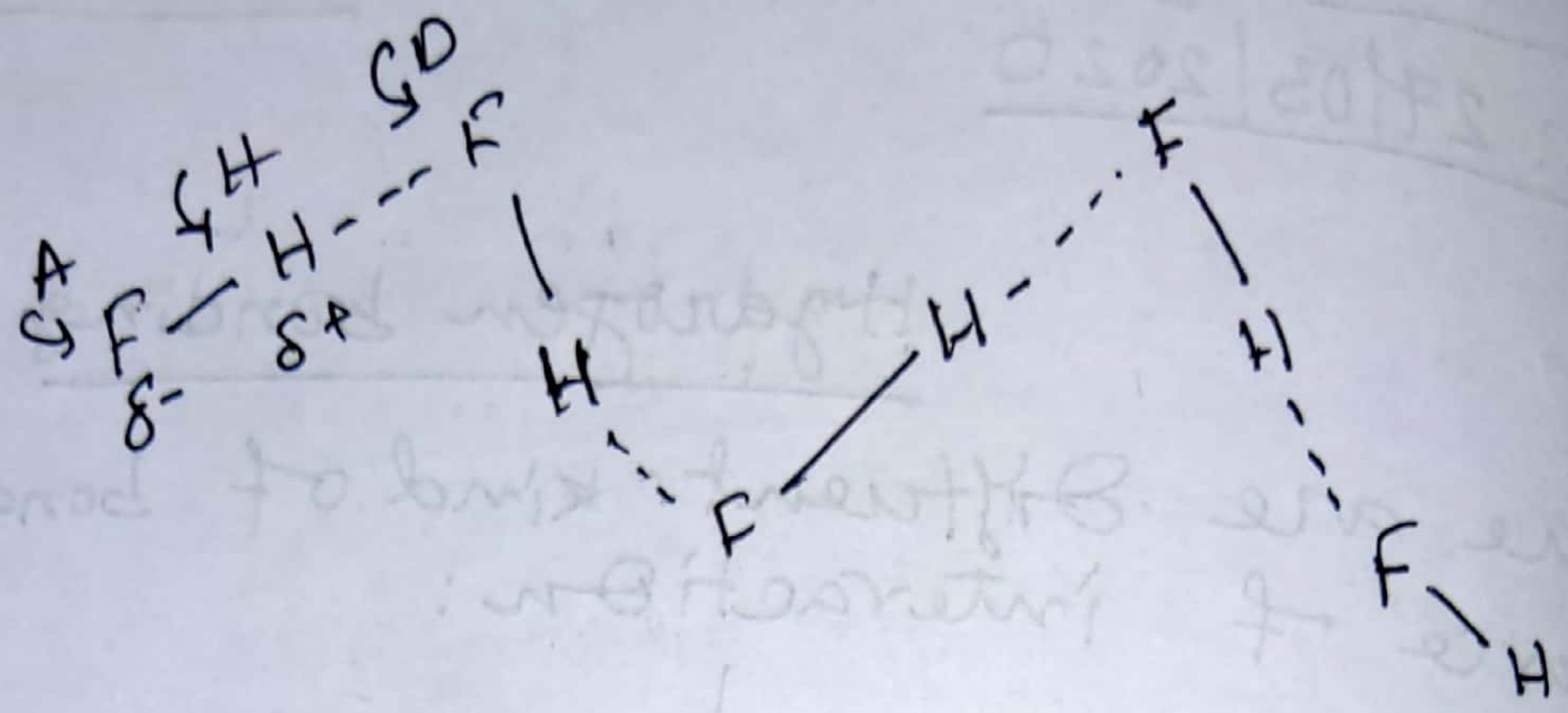
Condition for H-bond formation:

(i) A should be sufficiently electronegative (e.g F, O, N) to polarise the A-H bond as $\overset{\delta-}{A}—\overset{\delta+}{H}$

(ii) D should have lone pair of electron to act as lewis Base. In some cases D may be only

π-electron cloud.

