This Class

Chap 6 Acid and Bases

Next Class

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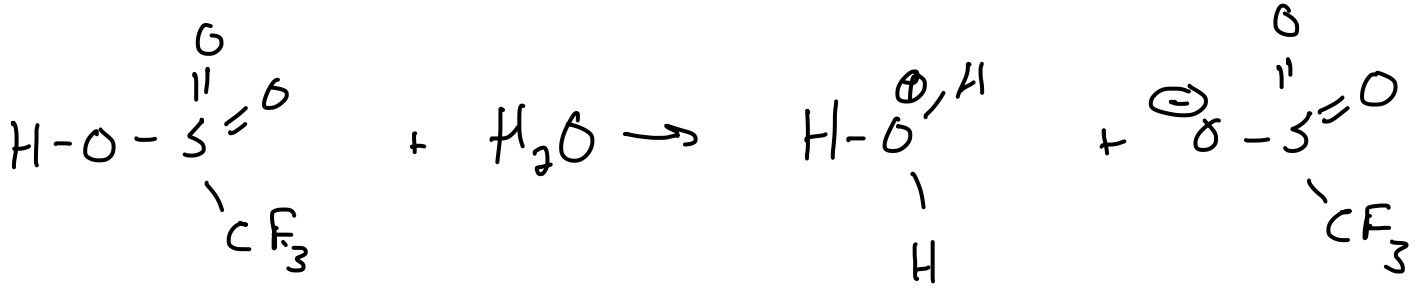
Strong $HCl + H_2O \rightarrow H_3O^{\oplus} + Cl^{\ominus}$

Leveling

Weak $CH_3CO_2H + H_2O \rightleftharpoons H_3O^{\oplus} + CH_3CO_2^{\ominus}$

H_3O^+ is the strongest acid you can make in H_2O. Add a stronger acid to water & it is converted to H_3O^+

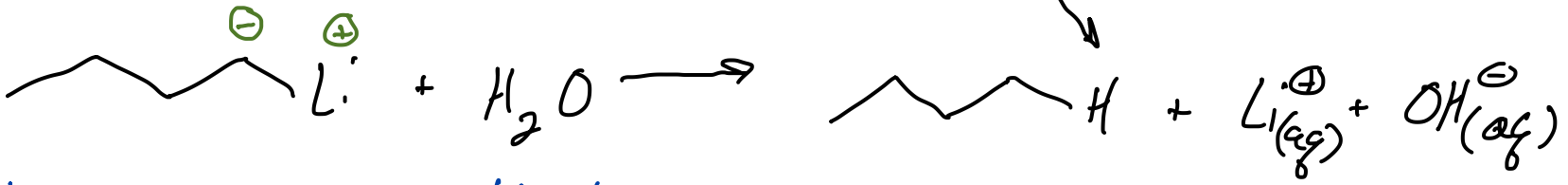
What's the strongest acid that can exist in aqueous solution?



$H\text{-}Cl + H_2SO_4$ would have ionized completely, too acid to water & it is converted to H_3O^+

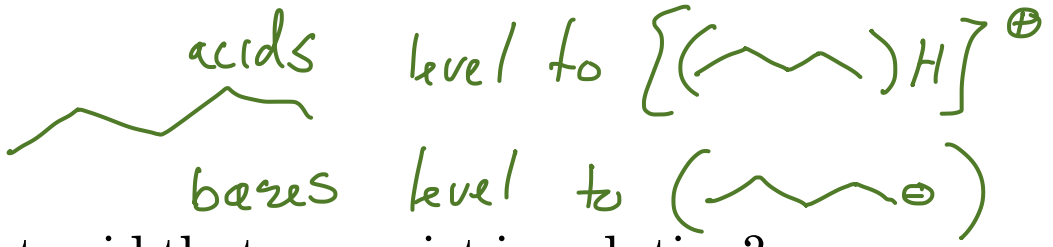
What's the strongest base that can exist in aqueous solution?

$C^{\ominus}$ grabbed an $H^{\oplus}$



Strongest base that can exist in H_2O is $OH^{\ominus}$

Anything stronger is converted to $OH^{\ominus}$



What's the strongest acid that can exist in solution?

$HA + solvent \longrightarrow (solvent)H^+ + A^-$

the conjugate acid of the solvent is the strongest acid that can exist in that solvent

$R\text{-}OH + HA \longrightarrow R\text{-}\overset{\oplus}{O}(H)\text{-}H + A^\ominus$ water + alcohols level acids to $(ROH_2)^+$

What's the strongest base that can exist in solution?

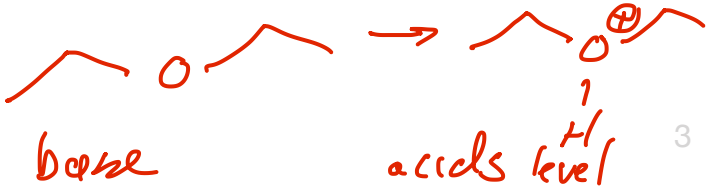
$B + solvent \longrightarrow (solvent)^\ominus + H{:}B^\oplus$

the conjugate base of the solvent is the strongest base that can exist in the solvent

$R\text{-}O\text{-}H + B \longrightarrow R\text{-}O^\ominus + BH^\oplus$ water and alcohols level bases to $RO^\ominus$

$CH_2Cl_2 + B \longrightarrow :CHCl_2^- \; HB^+$

acids ✓ base ✗



Trends in Acid Strength

Brønsted-Lowry

Section 6.3.7, 6.3.8, 6.3.9

across a period

LiH BeH_2 BH_3 CH_4 NH_3 HF $HNe^{\oplus}$

weaker acid

stronger acid

The stability of the conjugate base determines the acids proton donor ability.

