

Arrhenius Theory
Svante Arrhenius (Swedish)
1880s

Acid - a substance that produces $\text{H}^+(\text{aq})$ in solution

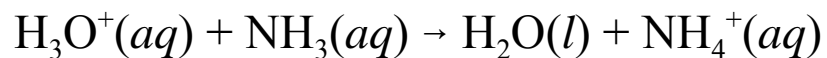
Base - a substance that produces $\text{OH}^-(\text{aq})$ in solution

Brønsted-Lowry Theory
Johannes Brønsted (Danish)
Thomas Lowry (English)
1923

Acid - a substance that donates protons (H^+)

Base - a substance that accepts protons (H^+)

Proton Transfer Reaction

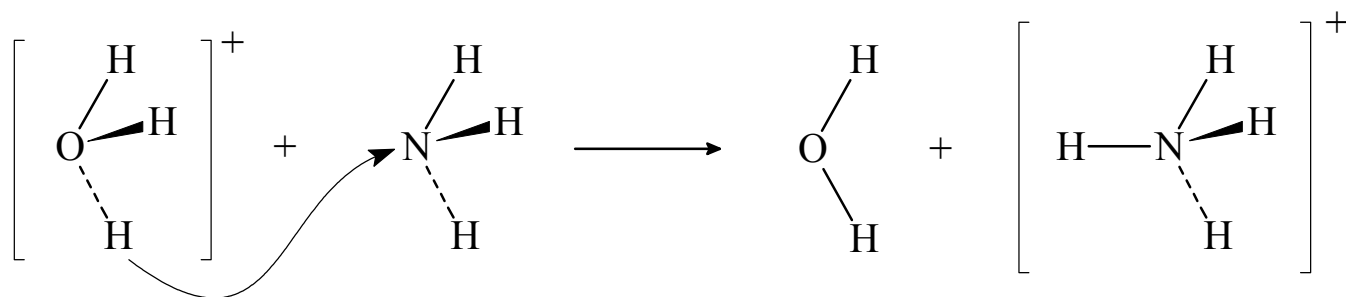


hydronium ion

ammonia

water

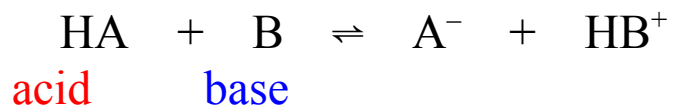
ammonium ion



proton donor
= acid

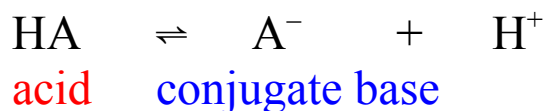
proton acceptor
= base

☞ In general terms, all acid-base reactions fit the general pattern

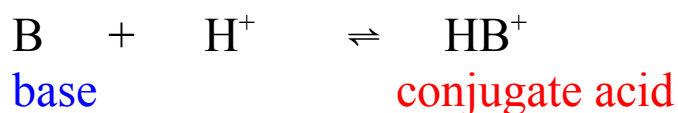


Conjugate Acid-Base Pairs

- ☞ When an acid, HA, loses a proton it becomes its **conjugate base**, A^- , a species capable of accepting a proton in the reverse reaction.

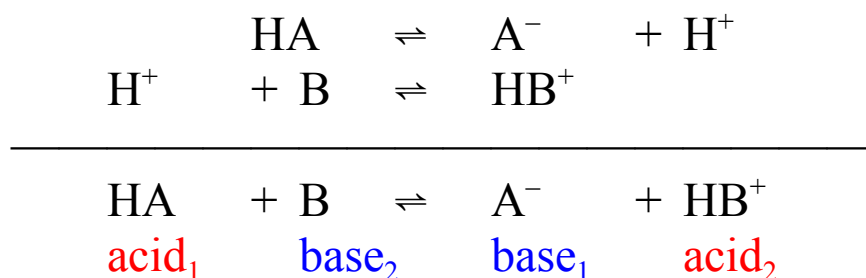


- ☞ When a base, B, gains a proton, it becomes its **conjugate acid**, BH^+ , a species capable of donating a proton in the reverse reaction.



Acid-Base Reactions

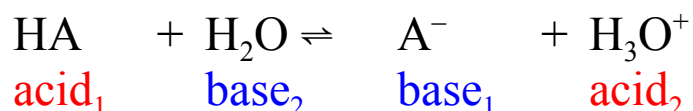
☞ We can analyze Brønsted-Lowry type proton transfer reactions in terms of conjugate acid-base pairs. The generic reaction between HA and B can be viewed as



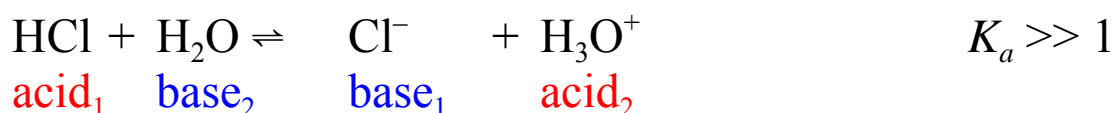
- Species with the same subscripts are conjugate acid-base pairs.

Acid Hydrolysis and the Role of Solvent Water

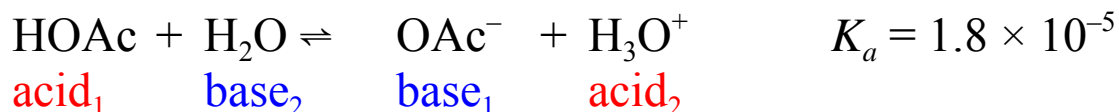
- ☞ When any Brønsted-Lowry acid HA is placed in water it undergoes *hydrolysis* to produce hydronium ion, H_3O^+ , and the conjugate base, A^- , according to the equilibrium:



- The acid HA transfers a proton to H_2O , acting as a base, thereby forming the conjugates A^- and H_3O^+ , respectively.
- The position of this equilibrium indicates the strength of the acid.



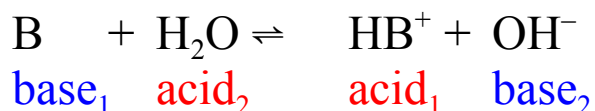
Equilibrium lies right. \Rightarrow HCl is a strong acid.