Example:



H-bonding

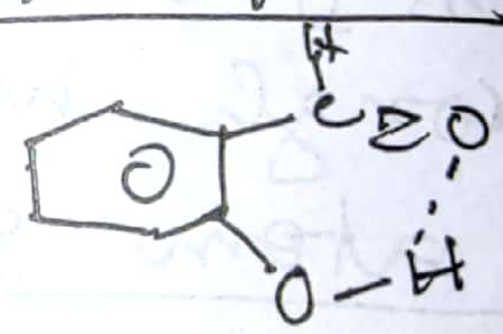
Intermolecular
(Donor atom "D" comes from different molecule)

Example: $(HF)_n$, $(H_2O)_n$, $(NH_3)_n$, $(ROH)_n$

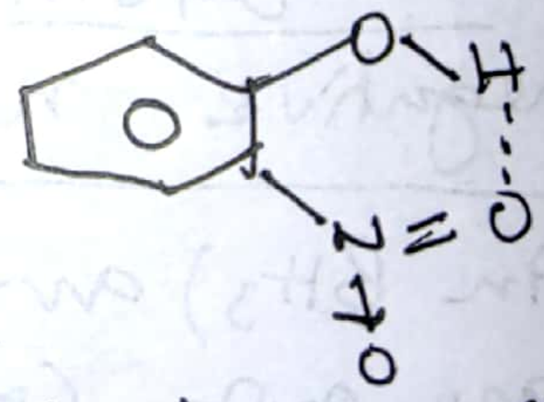
Intramolecular
(Donor atom "D" comes from the same molecule)

Examples:

(a)



(b)



Here

(*) H-bonding occurs through ring formation or chelation.

So, H-bonding

$\overset{\delta-}{A} \xleftrightarrow{\text{Covalent bond}} \overset{\delta+}{H} \cdots\cdots : D$ → E.N atom, small size, lone pair (F/O/N or cl for organic)

H-bond

E.N. atom (electronegative atom (F/O/N) and (C and cl for organic chemistry)

<u>Question:</u> if $A \overset{x}{-} H \cdots D$

Covalent bond H-bond

then

(a) $B.E.x > B.Ey$ → True always

(b) $B.Ex = B.Ey$ → (*) True only for one case

(c) $B.Ex < B.Ey$ → False

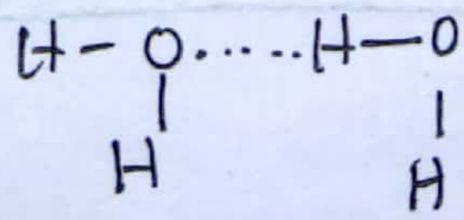
(*) Covalent bond = H-bond

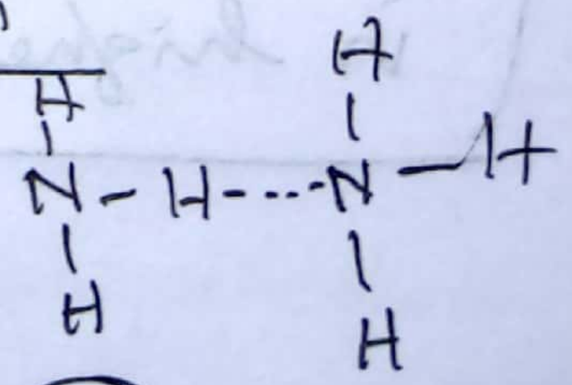
Example HF_2^- → $\overset{\delta-}{F} - \overset{\delta+}{H} \cdots \overset{\delta-}{F}$

F–H: 200 kJ/mol; H···F: 200 kJ/mol

<u>Comparison of H-bond strength</u>

(a) H–F ···· H–F

(b) 

(c) 

<u>H-bond strength</u> a > b > c

Reason: H-bond strength is directly proportional to the electronegativity of A atom. for HF_2 more A is the most electronegative F atom. then for (b) it 'O' atom and for (c) it is N atom.