$Li^{\ominus}$ vs $F^{\ominus}$

+3 nucleus
unlikely
to form

+9 nucleus
that is a lot
of charge to
stabilize the $\ominus$

extremely unlikely
these metal hydrides
act as $H^{\ominus}$ donor

Trends in Acid Strength

down a family

H - F

H - Cl

H - Br

H - I

H_2O

H_2S

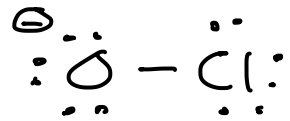
weaker

stronger

⊕ on nucleus grows & volume that e⁻ density is spread out over increases

for "oxy-acids"

$HOCl$ weakest

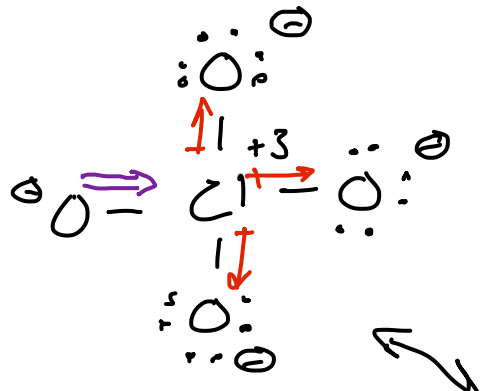


$HOClO$

$HOClO_2$

$HOClO_3$ strongest

H_2SO_4 or H_2SO_3



More O atoms means...

O atoms are eneg & draw e^- density away for the conjugate base to H⊕ bond

e^-'s will be distributed by resonance ... more O atoms more e^- delocalization

in general for Brønsted-Lowry acids

In general

1. resonance to spread out e^-
2. eneg atoms on adjacent atoms to spread out e^-
3. place the $\ominus$ on a large atom to spread out e^-
4. Get $\ominus$ close to a $\oplus$ nucleus

   $F^\ominus$ vs $OH^\ominus$
5. Get $\ominus$ close to nucleus by using high "s character" hybrids

   sp vs sp^3

For Lewis acids

e^- pair acceptors

more ⊕ more attractive to lp e^-

concentrated ⊕ ... small atoms

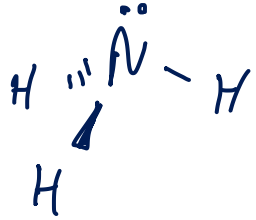
Fe^{3+} vs Fe^{2+}

↑ stronger Lewis acid

Fe^{3+} vs Al^{3+}

↑ stronger Lewis acid

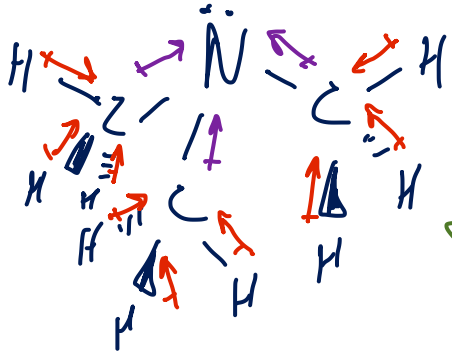
$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$ molten iron



Gas phase basicity

$: NMe_3 < NHEt_2 < NHBu_2 < NEt_3 < NBu_3$

due to the inductive effect the e^- rich C atoms push e^- density to the N



stronger than NH_3

each time we add more C-H bonds we are pushing more e^- density onto the N and the N is becoming more basic... better able to attract an H^+