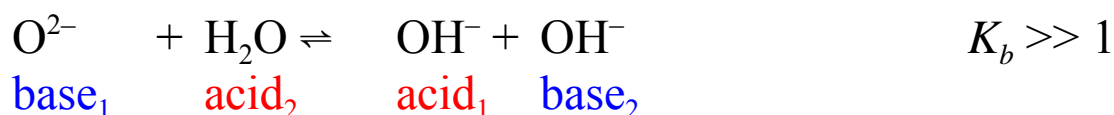
Equilibrium lies left. \Rightarrow HOAc is a weak acid.

Base Hydrolysis and the Role of Solvent Water

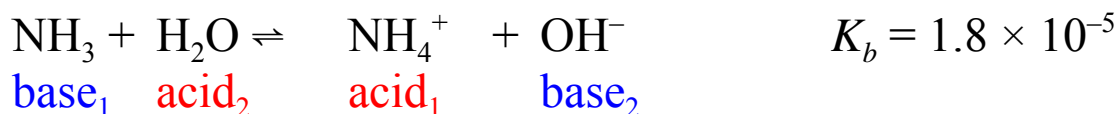
- ☞ Hydrolysis of a base also involves water as an active participant, functioning as an acid.



- H_2O acts as the acid, transferring a proton to B, thereby forming the conjugates OH^- and HB^+ , respectively.
- The position of this equilibrium indicates the strength of the base.



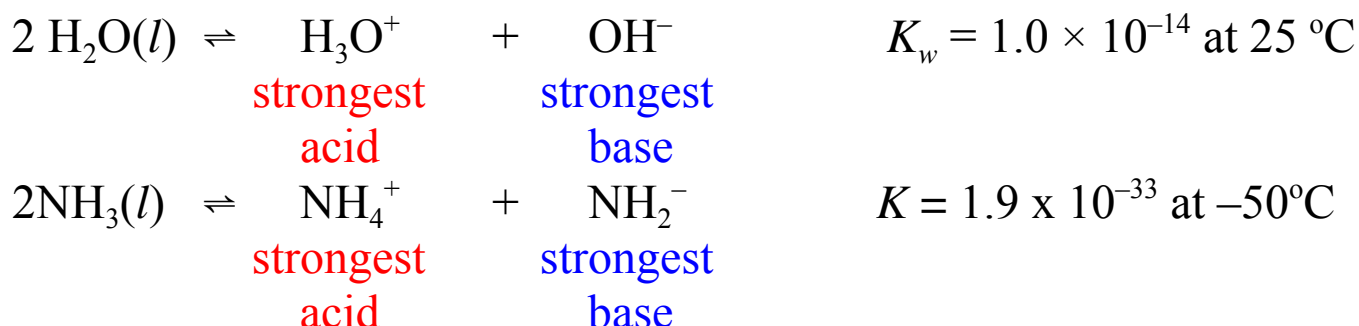
Equilibrium lies right. $\Rightarrow \text{O}^{2-}$ is a strong base.



Equilibrium lies left. $\Rightarrow \text{NH}_3$ is a weak base.

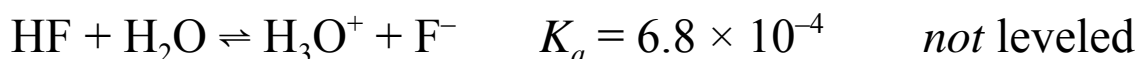
Strongest Acid and Base

☞ In Brønsted-Lowry theory, the strongest acid and strongest base that can exist in a protonic solvent is defined by the solvent's autoprotolysis reaction.



☞ Any stronger *molecular* acid or base is **leveled** to the strength of the strongest acid or base for the solvent.

- Any molecular acid or base that is completely dissociated in its solvent is a strong acid or base that has been leveled.
- Any acid or base that is only partially dissociated in its solvent is a weak acid or base and is *not* leveled.

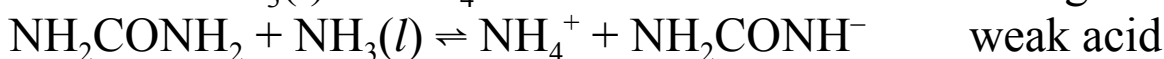
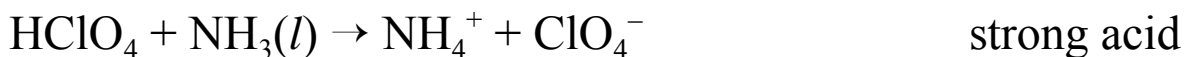


☞ An ionic compound whose anion is the strongest base of the solvent is not leveled, but merely dissociated.



Brønsted-Lowry Theory of $\text{NH}_3(l)$

☞ In $\text{NH}_3(l)$, any substance that reacts with $\text{NH}_3(l)$ to produce NH_4^+ in solution is an acid.



- HClO_4 and HOAc are leveled to the strength of NH_4^+ in $\text{NH}_3(l)$.
- NH_2CONH_2 is *not* leveled.

☞ In $\text{NH}_3(l)$, any substance that reacts with $\text{NH}_3(l)$ to produce NH_2^- in solution is a base.



- N^{3-} is leveled to the strength of NH_2^- in $\text{NH}_3(l)$

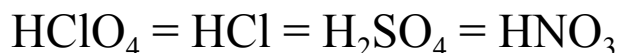
☞ Any ionic salt that contains NH_4^+ or NH_2^- is an acid or base in $\text{NH}_3(l)$.



- Dissociation of these ionic salts in $\text{NH}_3(l)$ is not leveling.

Acid Strength in Non-aqueous Solvents

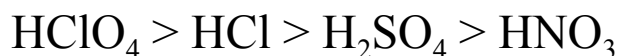
- In water, the well-known strong acids are equally strong, because they are completely dissociated (leveled):



- Differences in acid strength can be discerned in non-aqueous media.
- In glacial acetic acid, $\text{HOAc}(l)$, these acids are not completely dissociated, being weaker than H_2OAc^+ :



- In $\text{HOAc}(l)$ the acid strengths are in the following order:



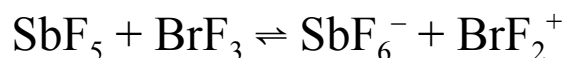
Solvent System Concept

- The solvent system concept of acid-base character can be applied to aprotic solvents that have significant autodissociation.
- ☞ In the solvent system concept, an acid is a substance that produces the cationic species of the autodissociation, and the base is a substance that produces the anionic species of the autodissociation.

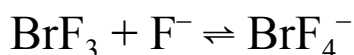
Example: Solvent system $\text{BrF}_3(l)$, m.p. = 9 °C, b.p. = 126 °C



Acidic solution: SbF_5 in BrF_3



Basic solution: F^- in BrF_3



- ☞ Solvent system concept and the corollary leveling effect cannot be applied to non-dissociating solvents.
- For example, strengths of acids in hydrocarbon solvents depend mainly on the reactivities of the solute species, and little on the solvent itself.