Q. (ii) Which H-bond is strongest

(a) O—H ... O (c) N—H ... N

(b) O—H ... N (d) N—H ... O

Ans: (b), $\overset{A}{O}-\overset{H}{H}\cdots\overset{D}{N}$

Reason: (i) H-bond strength $\propto$ E.N of A

(ii) H-bond strength $\propto \frac{1}{\text{E.N. of B}}$

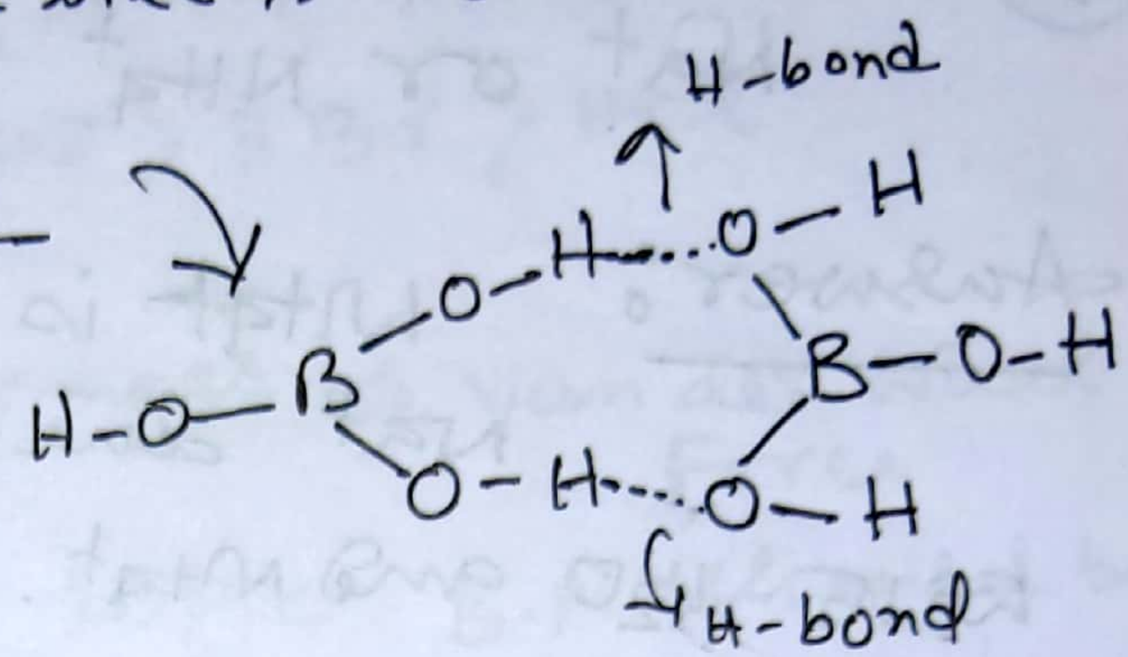
Isotopic effect

H-bond involving deuterium (D, heavier isotope of hydrogen) is stronger. Thus O—H ... O bond is weaker than O—D ... O bond. In fact, the boiling point of D_2O (heavy water) is higher than the normal water

Intermolecular H-bonding: Examples

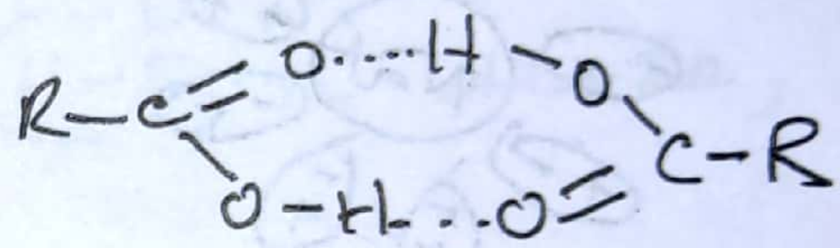
H_3BO_3 (Boric acid) exist as dimer due to H-bonding with cage like structure.

$H_3BO_3 \longrightarrow (H_3BO_3)_2$ Dimer



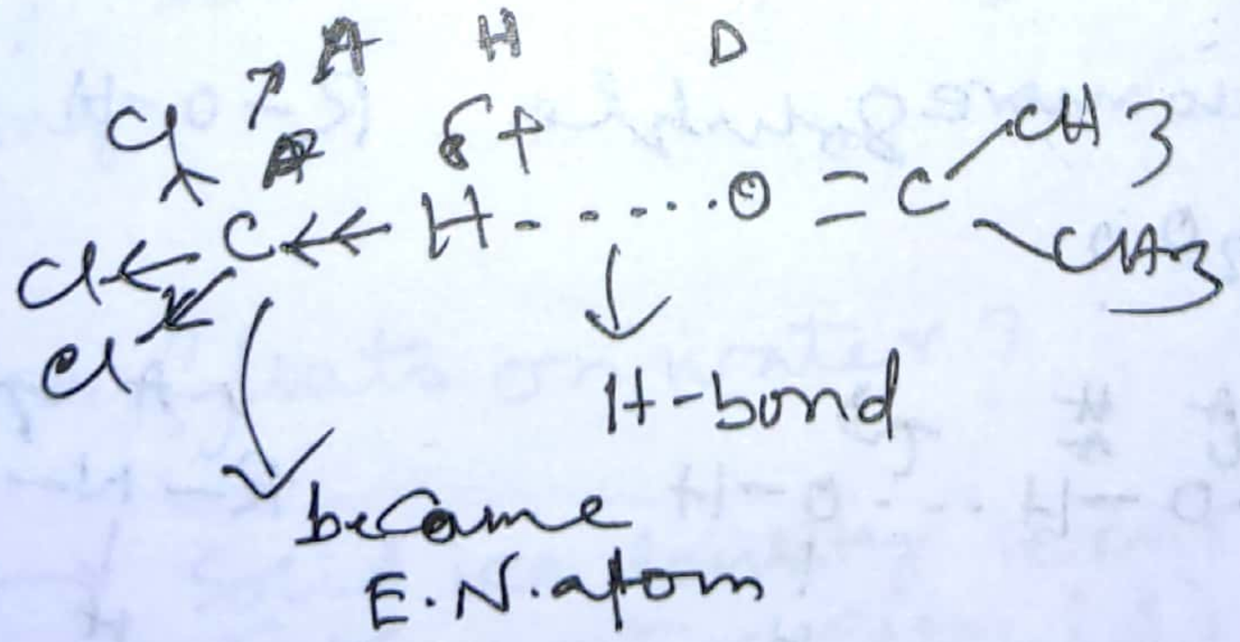
Carboxylic acid also exist as dimer.