eneg of C is 2.5
eneg of H is 2.1
so C attracts e^-'s in C to H bond

Me = methyl or CH_3 Et = ethyl or CH_2CH_3 Bu = butyl $CH_2CH_2CH_2CH_3$

Increasing base strength in water

the starting point

9 C-H bonds push e⁻ density toward N

$NH_3 < Me_3N < MeNH_2 < Me_2NH$

$NH_3 < EtNH_2 < Et_3N < Et_2NH$

NH_3 < Me_3N < $MeNH_2$ < Me_2NH

cannot be an H bond donor

can be H-bond donor

can be an H-bond donor

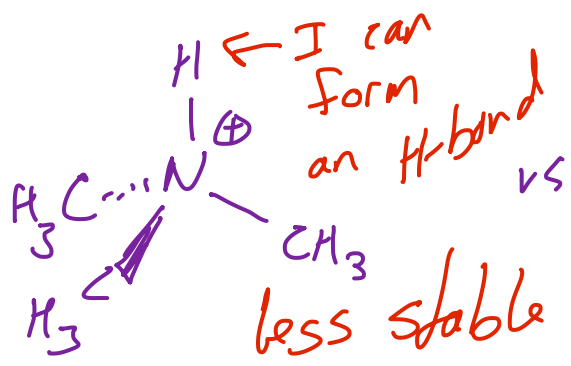
9 C-H bonds

3 C-H bonds

6 CH bonds

