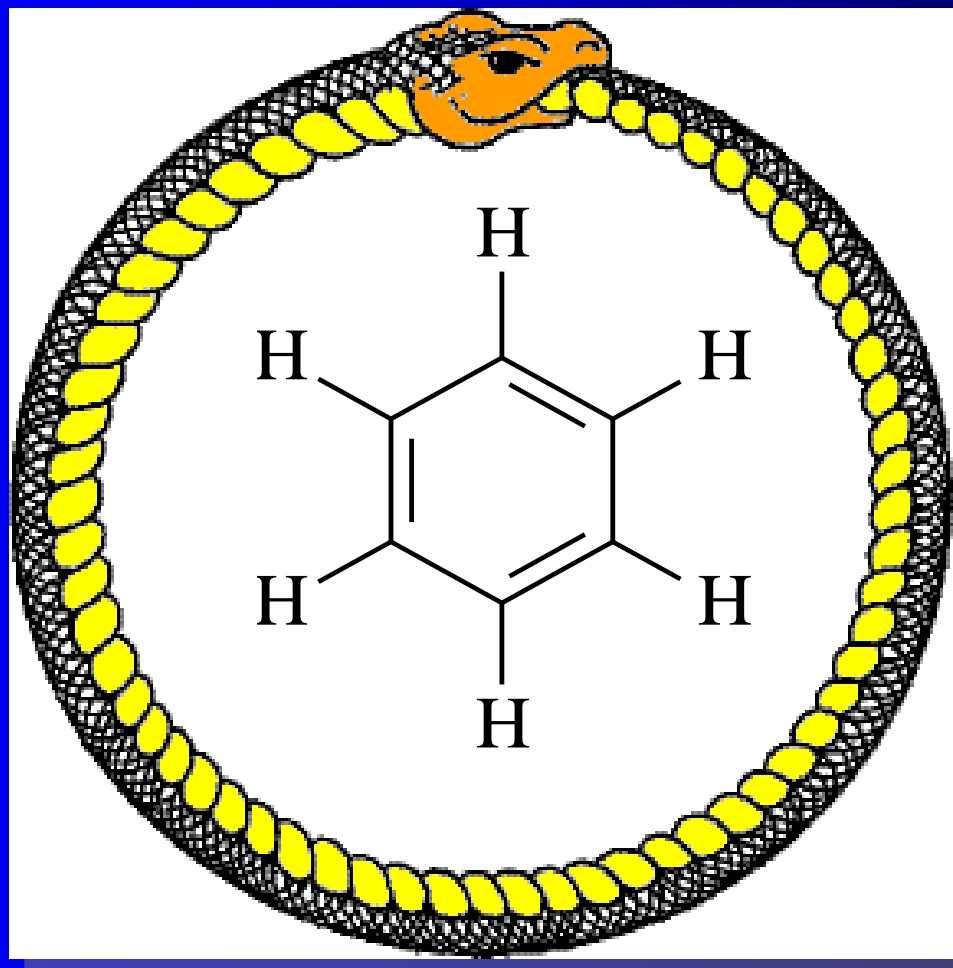


Lecture 8

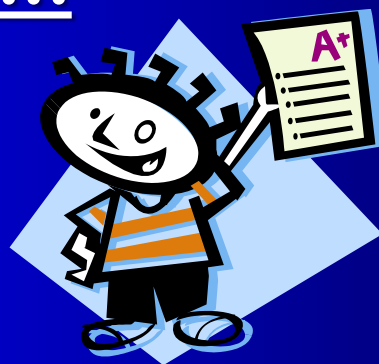
MOs and Benzene



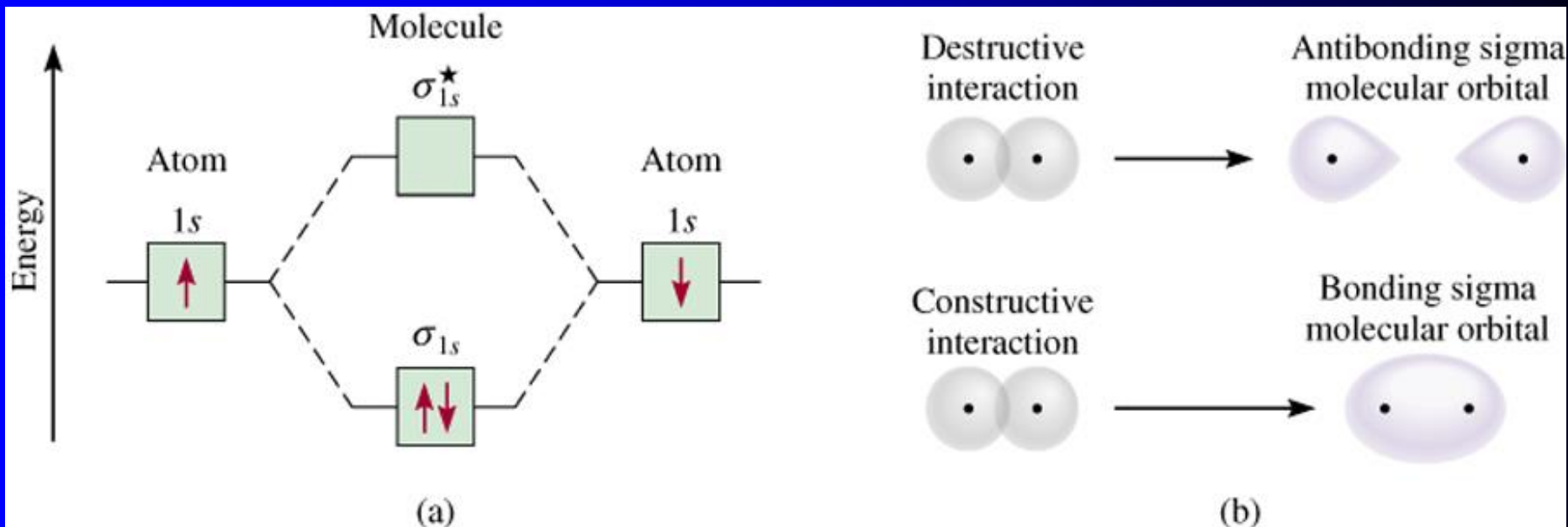
First Midterm Exam

- When: Wednesday, 2/17
- When: 7-9 PM (please do not be late)
- Where: WEL 3.502...enter from Inner Campus Drive
- What: Covers material through Thursday's lecture
- Remember: Homework problems!!
- Practice: Old exams will be posted on the web site
- Review Sessions: Mon Pharm 2.110, Tue Painter 4.42.
- Please...bring pencils, an eraser and a calculator only andDo a good job!!!

I will bother you! 😊



Bonding and antibonding molecular orbitals in hydrogen (H_2).