$R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow (RCOOH)_2$ Dimer $\equiv$



H-bonding due to carbon (C) Rather than F|O|N, forming adduct.

Example: $CHCl_3$ chloroform + CH_3COCH_3 Acetone

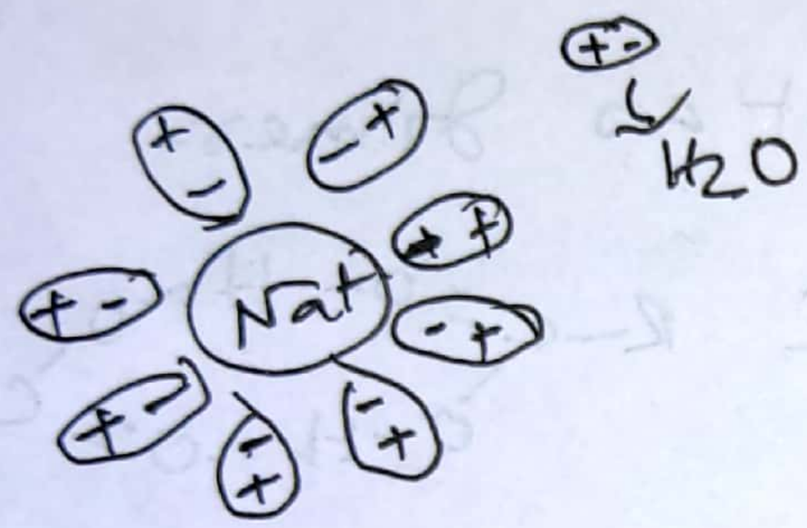


Effect of H-bonding

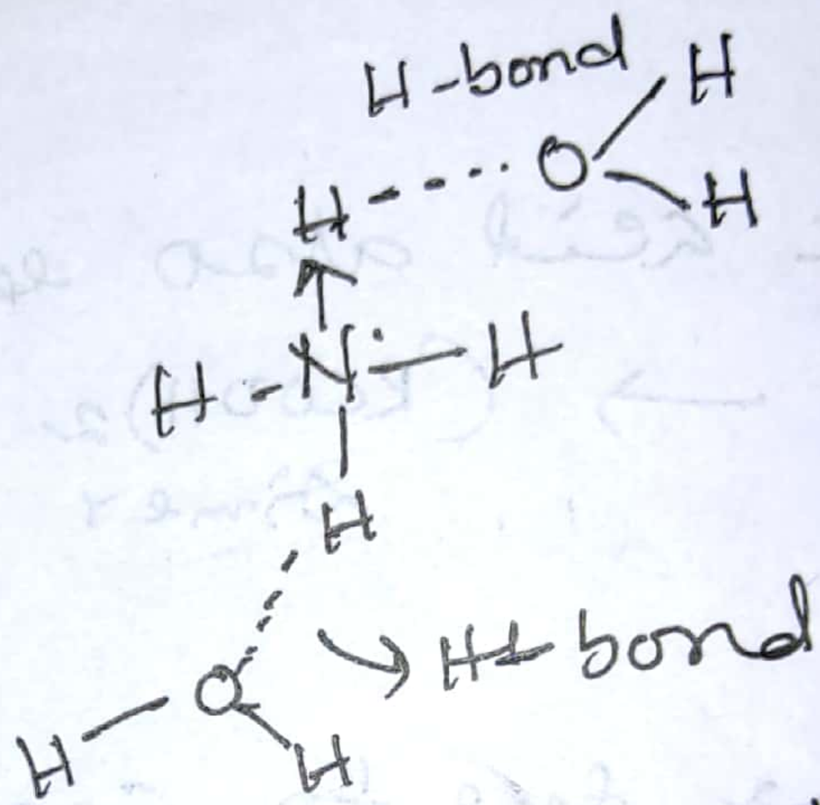
(i) Solubility

(Q) Which is more soluble in water
Na^+ or NH_4^+

Answer: NH_4^+ is more soluble in H_2O than Na^+ due to formation of H-bond with H_2O and NH_4^+.