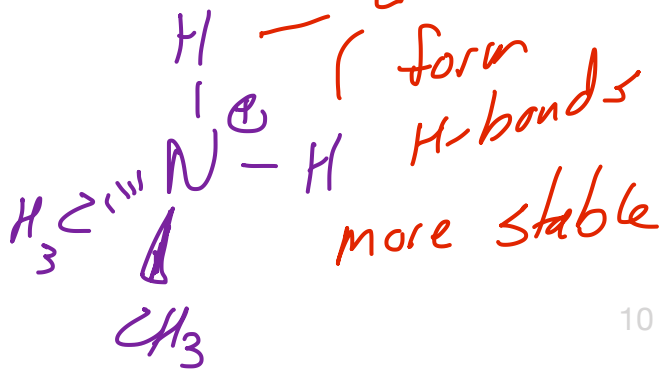
pushing e⁻ density toward N

NH_3 can be an H bond donor



I can form an H-bond vs

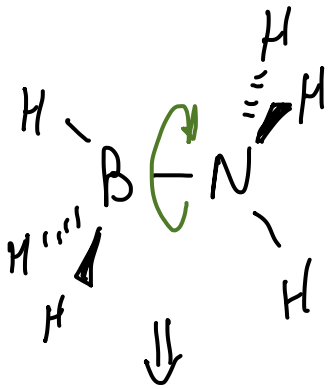
less stable

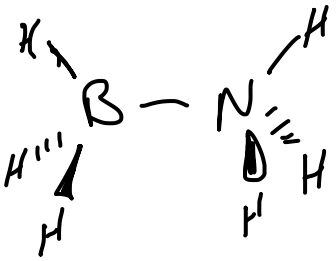


H can form H-bonds

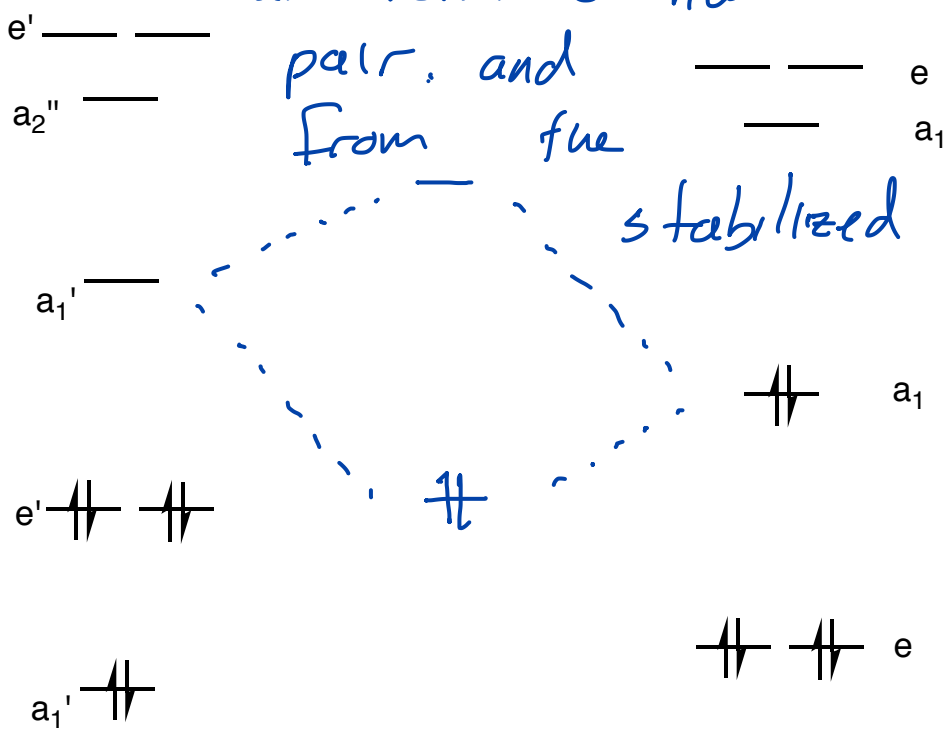
more stable

BH_3 exists as B_2H_6

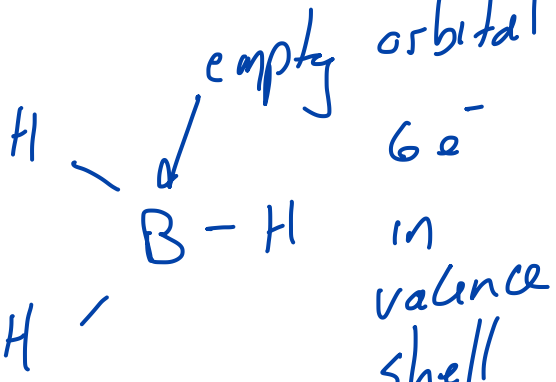




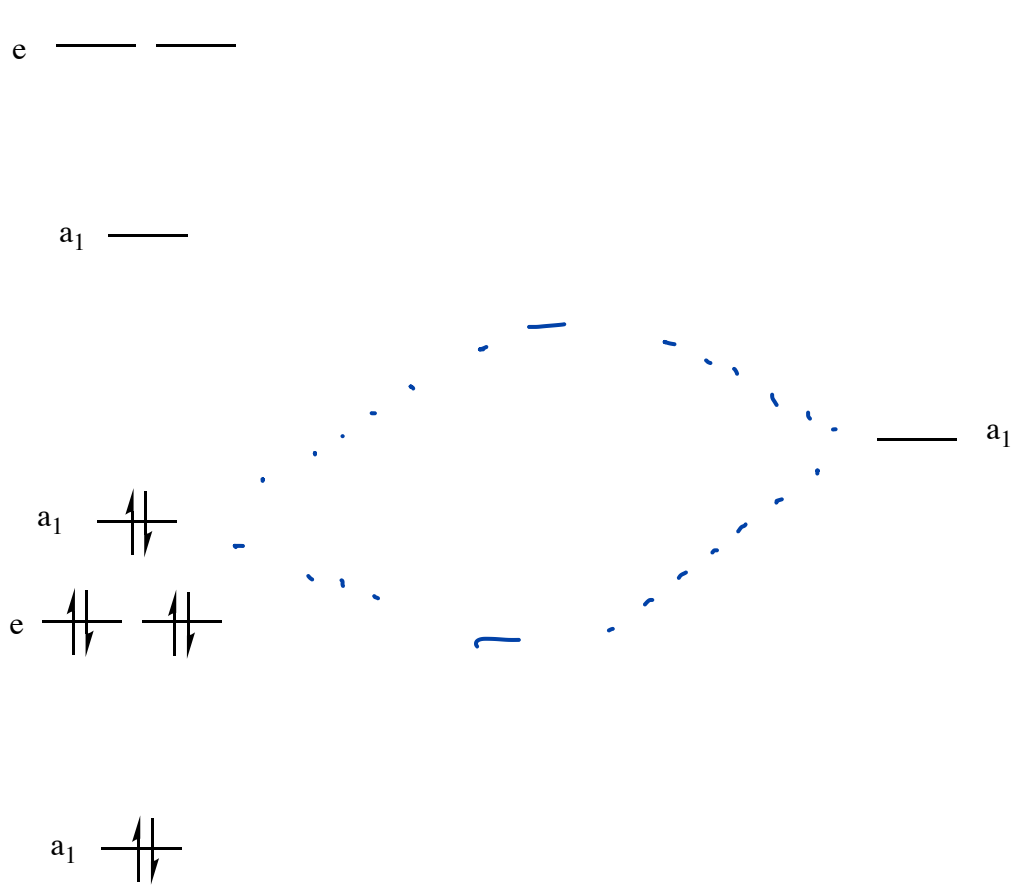
HOMO of base & LUMO of acid interact and form a new bonding/antibonding pair. and from the stabilized the e⁻'s base are