Lewis Acid-Base Theory

G. N. Lewis - 1923

Lewis acid - an electron-pair acceptor

Lewis base - an electron-pair donor

- ✓ Lewis acids are *electrophiles*.
- ✓ Lewis bases are *nucleophiles*.
- ✓ The product of a Lewis acid-base reaction is often called an *adduct*.

Comparison of Theories

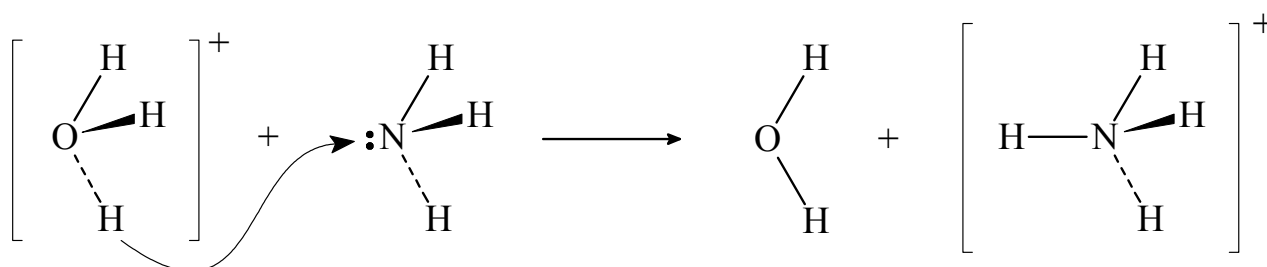
- ✓ Acids and bases in Arrhenius and Brønsted-Lowry theories are also acids and bases in Lewis theory:

hydronium ion

ammonia

water

ammonium ion

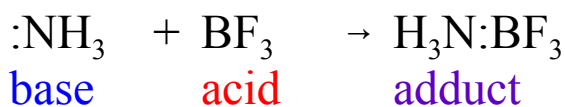


e-pair acceptor
= acid = electrophile

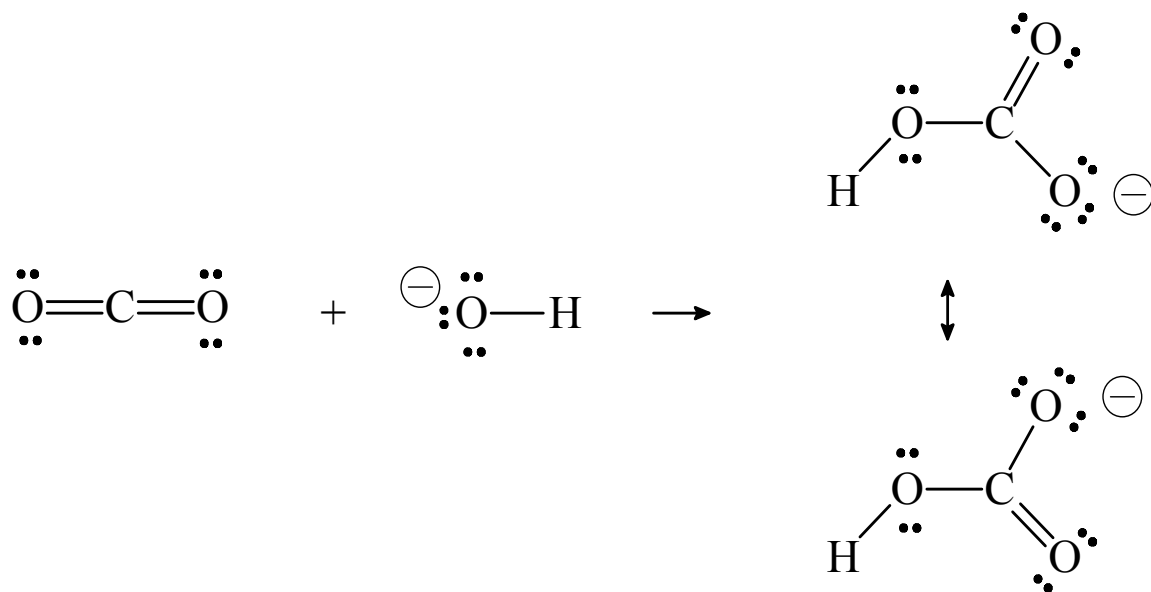
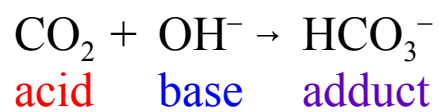
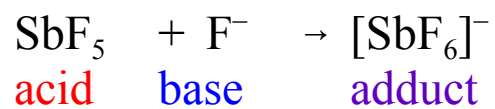
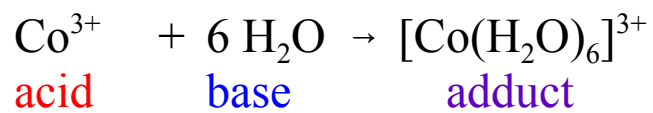
e-pair donor
= base = nucleophile

adduct

- ✓ Some acid-base reactions in Lewis theory are not seen as such by the other theories:

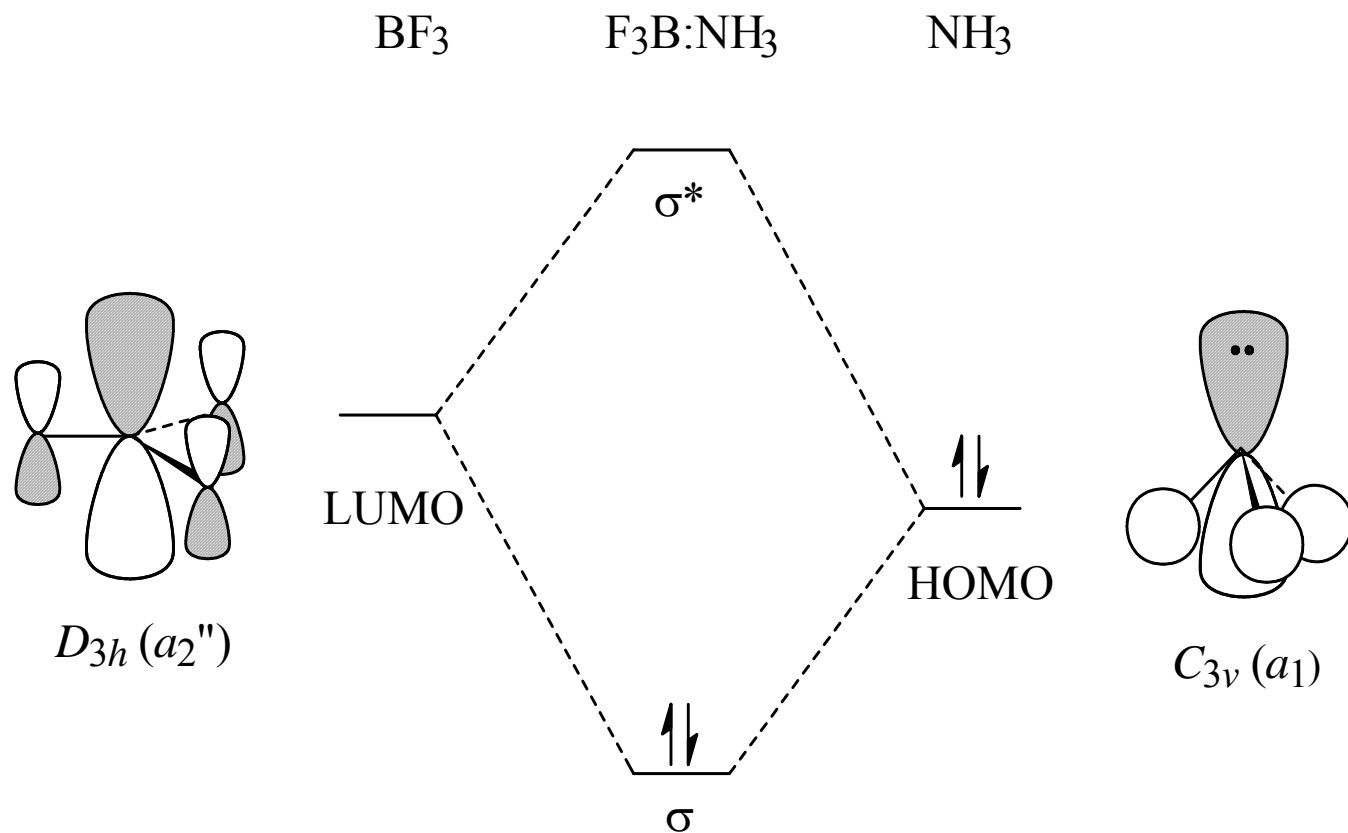


Examples of Lewis Acid-Base Reactions



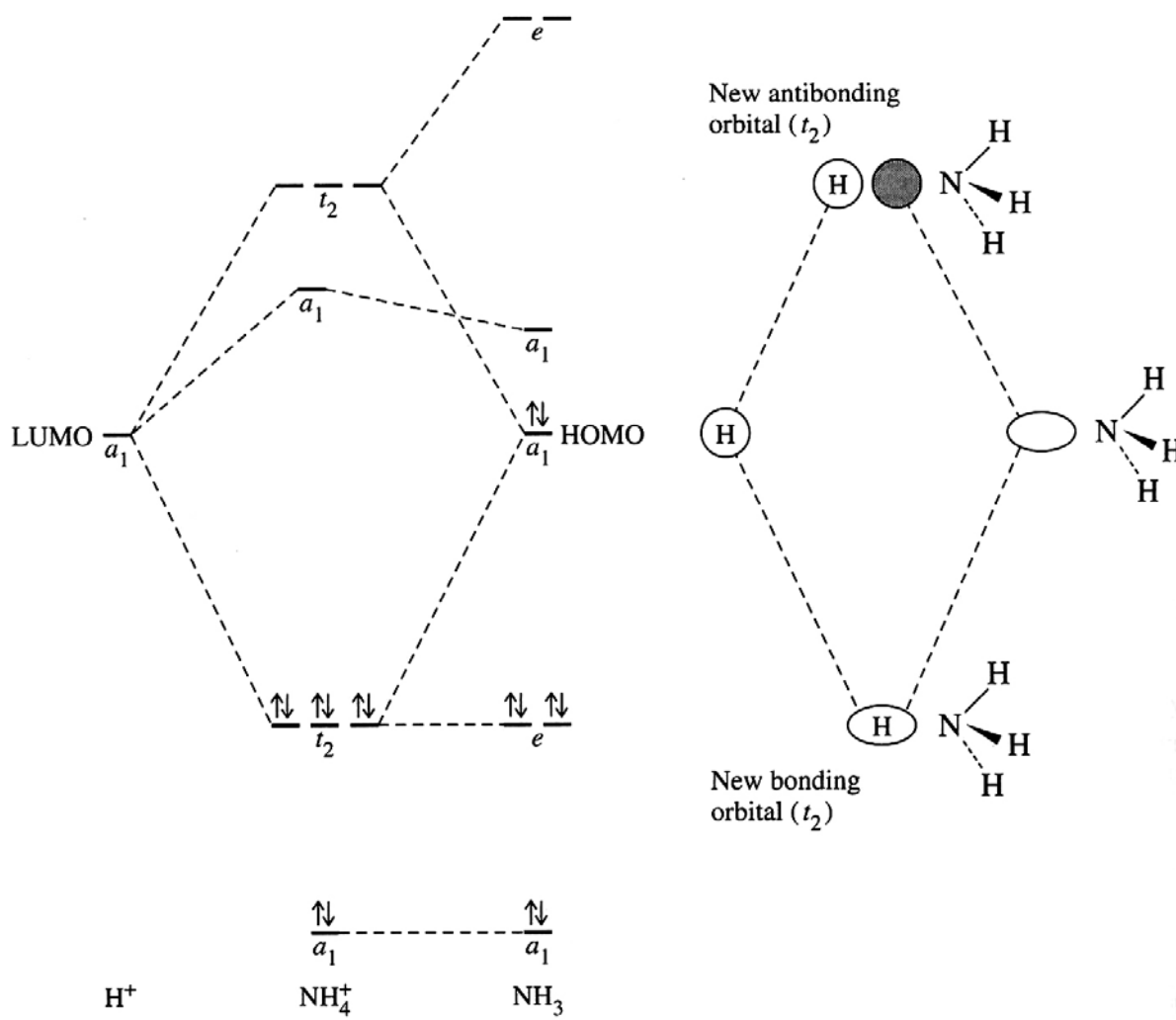
Frontier Orbital Concept

- ☞ The frontier orbital concept sees Lewis acid-base interactions in terms of the base donating an electron pair from its highest occupied molecular orbital (HOMO) into the acid's lowest unoccupied molecular orbital (LUMO).