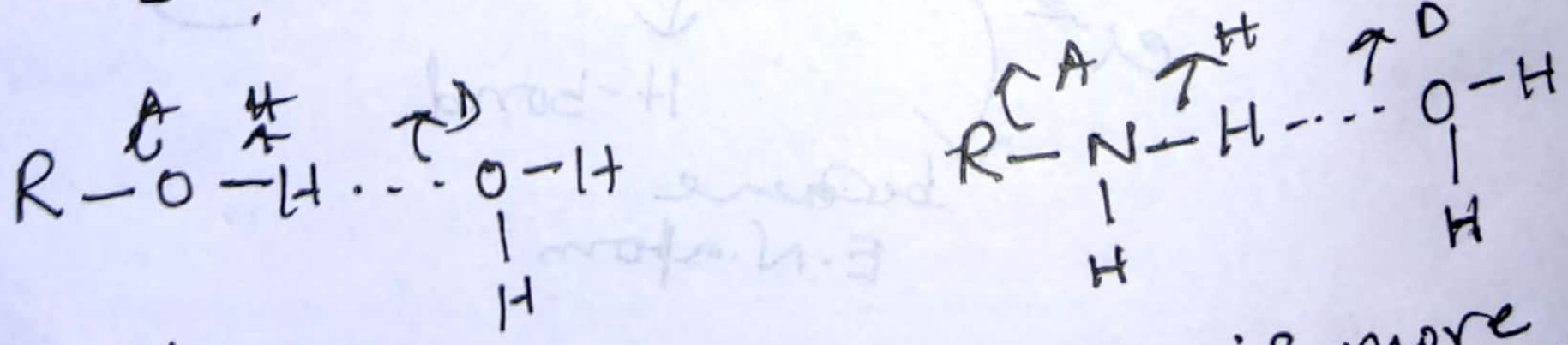
Ion-dipole interaction
Van der Waals force



H-bonding interaction

<Q> Which is more soluble $R-O-H$ or $R-\underset{H}{\underset{|}{N}}-H$ in H_2O?

Ans:



H-bonding strength in $R-O-H\cdots O$ is more stronger than $R-N-H\cdots O$. We have already discussed H-bond strength depends on the electronegativity of the atom 'A'. Hence R-OH is soluble in H_2O than $R-NH_2$.

(ii) Boiling point / Melting point (B.P)

ⓐ HF HCl HBr HI (Gr. 17)

Compare the boiling point

The sequence is HF > HI > HBr > HCl

We know B.P. ∝ molar mass ∝ Van der Waal Force

So, according the above logic B.P. should be HI > HBr > HCl > HF

But H–F undergoes strong H-bonding interaction to exist as $(H-F)_n$. Hence, it has highest B.P.