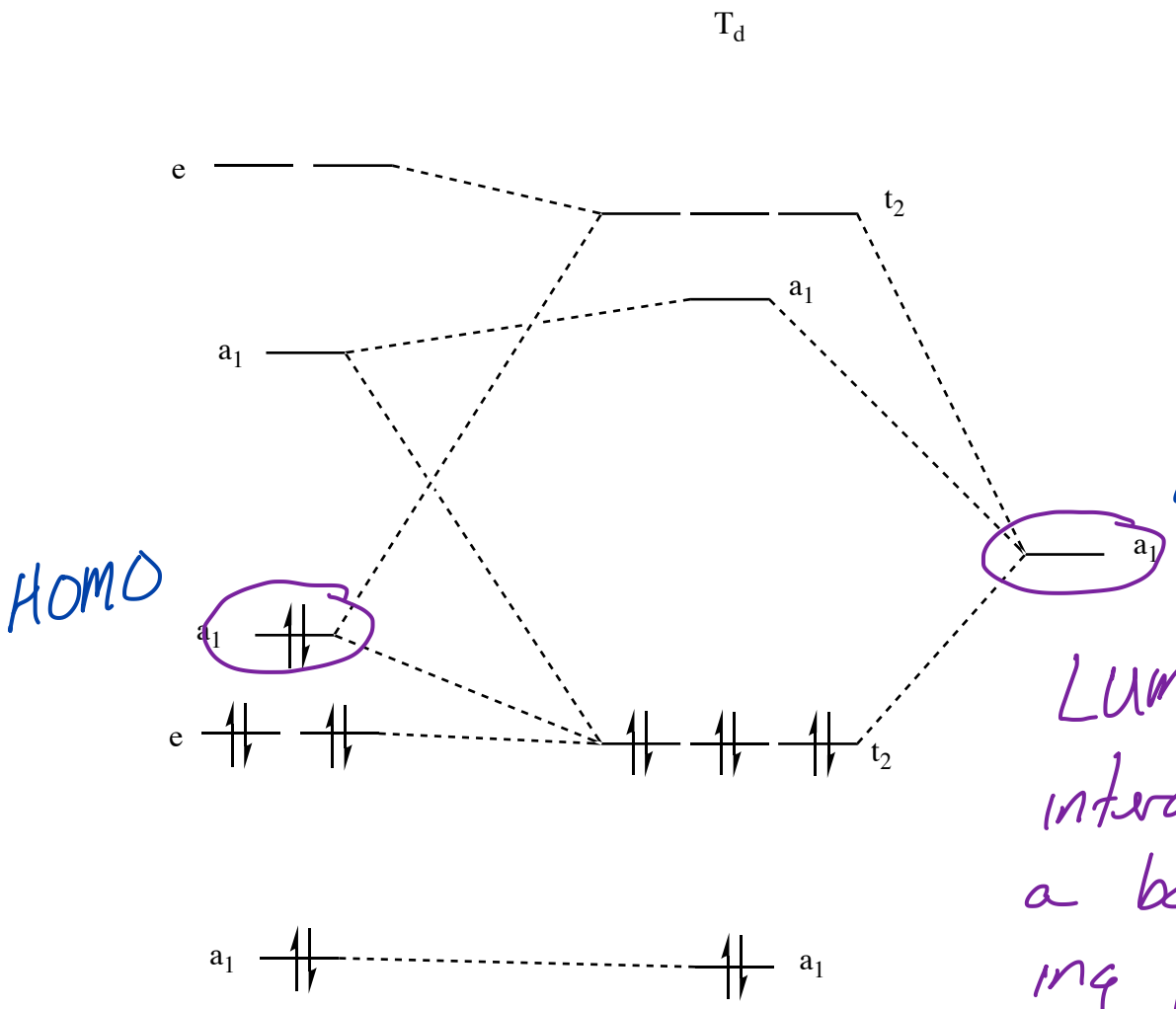


Lewis acid



Lewis base


e
a1
a1
a1
e
a1
NH3
H+
C3V
Td



HOMO

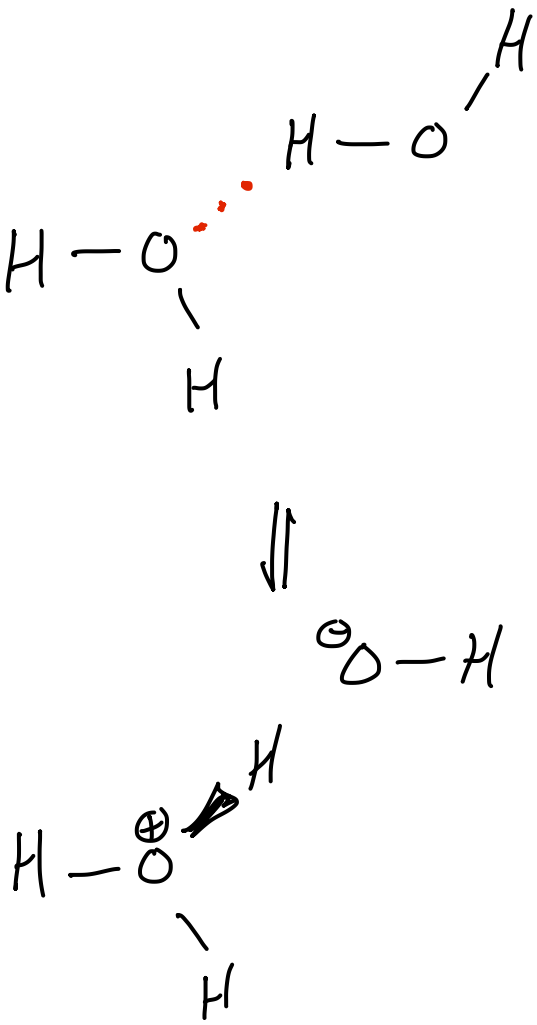
LUMO

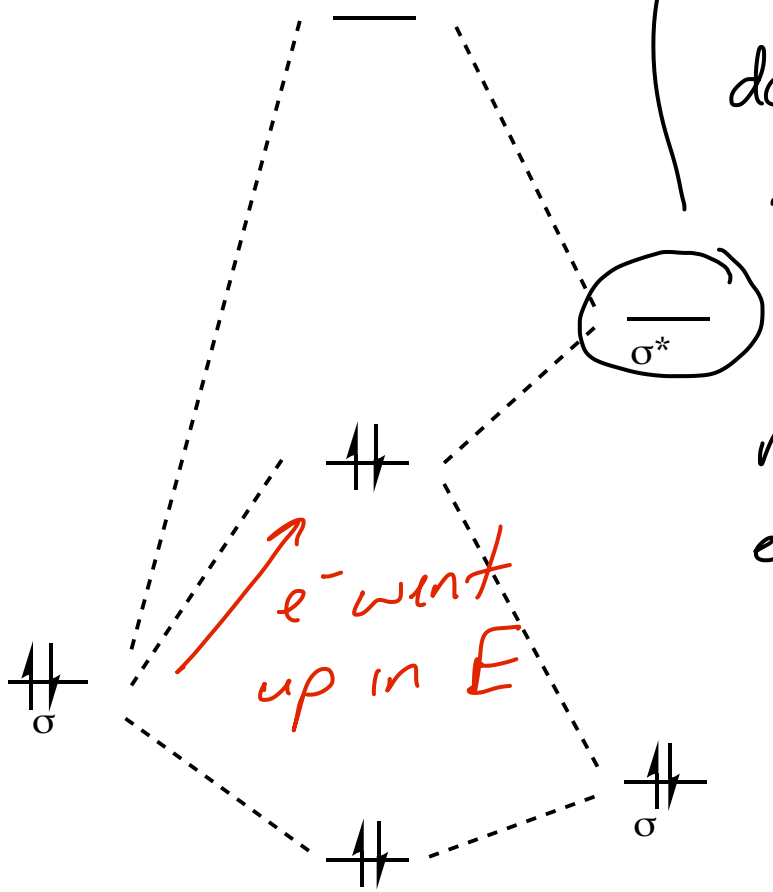
LUMO + HOMO still interact an create a bonding/anti bonding pair. e⁻'s from base are stabilized