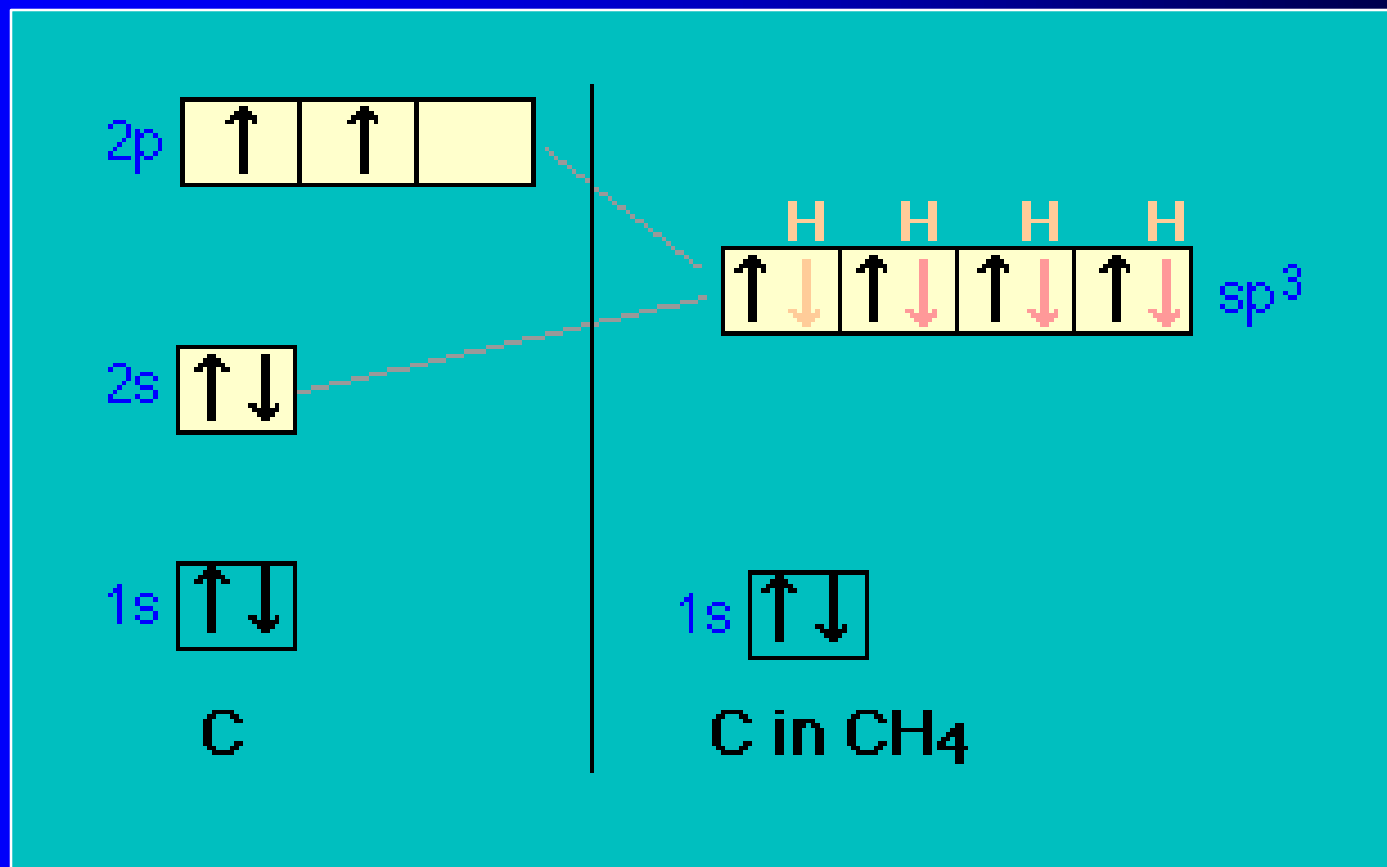


A **bonding molecular orbital** has lower energy and greater stability than the atomic orbitals from which it was formed.

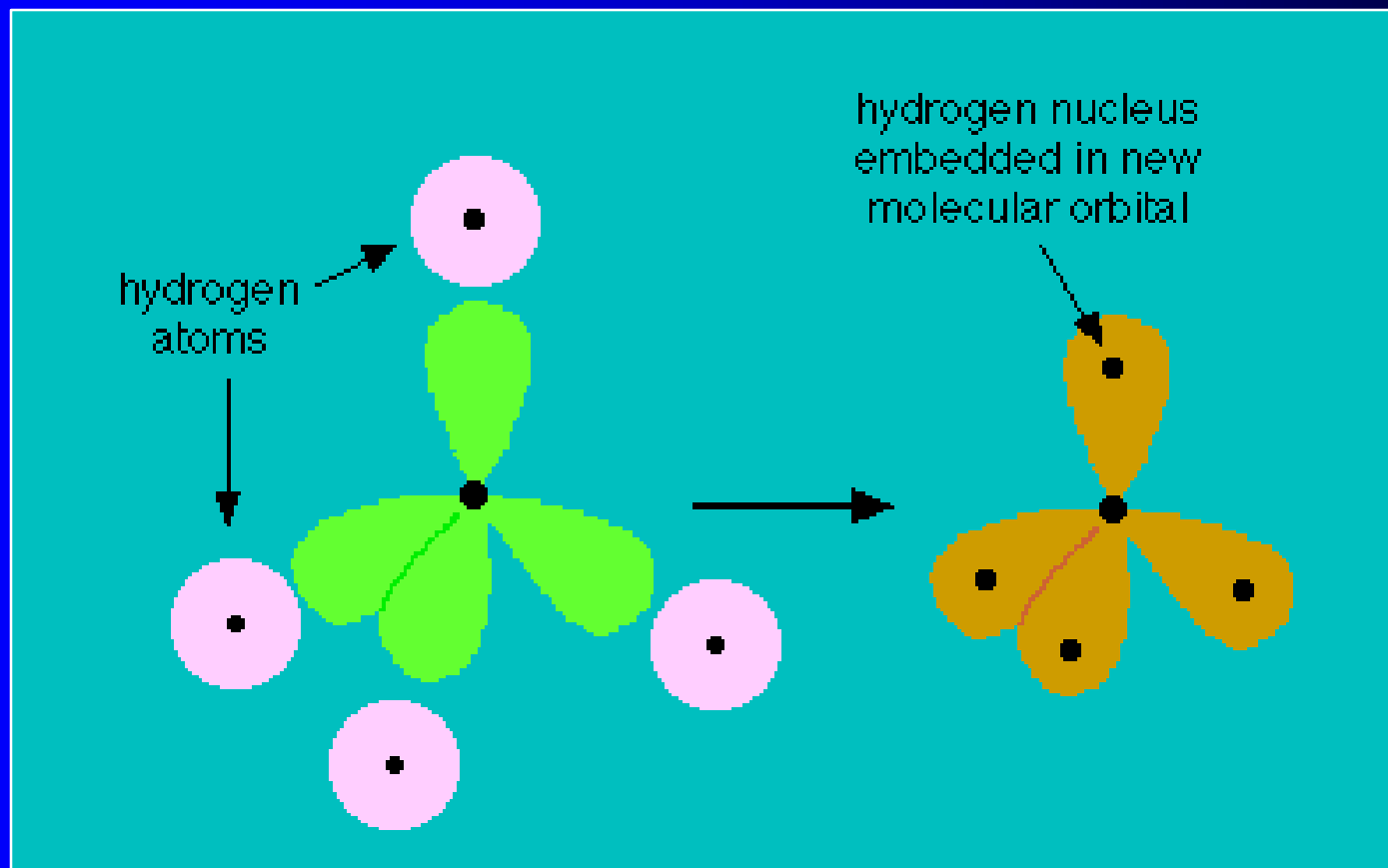
An **antibonding molecular orbital** has higher energy and lower stability than the atomic orbitals from which it was formed.



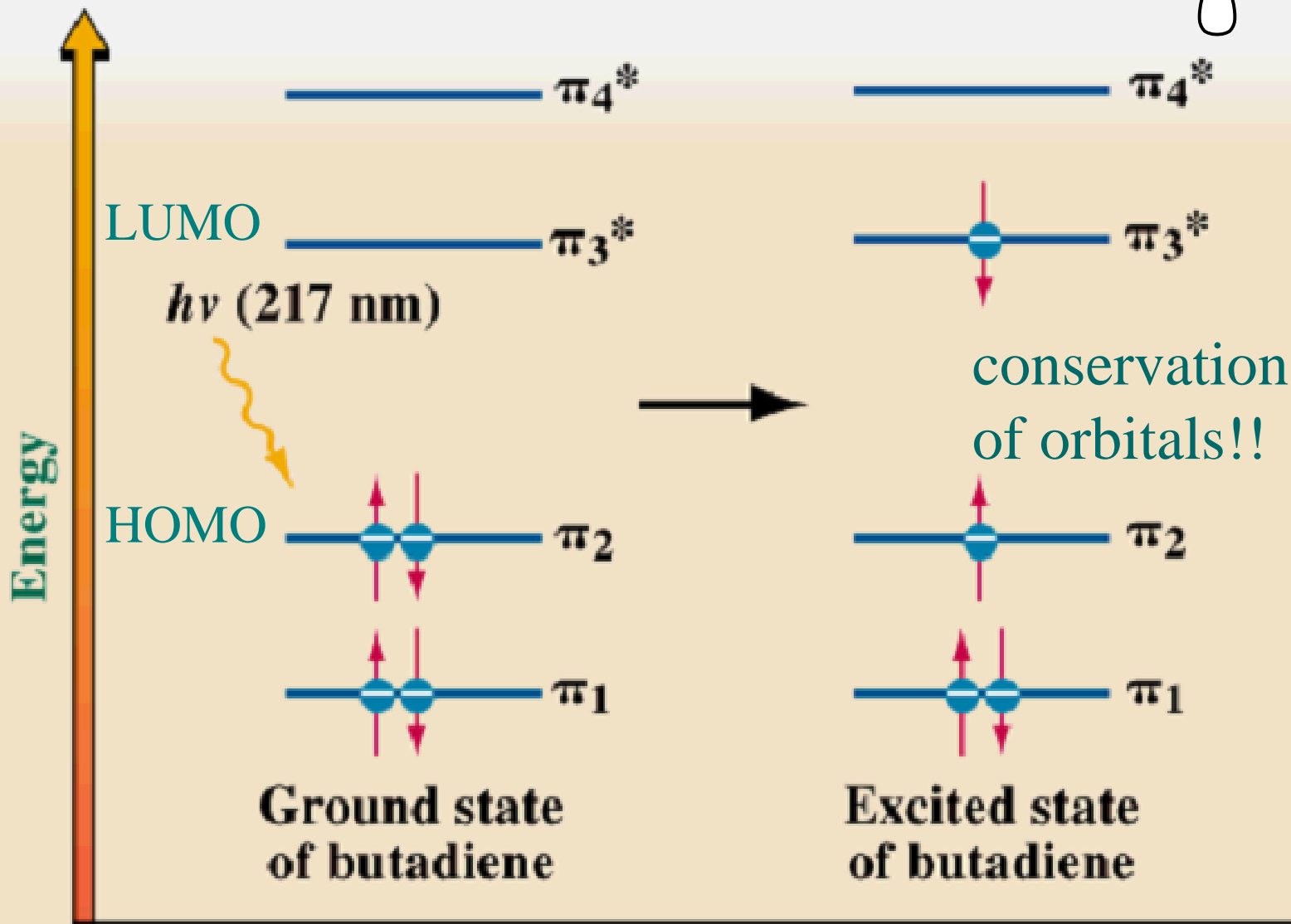
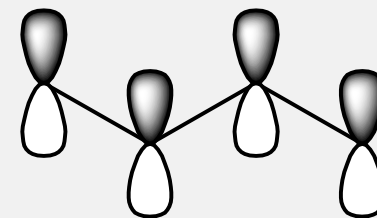
Hybridization of Atomic Orbitals