⊛ Similar B.P. trend observed for gr. 16 and gr. 15 elements also,

$H_2O > H_2Te > H_2Se > H_2S$

H-bonding

and

$NH_3 > SbH_3 > AsH_3 > PH_3$

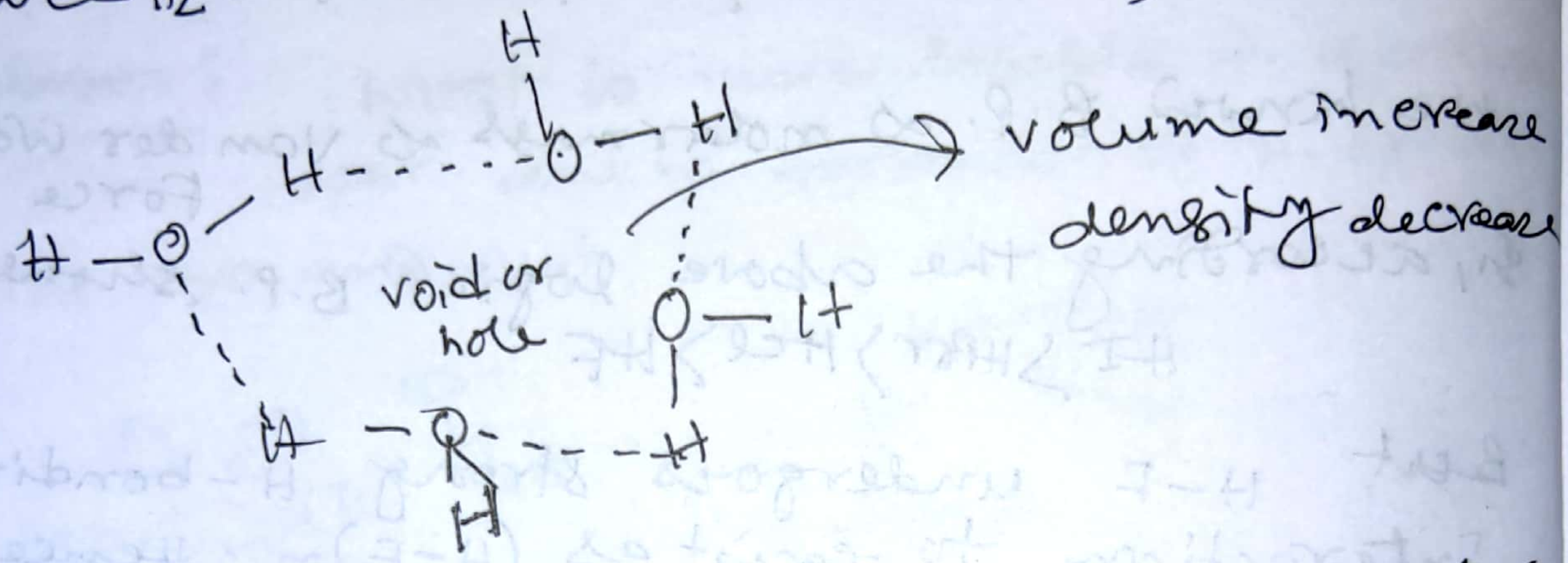
H-bonding

⟨8⟩ Why ice floats on water?

→ Solid ice density lesser than density of water (liquid)

(0.9 g/cm³) → (1 g/cc)

Ans: Ice got cage like structure due to formation of intermolecular H-bond among H_2O mole and due to presence of void or cavity, it got less density ($\frac{mass}{volume}$). Than pure H_2O



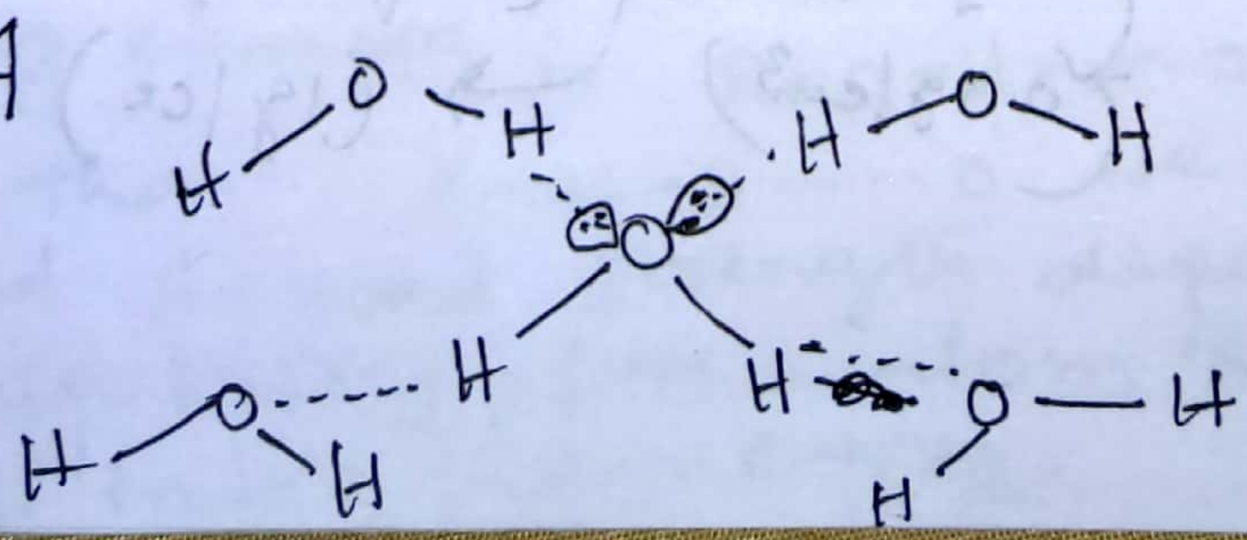
ice (0°c) → water (0°c) → water (4°c) → water (50°c)

density (d) = < < >

water at 4°c has max density, ~~if we heat~~ because no H-bonding. If we heat at high temperature volume increase due to expansion and density decrease.