MO's for a T_d molecule

is like an incomplete

H^+ transfer





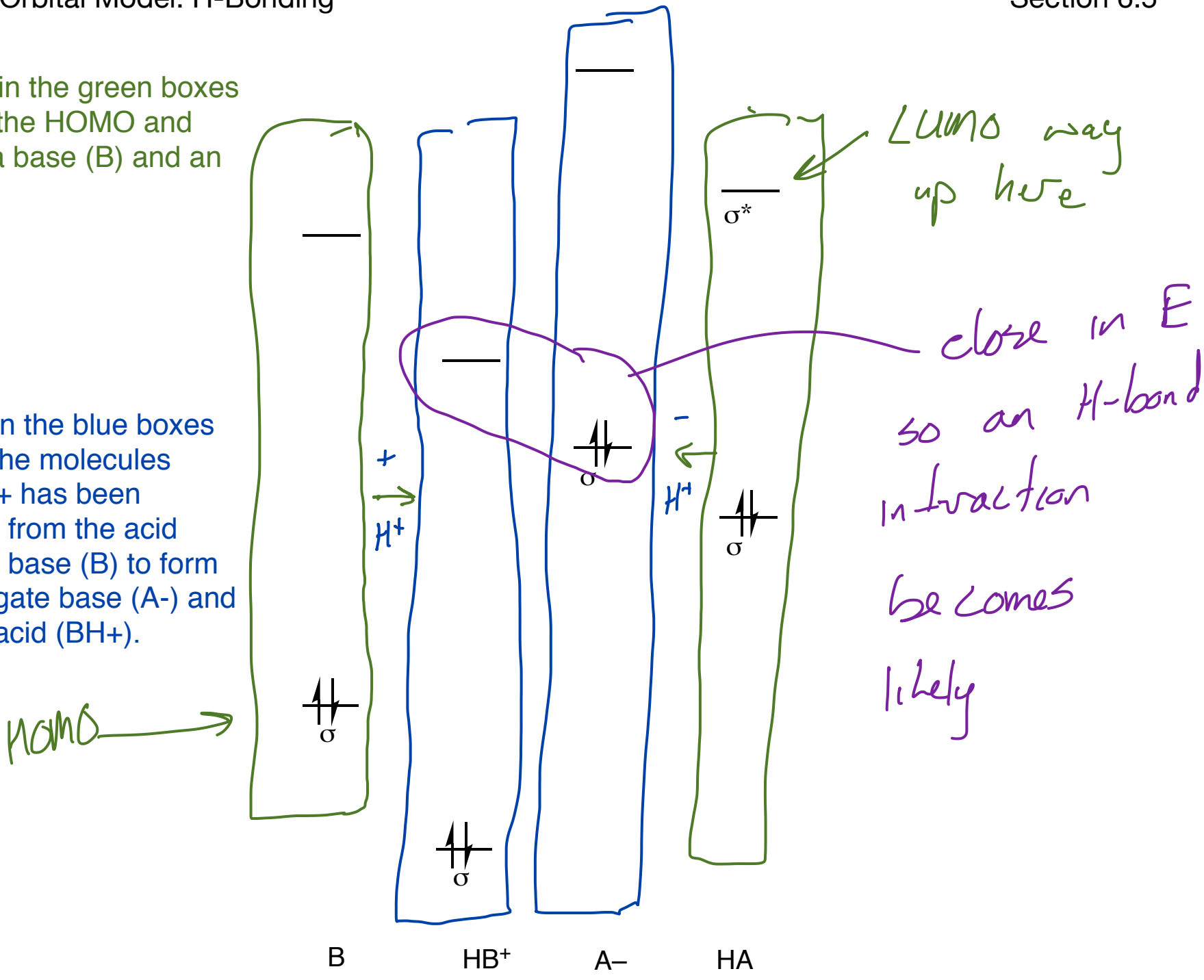
if the LUMO on our H-bond donor candidate is too high, then forming a new bonding / anti bonding pair will not stabilize e⁻