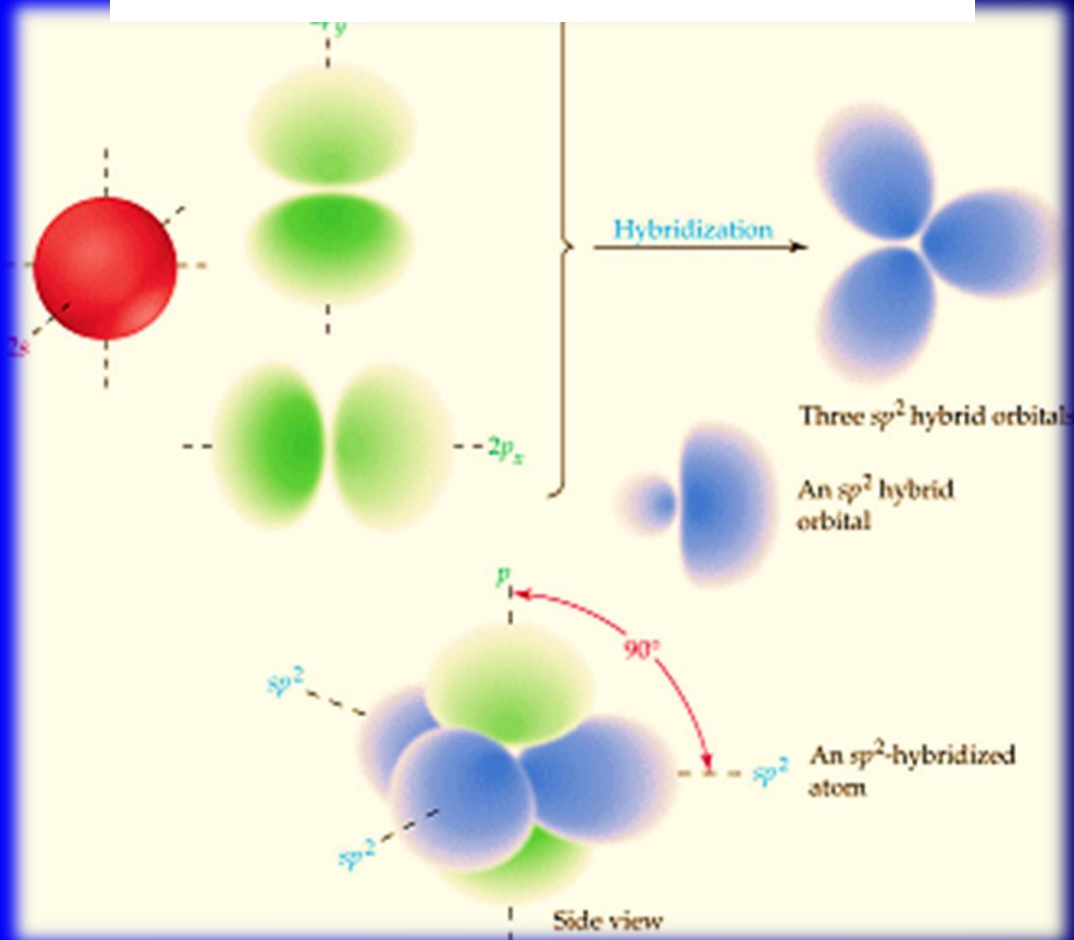
A “good” cartoon



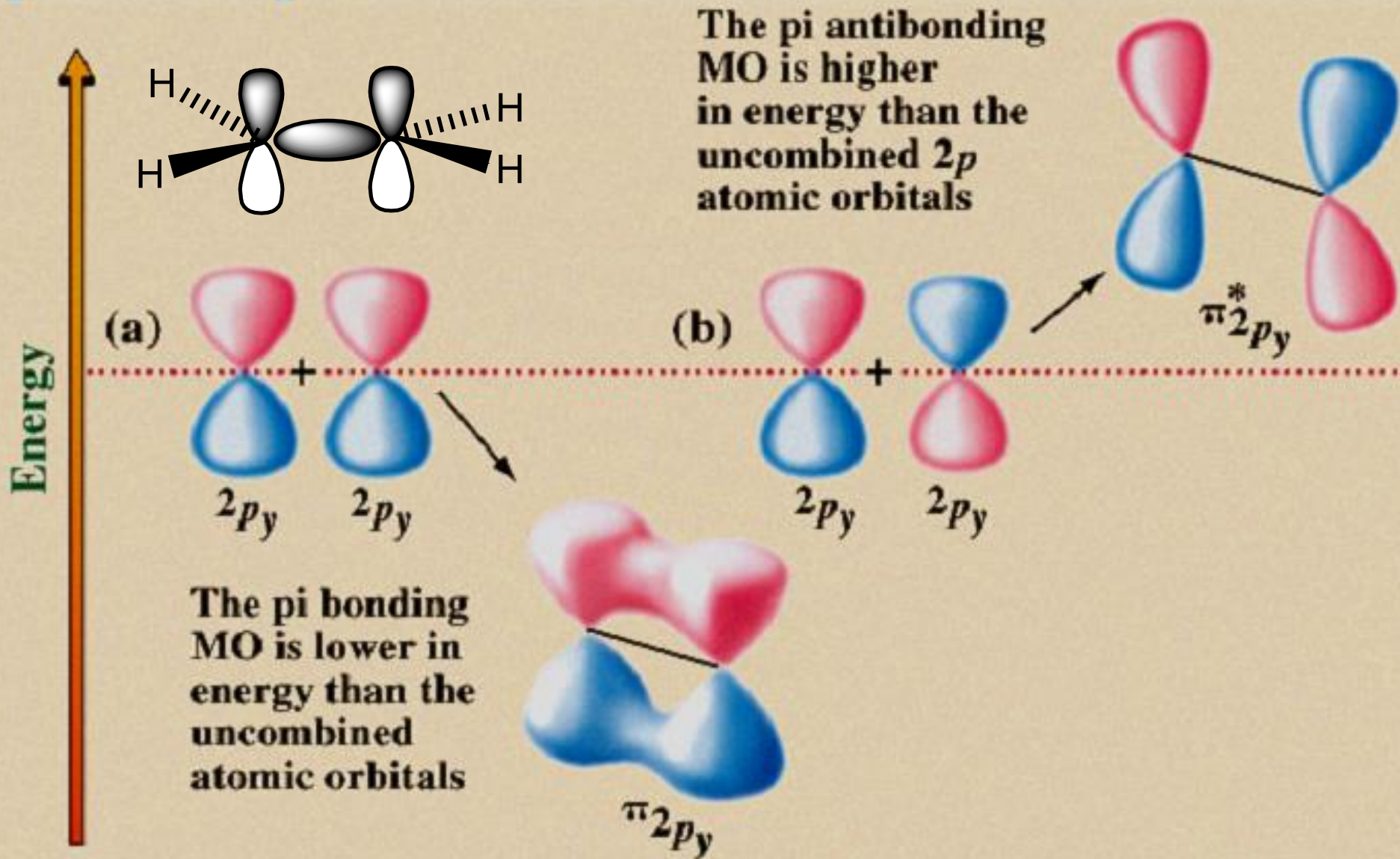
Electronic excitation 1,3-butadiene



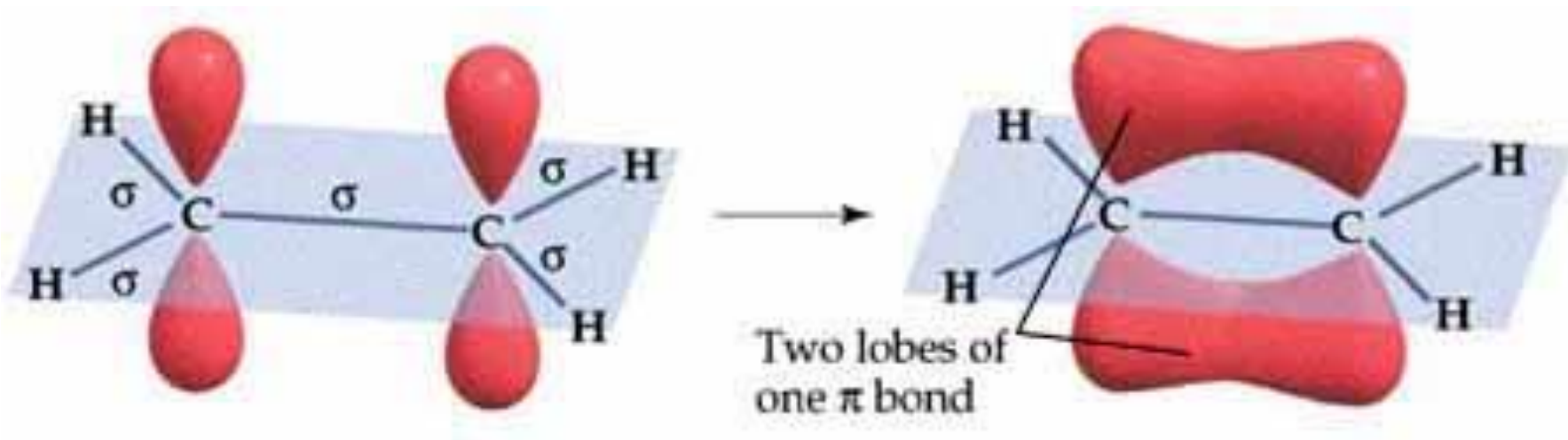
sp^2 hybrid orbitals



MOs formed by combination of parallel 2p orbitals