- ☞ The base-acid HOMO-LUMO pairing creates new MOs for the adduct, which are its HOMO and LUMO.

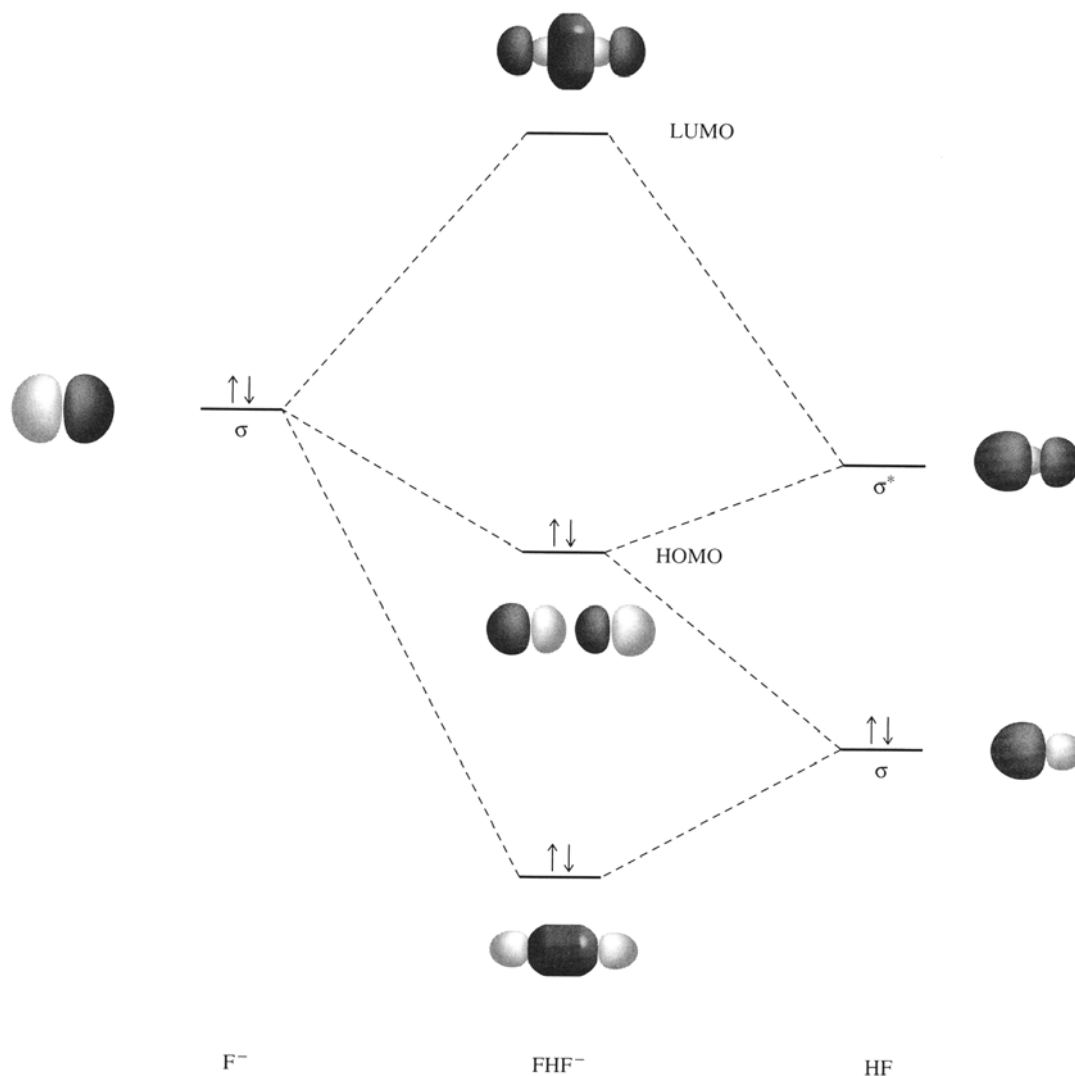
HOMO-LUMO Model of NH_4^+ Formation



- ☞ In frontier orbital terms, a Lewis base has an electron pair in a HOMO of suitable symmetry to interact with the LUMO of the acid.
- ☞ The more similar the energies of the HOMO and LUMO the stronger the interaction will be.

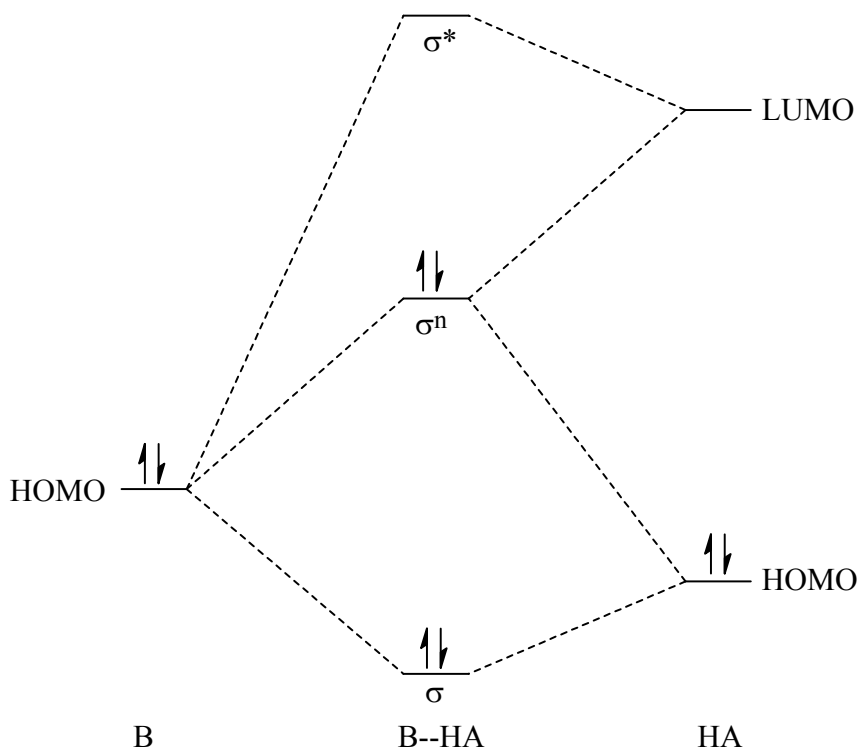
Hydrogen Bonding

- Hydrogen bonding can be understood in terms of frontier orbital concepts.
- For a very strong hydrogen bond, such as in FHF^- , the LUMO of the acid species (HF) has comparable energy to the HOMO of the base species (F^-), resulting in a complex with a lower overall energy.