e⁻ rich O or N

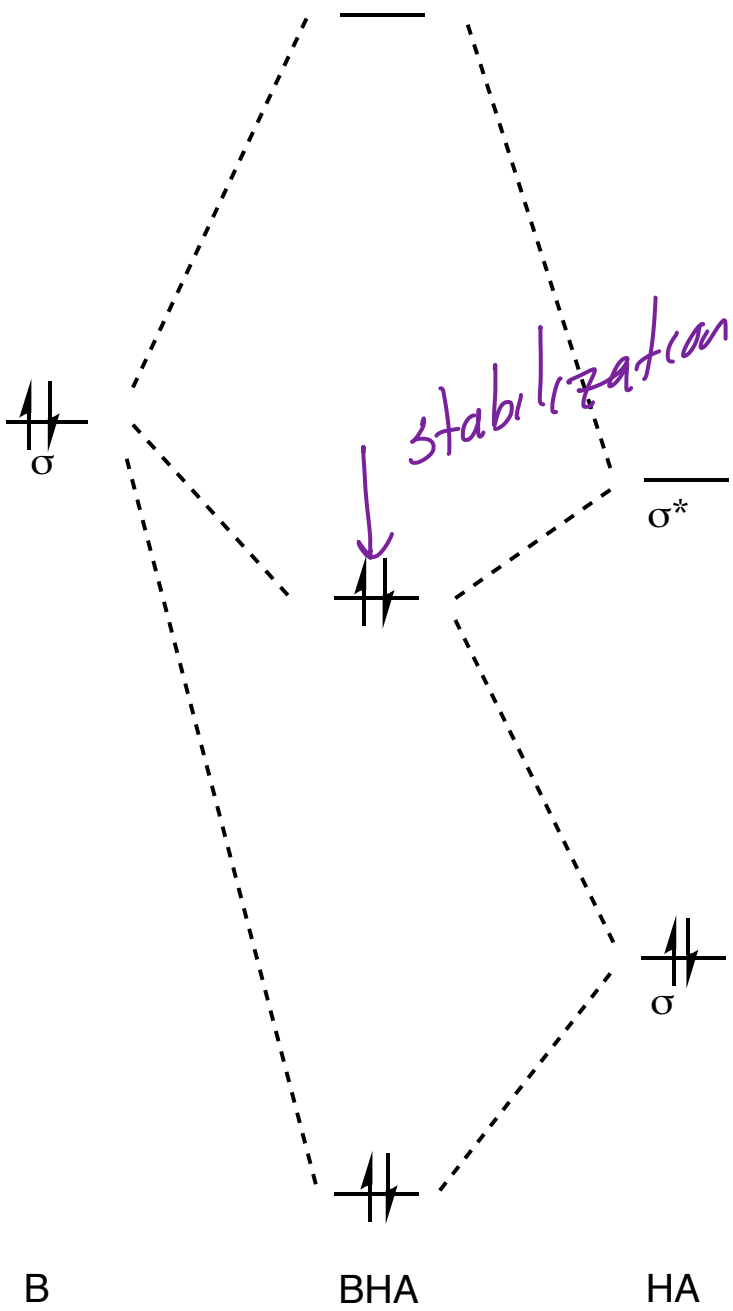
H-C

The MO's in the green boxes represent the HOMO and LUMO of a base (B) and an acid (HA).

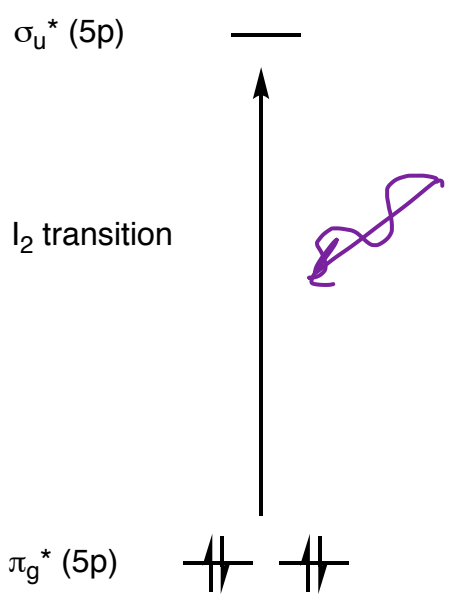
The MO's in the blue boxes represent the molecules after the H+ has been transferred from the acid (HA) to the base (B) to form their conjugate base (A-) and conjugate acid (BH+).



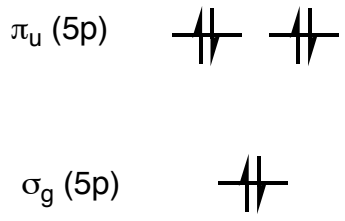
When LUMO of H-bond donor & HOMO of H-bond acceptor have a good energy match, a bonding antibonding pair can form, and the e⁻'s will stabilize