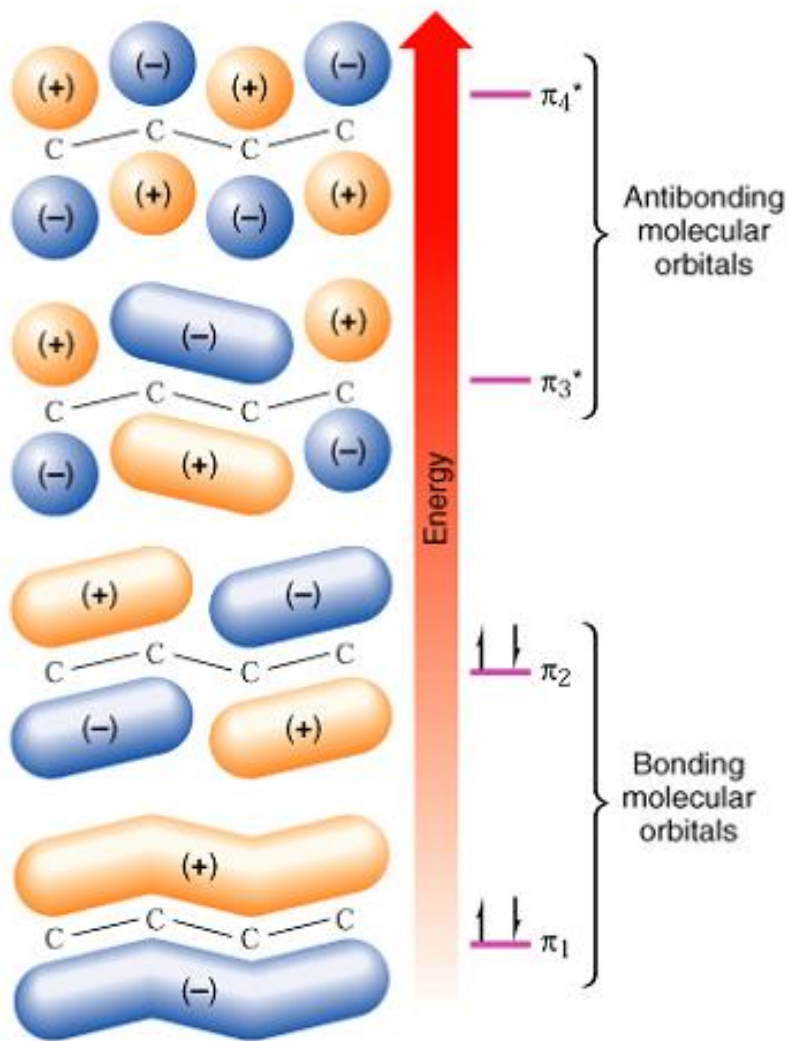
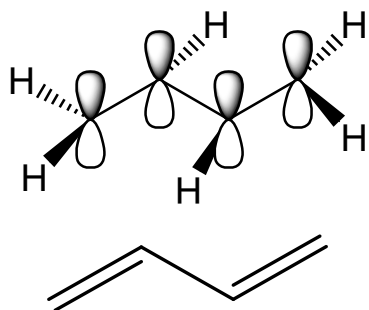


sp^2 hybrid orbitals and ethylene

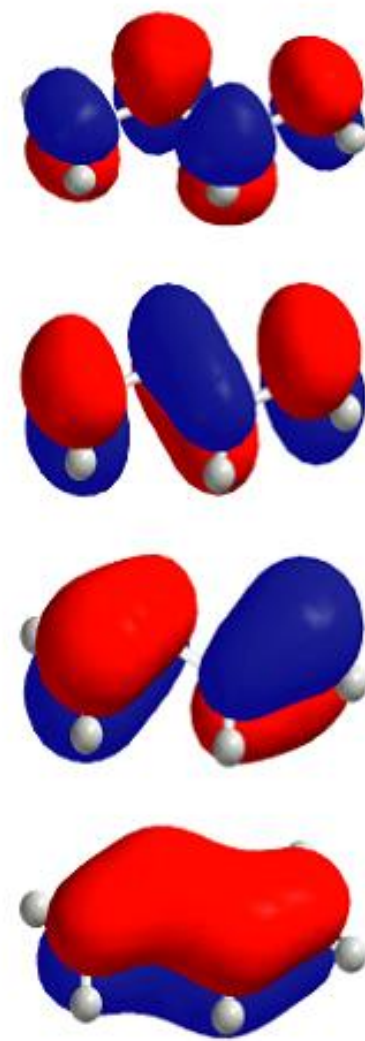


1,3-butadiene

Four isolated p orbitals
(with an electron in each)