Variations in B···H–A Interactions

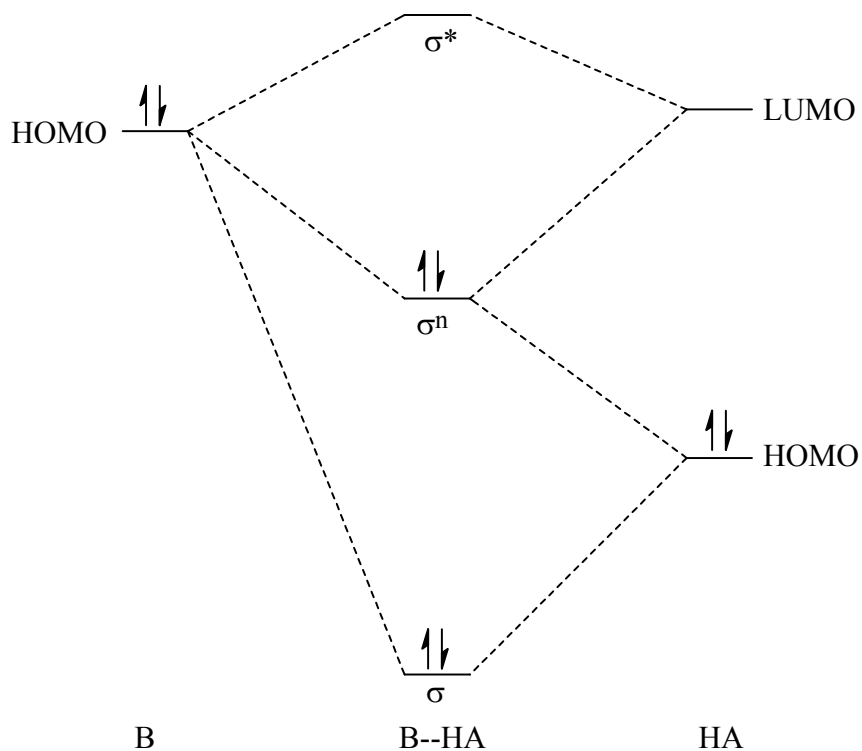
B HOMO \ll HA LUMO



- Bonding σ MO of B···H–A only slightly more stable than HA HOMO
 - Non-bonding σ^n MO of B···H–A much higher than B HOMO
- ☞ B···H–A energy higher (less stable) than separate B and HA energies, so no interaction. (Example: $\text{CH}_4 + \text{H}_2\text{O}$)

Variations in B...H-A Interactions

B HOMO \approx HA LUMO

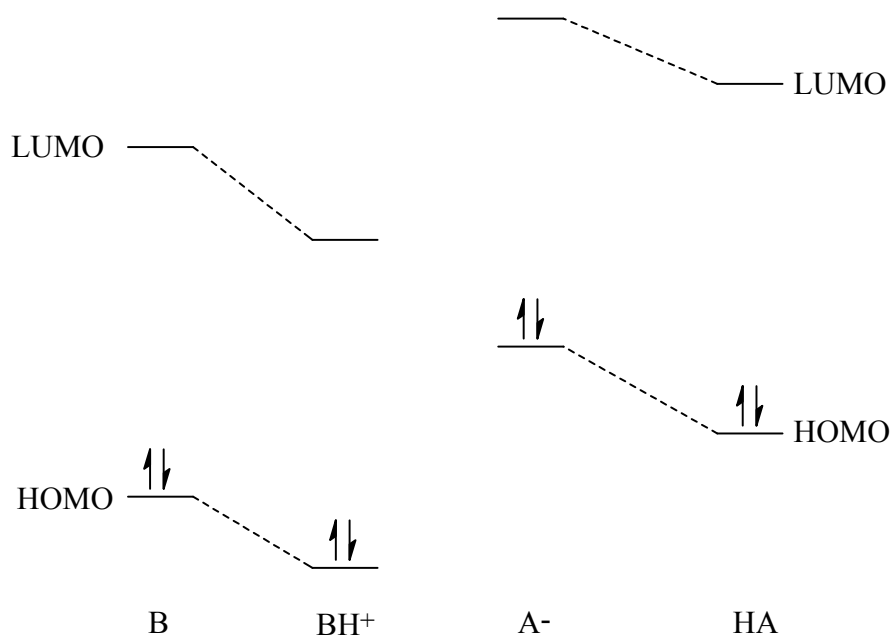


- Bonding σ MO of B...H-A much more stable than HA HOMO
 - Non-bonding σ^n MO of B...H-A much more stable than B HOMO
- ☞ B...H-A energy lower (more stable) than separate B and HA energies, so strong interaction. (Example: FHF⁻)

Variations in B···H–A Interactions

B HOMO \ll HA HOMO

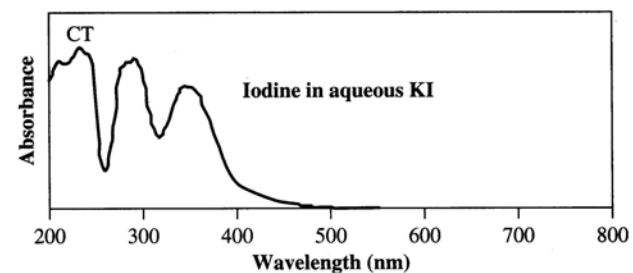
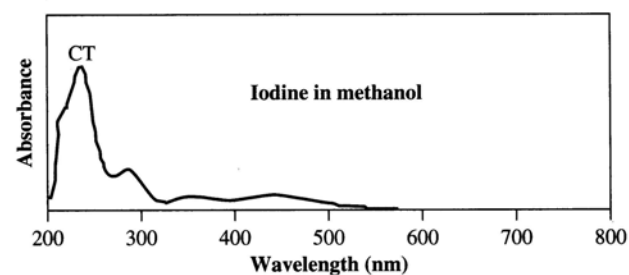
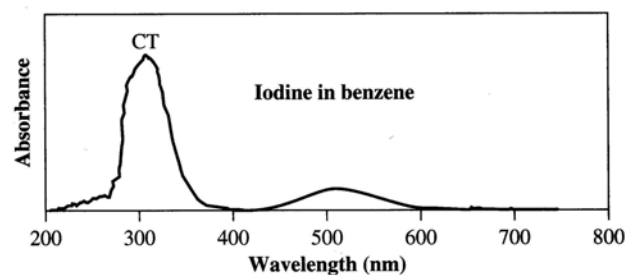
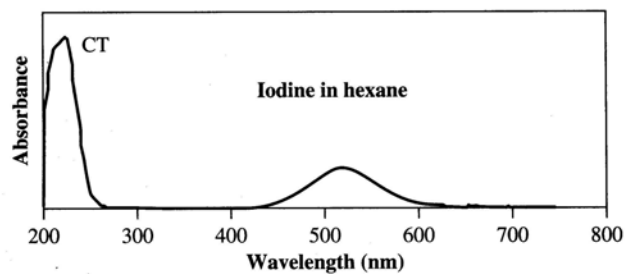
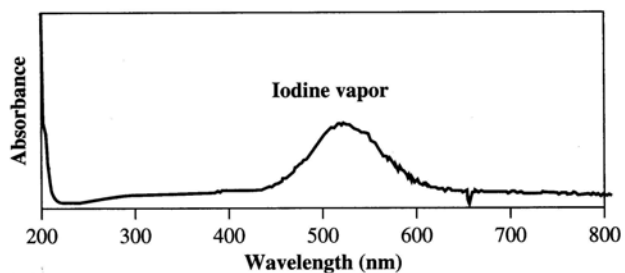
B LUMO \ll HA LUMO