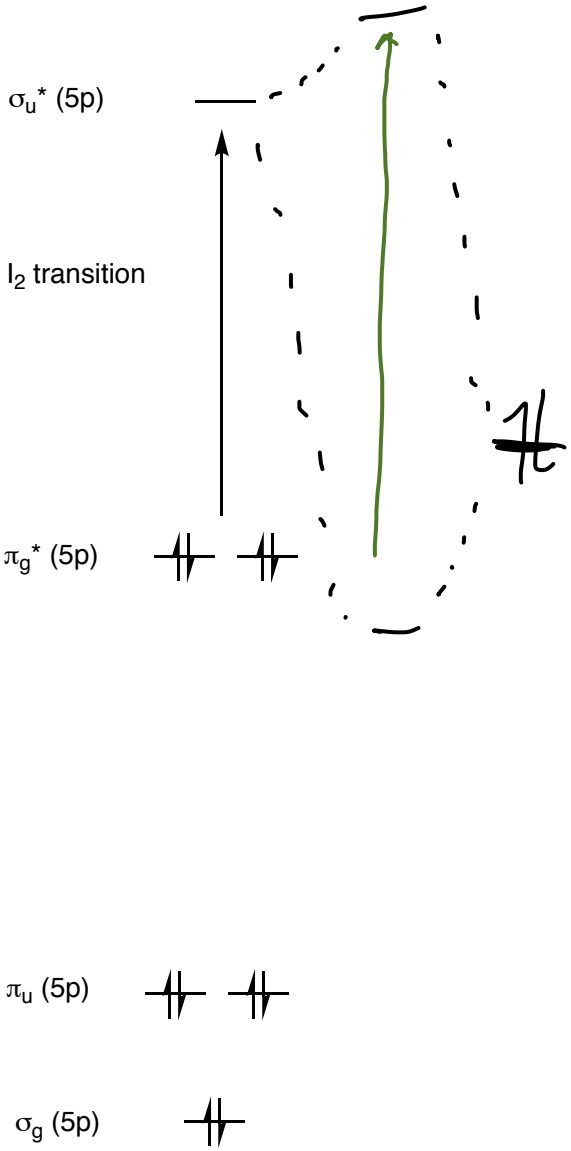
due to H bond interaction

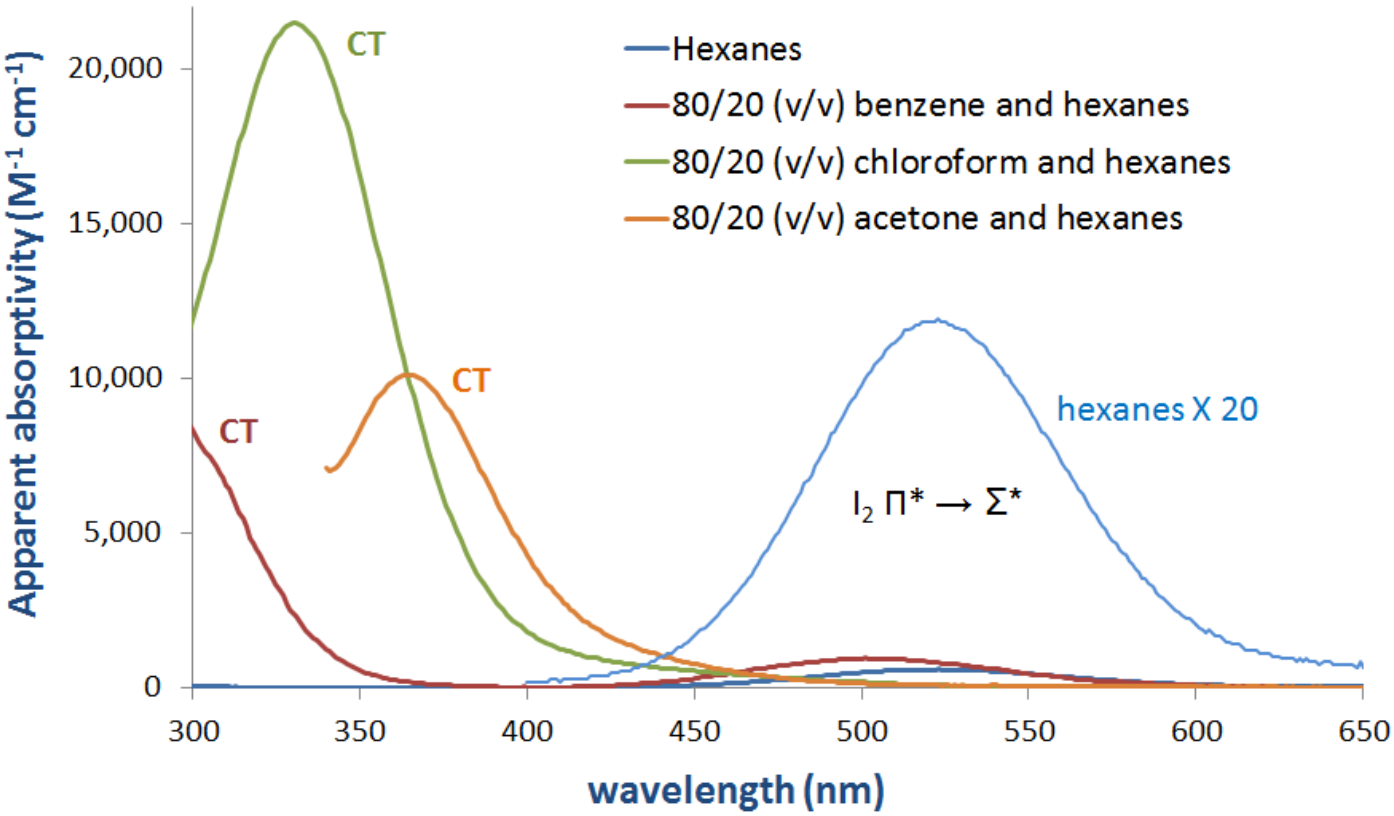


I_2 absorbs photons, but in different solvents the color is different



Frontier Orbital Model: Iodine





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