Schematic molecular orbitals

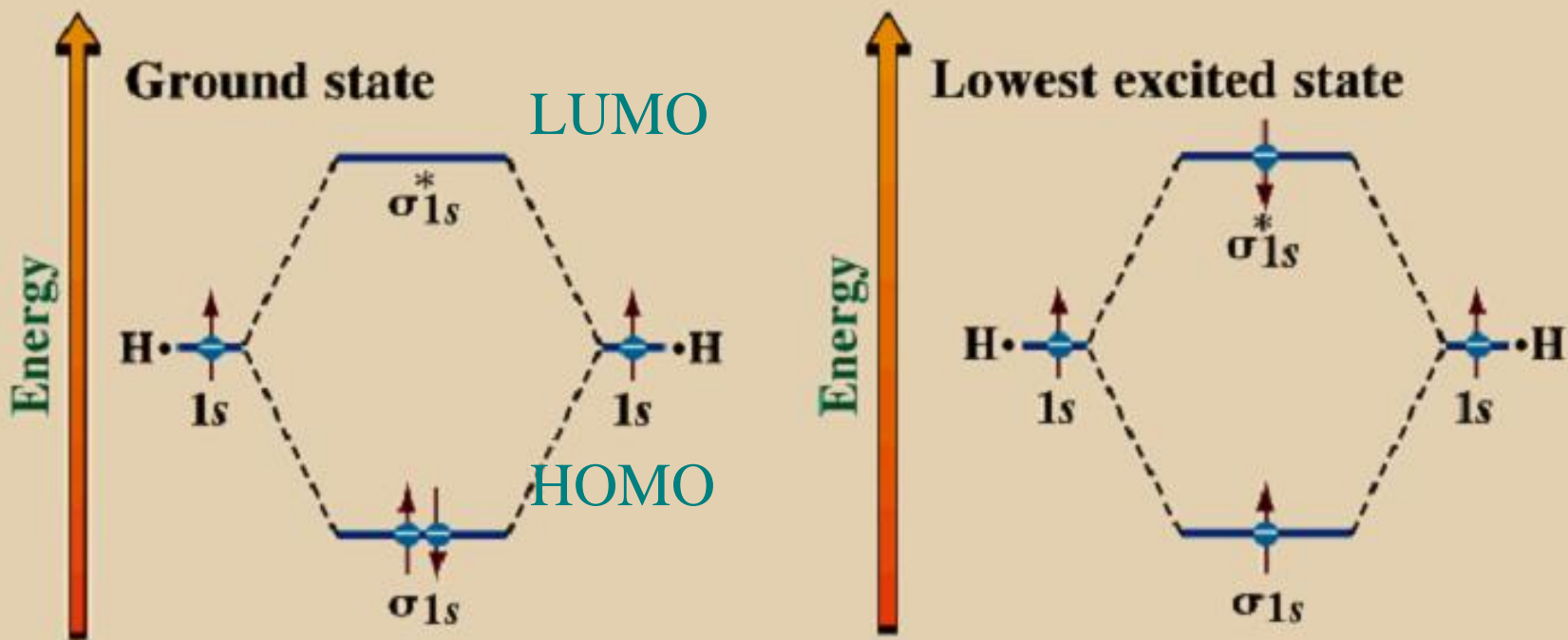


Calculated molecular orbitals

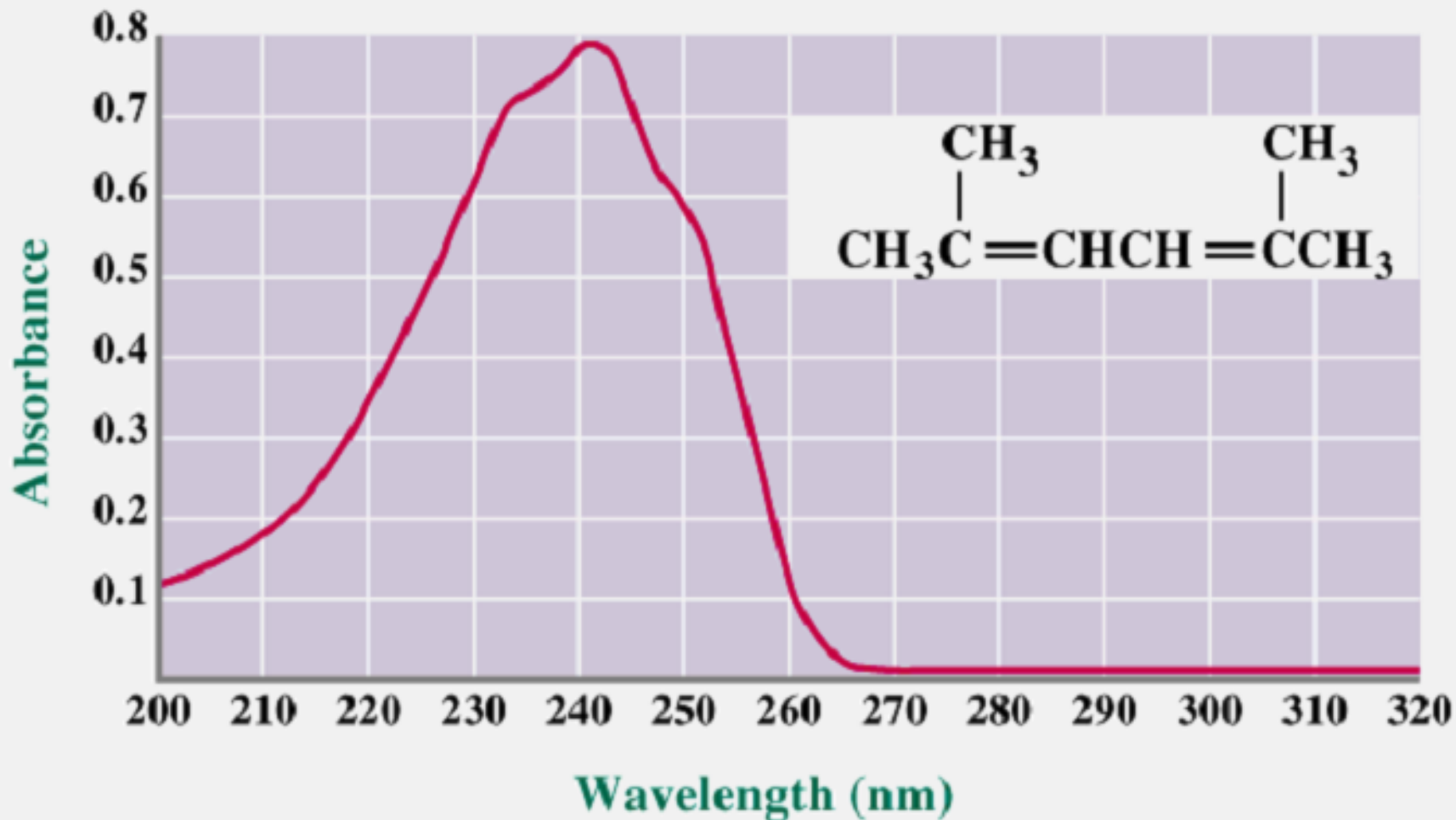


Origin of UV-Vis Absorbance MO Theory

MO energy diagram for the hydrogen molecule, H₂

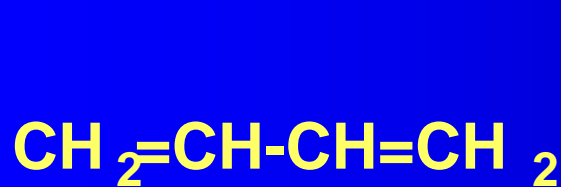


UV spectrum of 2,5-dimethyl-2,4-hexadiene

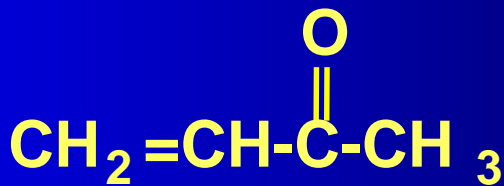


Electronic Transitions

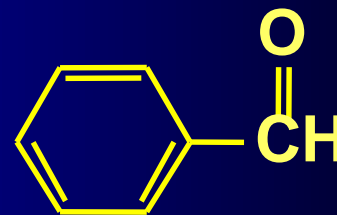
- Absorption of UV-vis radiation results in transition of electrons from a lower energy occupied MO to a higher energy unoccupied MO
- For example, π to π^* transitions in conjugated systems such as