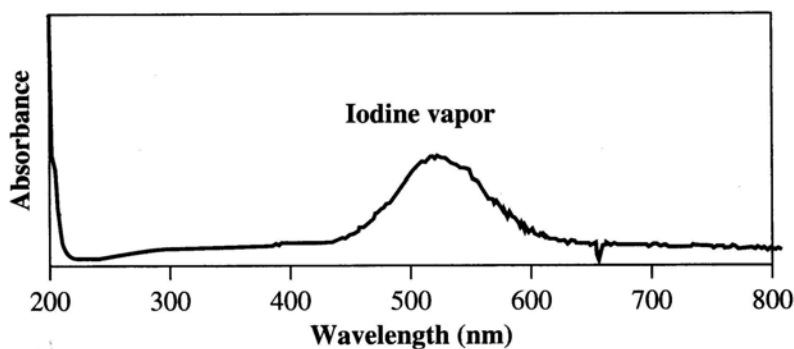
- Extreme mismatch of B HOMO and HA LUMO with B HOMO $<$ HA HOMO, so no MO formation

☞ Proton transfer from HA to B favored (e.g., $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$)

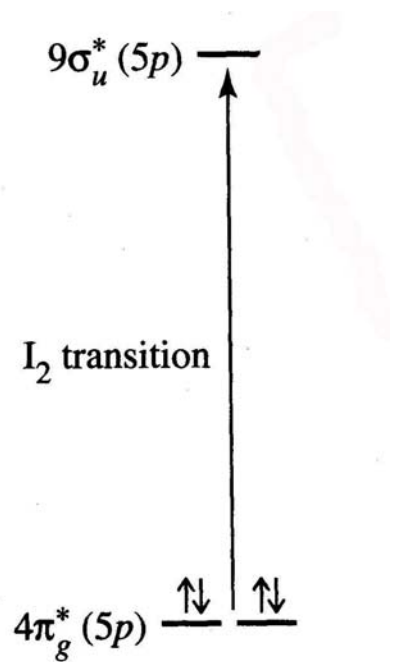
Visible and UV Absorption Spectra of $I_2(g)$ and $I_2(soln)$ in Donor Solvents



UV/Vis of $I_2(g)$

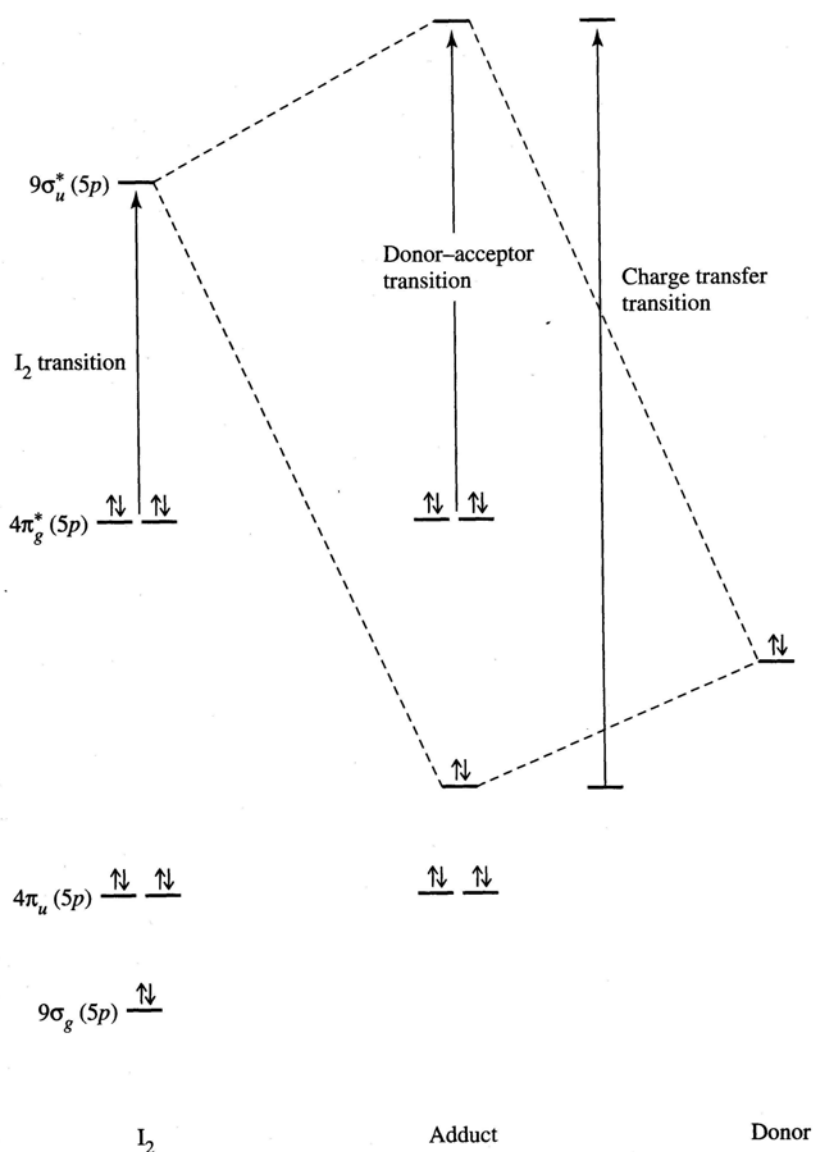


- The characteristic purple color of $I_2(g)$ is due to absorption at ~ 500 nm, due to promotion of electrons from the $4\pi_g^*$ MO (HOMO) to the $9\sigma_u^*$ MO (LUMO).