Q) How many H-bonds are in molecule of H_2O.

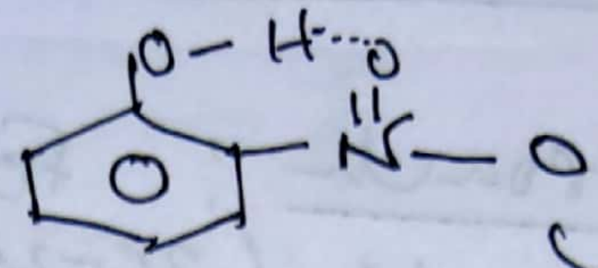
Ans: 4



=> sp^3 hybrid pyramidal structure. Tetrahedral

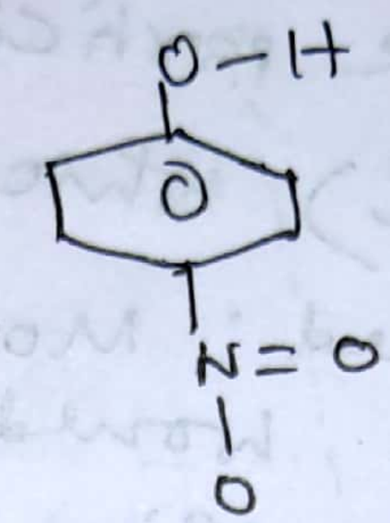
Intramolecular H-bonding example

O- nitrophenol



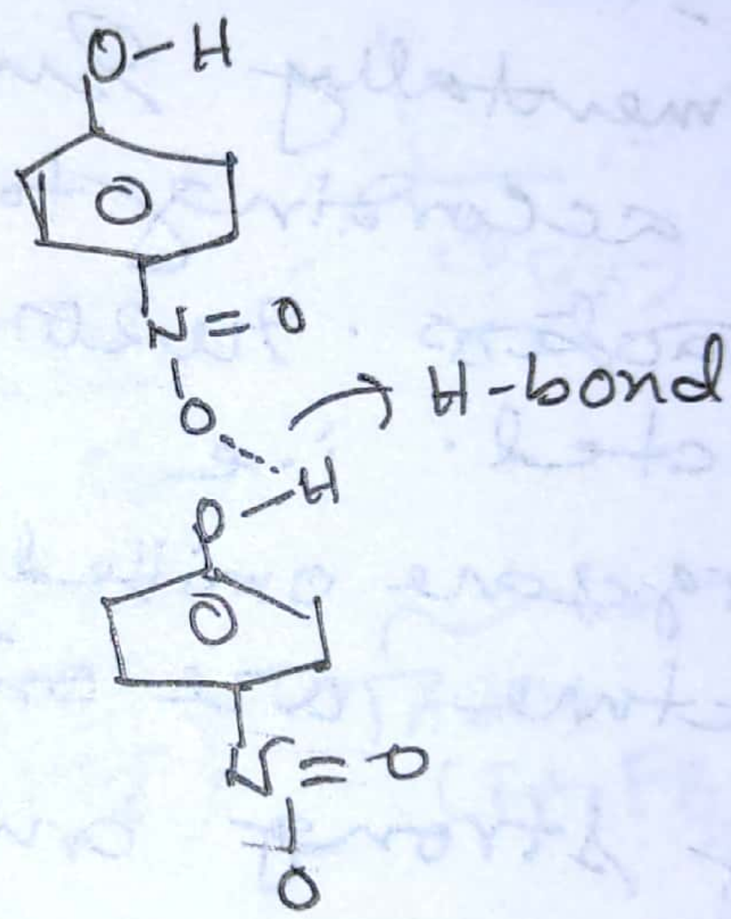
O-nitro phenol

→ intramolecular H-bond



P- nitrophenol

intermolecular H-bond in P-nitrophenol.



B.P. of P-nitrophenol > O-nitrophenol.
Hence, P- and, O- nitrophenol can be seperate from a mixture by fractional distillation process.

Also, O-nitrophenol is more volatile because it present as single molecule than P-nitrophenol.

Theories of H-bonding

(i) VBT approach: Formation of two covalent bonds (2c-2e) by H, i.e A–H–D, requires the participation of its 2s-orbital (~962 kJ/mol) which is not energetically ~~fav~~ favoured. Moreover, if it were so, all H-bonds would be symmetrical (for A = D) but this prediction is not experimentally supported. This is why according to VBT, covalent ionic ~~character~~ resonating structure is predicted. i.e A–H : D ⇌ A : H–D (charges are omitted). But such resonating structure are only meaningful for very strong and short (e.g. HF_2^-), H-bonds which leads to symmetrical position of H-bond.