1,3-Butadiene



3-Buten-2-one



Benzaldehyde

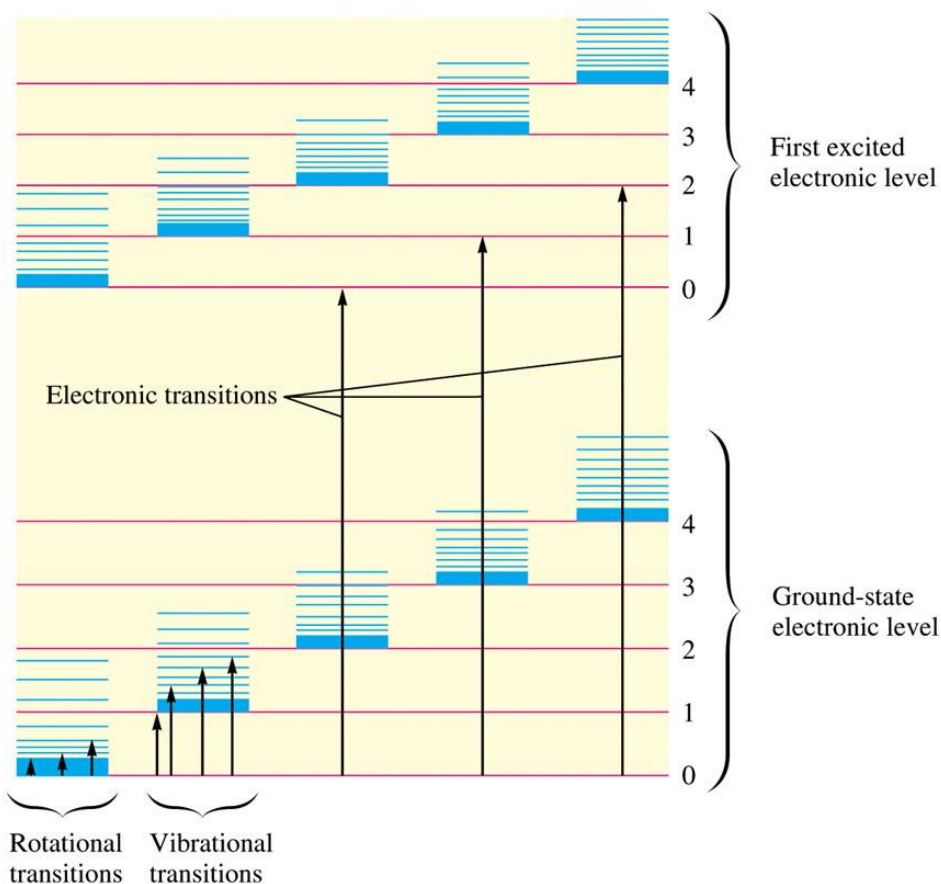


Electronic Transitions

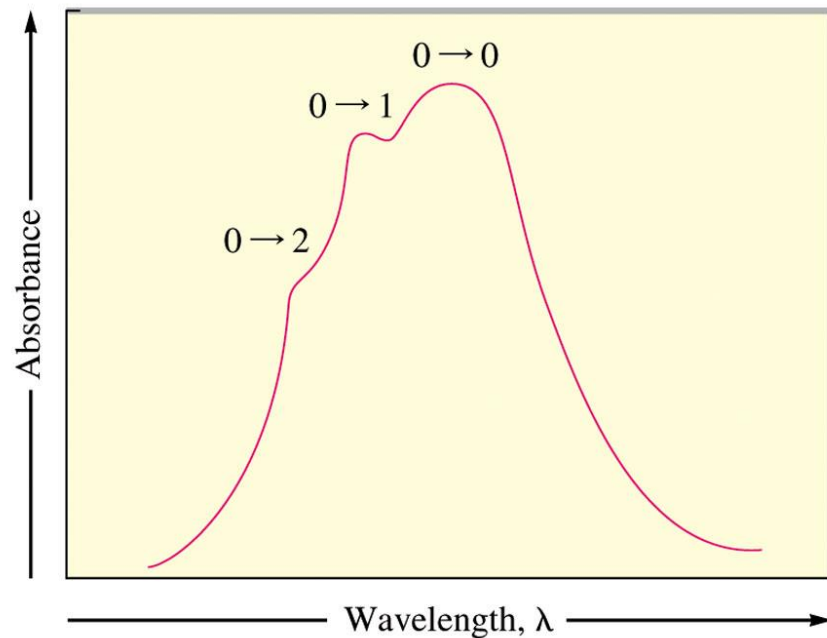
- Transitions between vibrational and rotational energy levels are superimposed on the electronic excitations
- The result is a large number of UV-Vis absorption peaks so closely spaced that the spectrophotometer cannot resolve them
- For this reason, UV-Vis absorption peaks usually are much broader than IR peaks



The various types of transitions are shown by vertical arrows.



An electronic absorption spectrum arising from electronic transitions



Electronic Transitions

- Wavelengths and energies required for π to π^* transitions of ethylene and three conjugated (alternating) polyenes
- The “longer the wire, the redder the absorbance”

Name	Structural Formula	λ_{\max} (nm)	Energy (kcal/ mol)
ethylene	$\text{CH}_2=\text{CH}_2$	165	173
1,3-butadiene	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	217	132
(3E)-1,3,5-hexatriene	$\text{CH}_2=\text{CHCH}=\text{CHCH}=\text{CH}_2$	268	107
(3E, 5E)-1,3,5,7-octatetraene	$\text{CH}_2=\text{CH}(\text{CH}=\text{CH})_2\text{CH}=\text{CH}_2$	290	92



UV-Vis Spectroscopy Summary

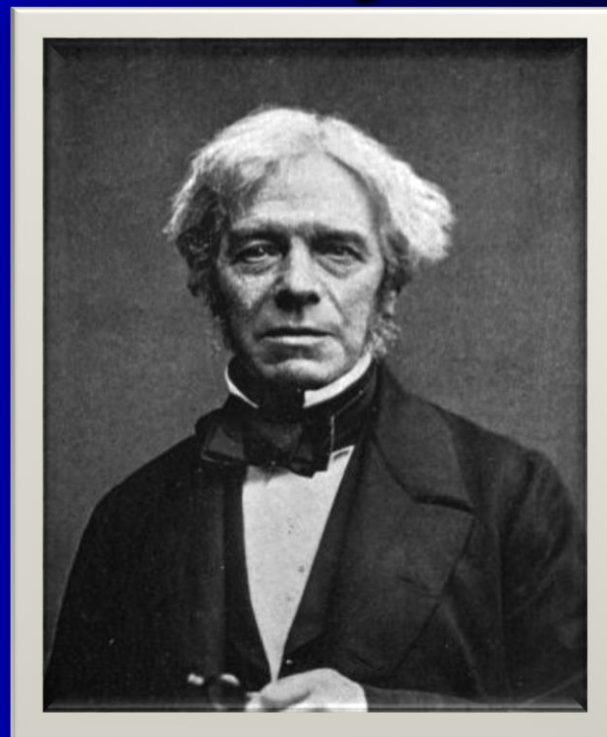
- Electronic Transitions
 - HOMO to LUMO
- Know definitions
 - A , ϵ , λ , C , T , I , I_0
- Practice quantitative analysis calculations
 - Beer – Lambert Law



Some History



Michael Faraday 1791-1867



British physicist and chemist, best known for his discoveries of electromagnetic induction and of the laws of electrolysis. He also discovered benzene!



What in the World is Benzene??

- C_6H_6 discovered by Michael Faraday in 1823
 - Empirical formula is CH
 - Synthesized in 1834 from benzoic acid
 - Remarkable chemical stability
 - Unsaturation number is very high but....
- Does not add Bromine
- Substitution with $Br_2 / FeBr_3$
- Not oxidized by Permanganate or ozone
- No reaction with strong HBr (aq)
- No reaction with Hydrogen on Pd..???????





Friedrich August Kekulé (1829-1896)