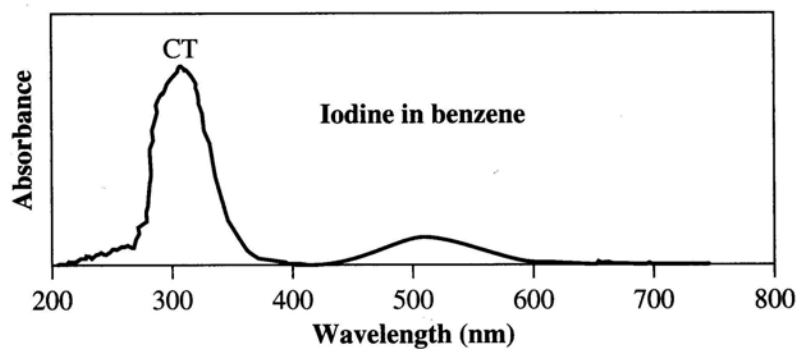
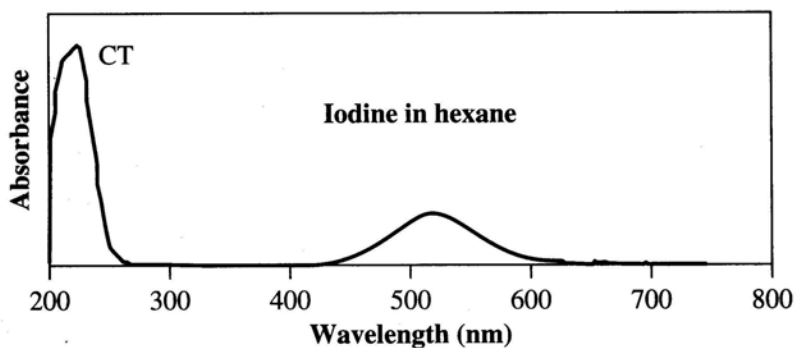
Visible and UV Absorption of I₂ in Donor Solvents

- Donor solvents form adducts with I₂ through interaction of the solvent's HOMO and iodine's LUMO ($9\sigma_u^*$), causing the adduct LUMO to rise and shifting the absorption to higher energy ("blue shift").
 - Donor-acceptor transition is $\pi_g^* \rightarrow \sigma_u^*$.
 - Charge transfer (CT) band results from adduct $\sigma_u \rightarrow \sigma_u^*$ promotions.



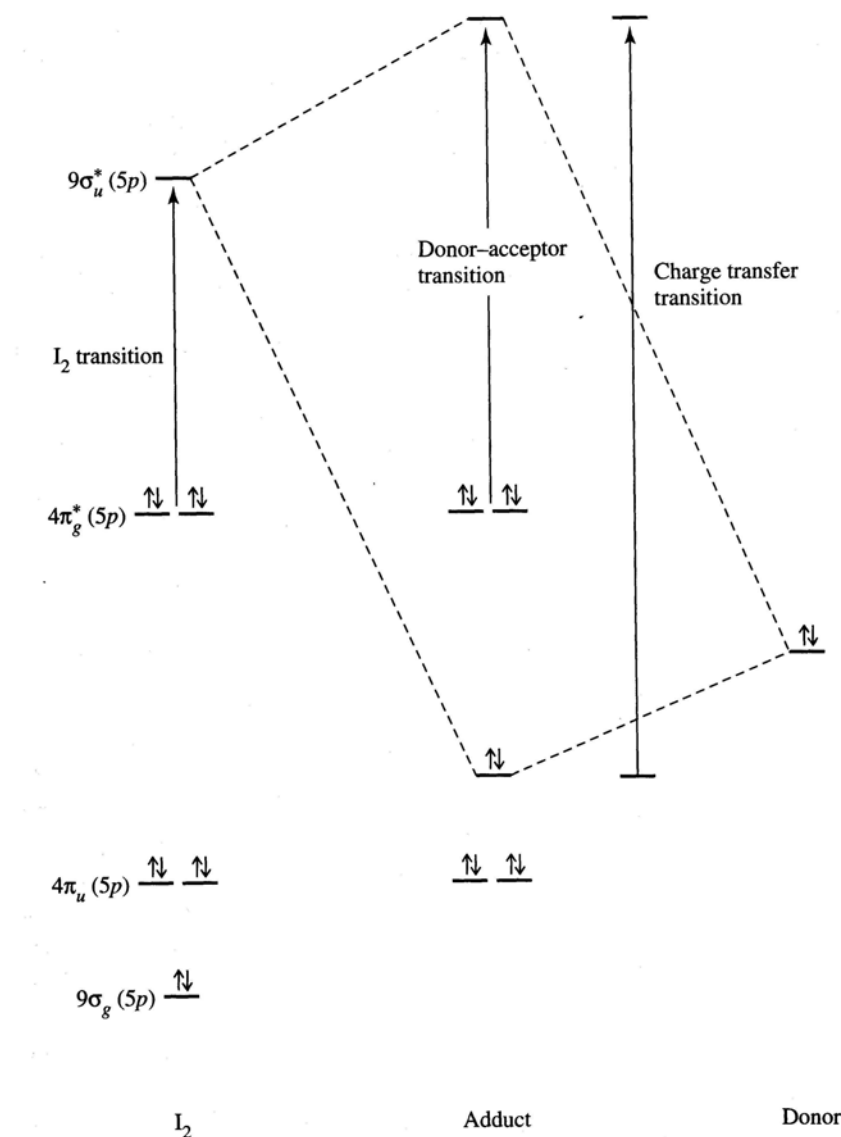
Non-donor Solvents

- Non-donor or weak donor solvents do not have effective HOMO-LUMO interactions, so visible absorption is similar to that of $I_2(g)$.
 - Solutions in hexane and benzene have purple color similar to $I_2(g)$



Strong Donor Solvents

- Strong donors have effective LUMO-HOMO interactions between I_2 (acid) and the solvent (base).
 - This causes greater energy separation between the adduct HOMO and LUMO, shifting the donor-acceptor visible absorption to higher energy (“blue shift”).



Uv/vis Spectra of I₂ in Donor Solvents

- Solution colors in strong donor solvents like methanol, water, or aqueous KI (where I₃⁻ forms) are yellow or brown.