In VBT approach, one can invoke resonance among the structures

$$F-H\cdots\bar{F} \longleftrightarrow \bar{F}\cdots H-F$$

MOT approach

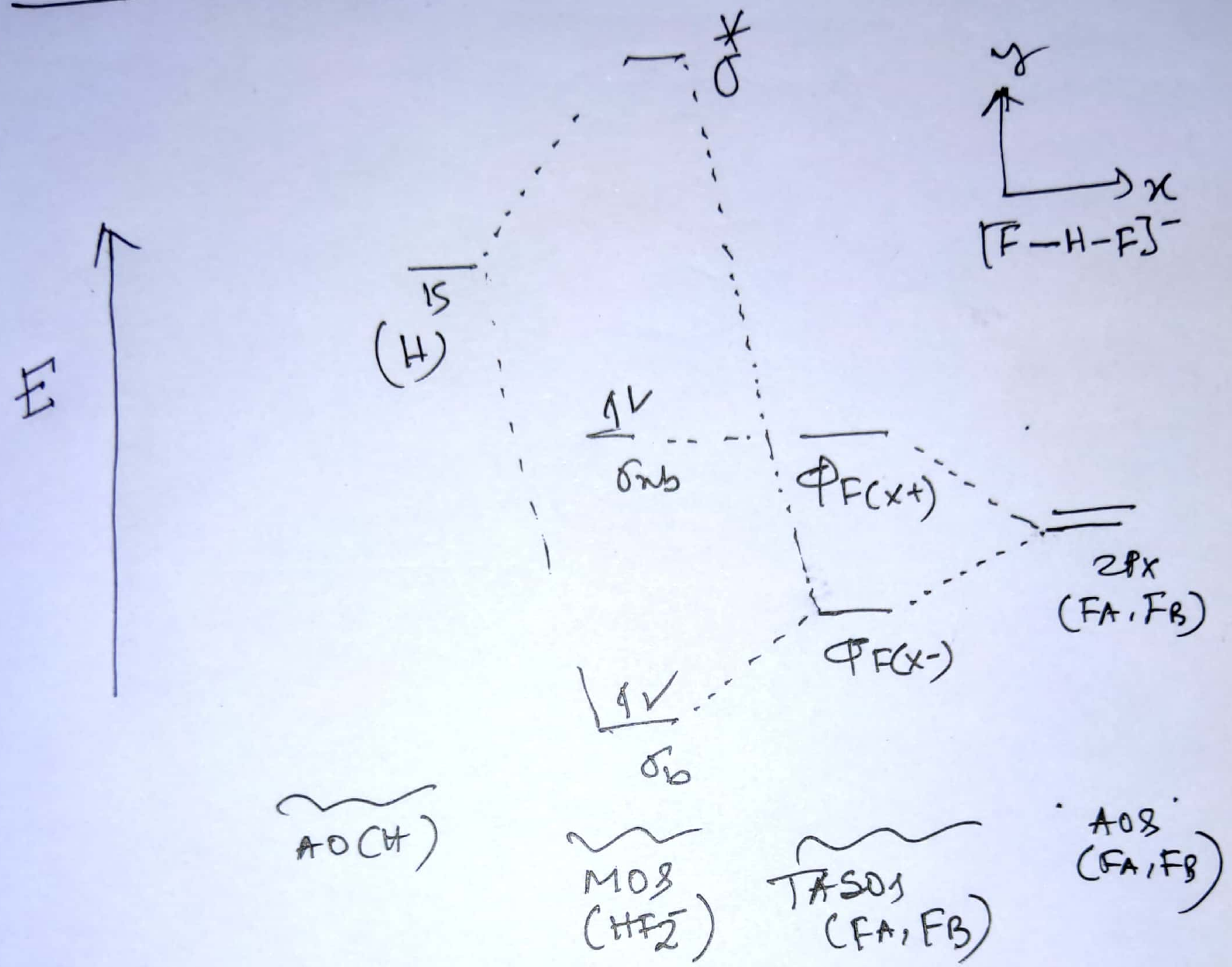


Fig: MOT diagram of HF_2^- molecule.

MOT ~~explains~~ describes the 3C–4e bonding model to explain the H-bonding behaviour and of HF, HCl, HBr and HI molecules.