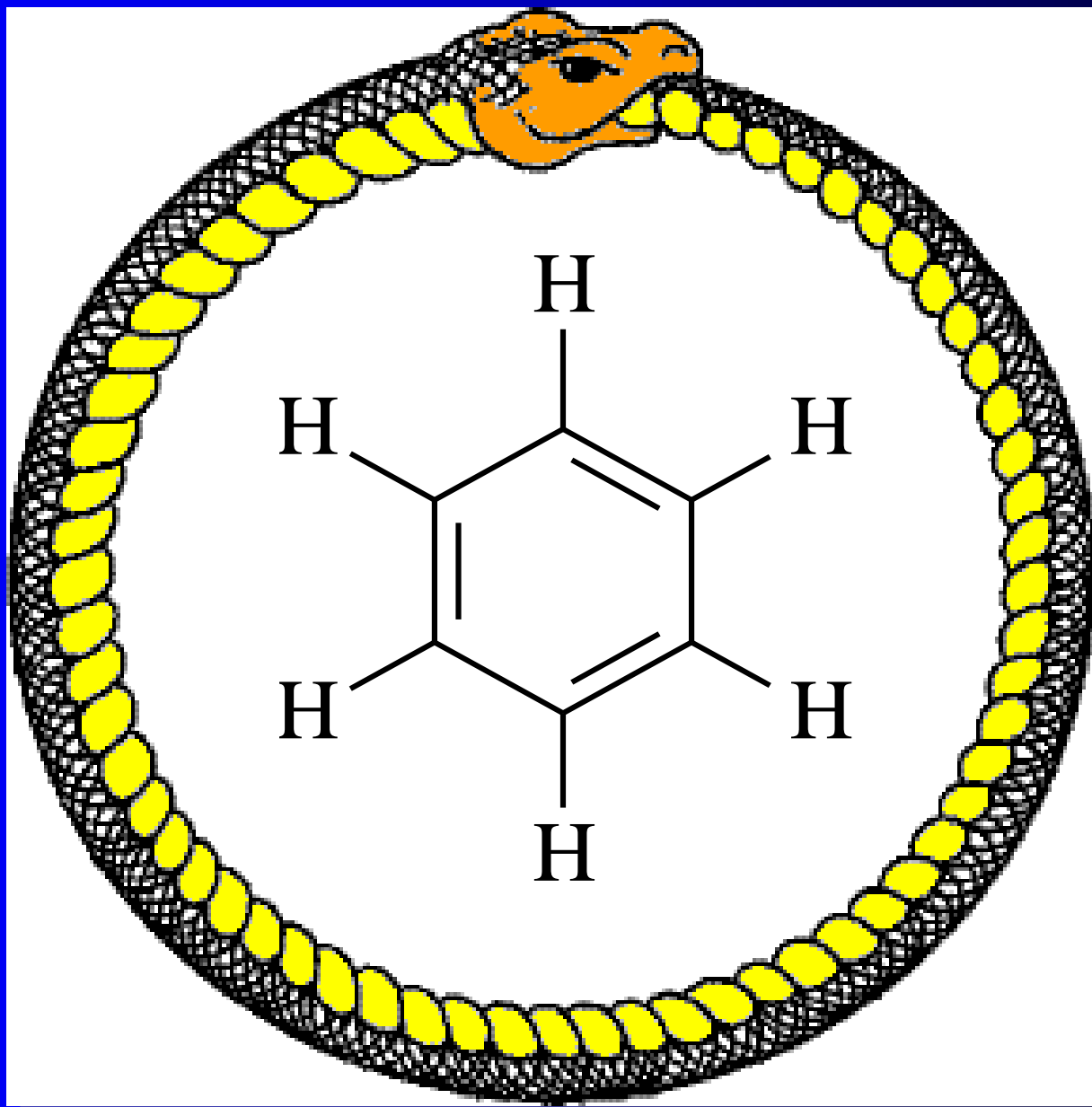
Midnight Ride of Kekule

Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly to the background. My mental eye, rendered more acute by repeated vision of this kind, could now distinguish larger structures, of manifold conformation; long rows, sometimes more closely fitted together; all twining and twisting in snakelike motion. But look!

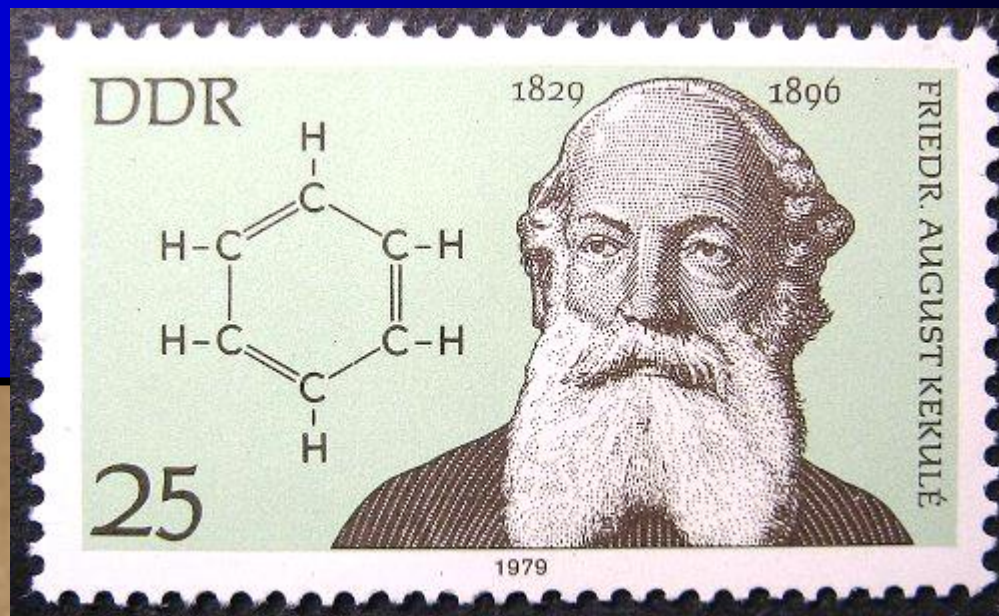
What was that?!?! One of the snakes seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lighting I awoke... Let us learn to dream, gentlemen.

Arthur Koestler (in "The Act of Creation") called this incident "probably the most important dream in history since Joseph's seven fat and seven lean cows.





The man and his snakes



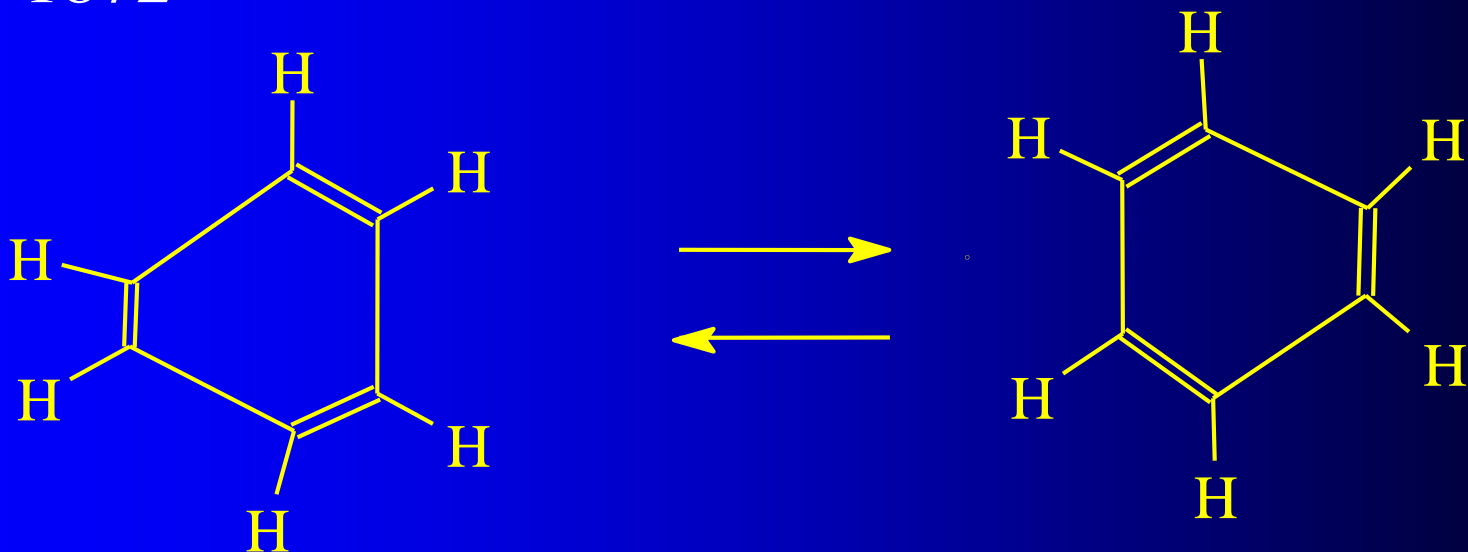
August Kekule





Benzene – per Kekulé

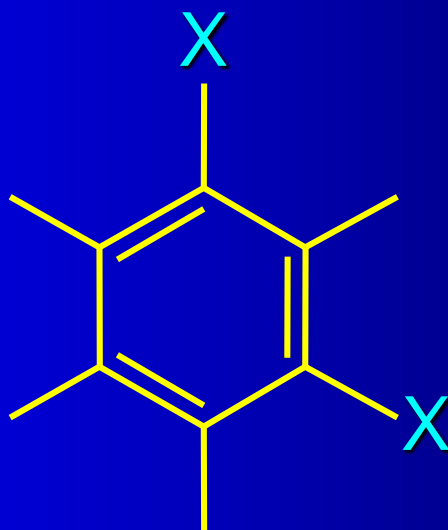
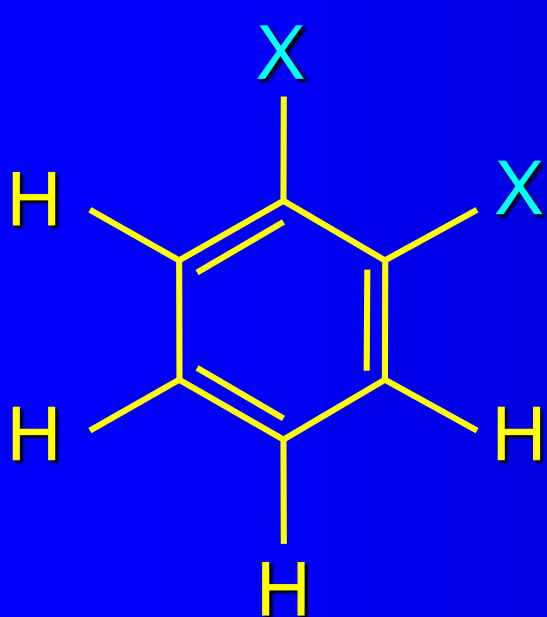
- August Kekulé proposed a structure for benzene in 1872



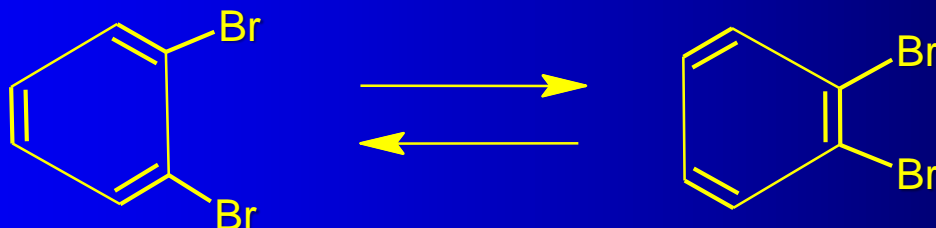
- This structure, however, did not really account for the unusual chemical reactivity of benzene



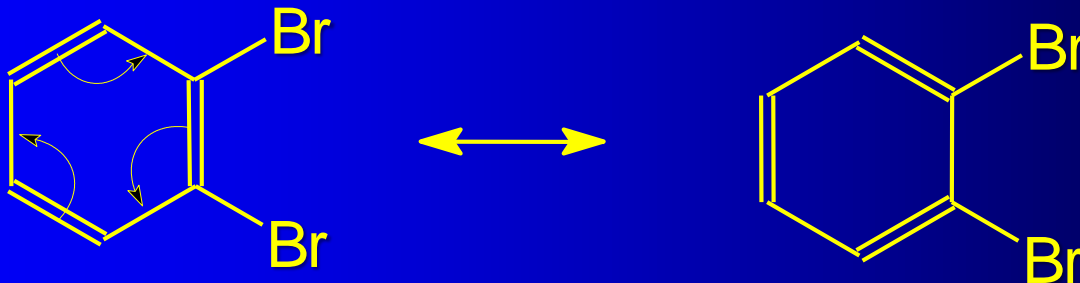
Kekule explains why there are only 3 isomers of dibromobenzene



- Kekule's proposal is an equilibrium between two structures

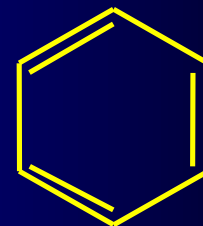
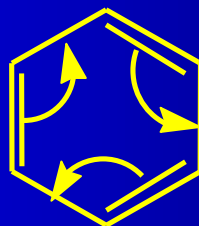
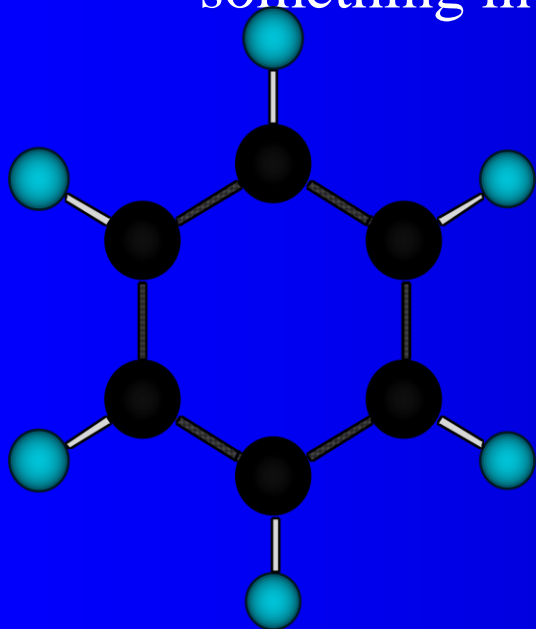


- Pauling's Resonance Theory describes resonance structures generated by electron movement (only!) that are not real, they are constructs the weighted sum of which describes the real molecule, which is presented as the resonance hybrid

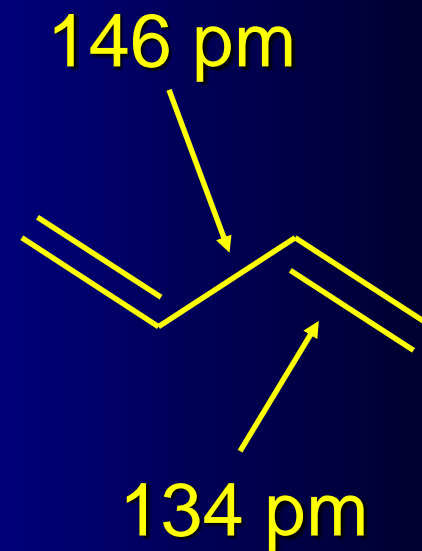
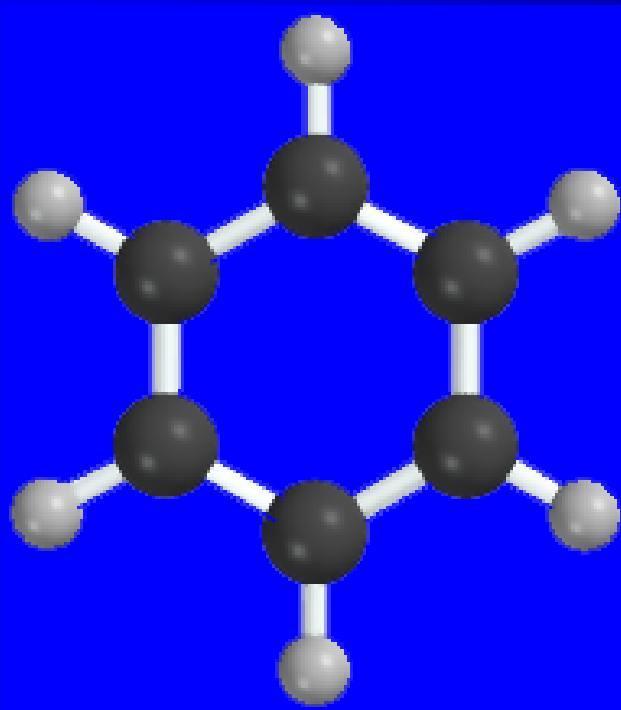


Benzene - Resonance

- We can represent benzene as the hybrid of two equivalent Kekulé structures
 - each makes an equal contribution to the hybrid, and thus the C-C bonds are neither double nor single, but something in between



All C—C bond distances = 140 pm (1.4 Å)



140 pm is the average between the C - C single bond length and the C=C double bond length in 1,3-butadiene.



Unusual Stability of Benzene

Benzene is the best and most familiar example of a substance that possesses "special stability" or "aromaticity"

Aromatic molecules have stability that is substantially greater for a molecule than would be expected on the basis of any of the Lewis structures written for it



Benzene - Resonance

- **Resonance energy:** the difference in energy between a resonance hybrid and the most stable of its hypothetical contributing structures in which electrons are localized on particular atoms and in particular bonds
- One way to estimate the resonance energy of benzene is to compare the heats of hydrogenation of benzene and cyclohexene that we saw earlier
- This theory provides an explanation for the reactivity of benzene



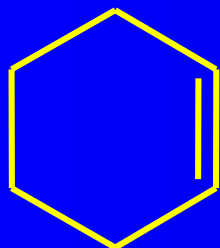
ΔH° of Hydrogenation

Name	Structural Formula	ΔH° (kcal/mol)
1-butene	$\text{CH}_3 \text{CH}_2 \text{CH}=\text{CH}_2$	-30.3
cis-2-butene	$\text{CH}_3 \text{CH}=\text{CHCH}_3$	-28.6
trans-2-butene	$\text{CH}_3 \text{CH}=\text{CHCH}_3$	-27.6
2-methyl-2-butene	$(\text{CH}_3)_2 \text{C}=\text{CHCH}_3$	-26.9
2,3-dimethyl-2-butene	$(\text{CH}_3)_2 \text{C}=\text{C}(\text{CH}_3)_2$	-26.6



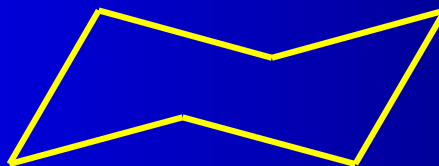
3 x cyclohexene

"expected" heat
of
hydrogenation
of benzene is 3 x
heat of
hydrogenation
of cyclohexene

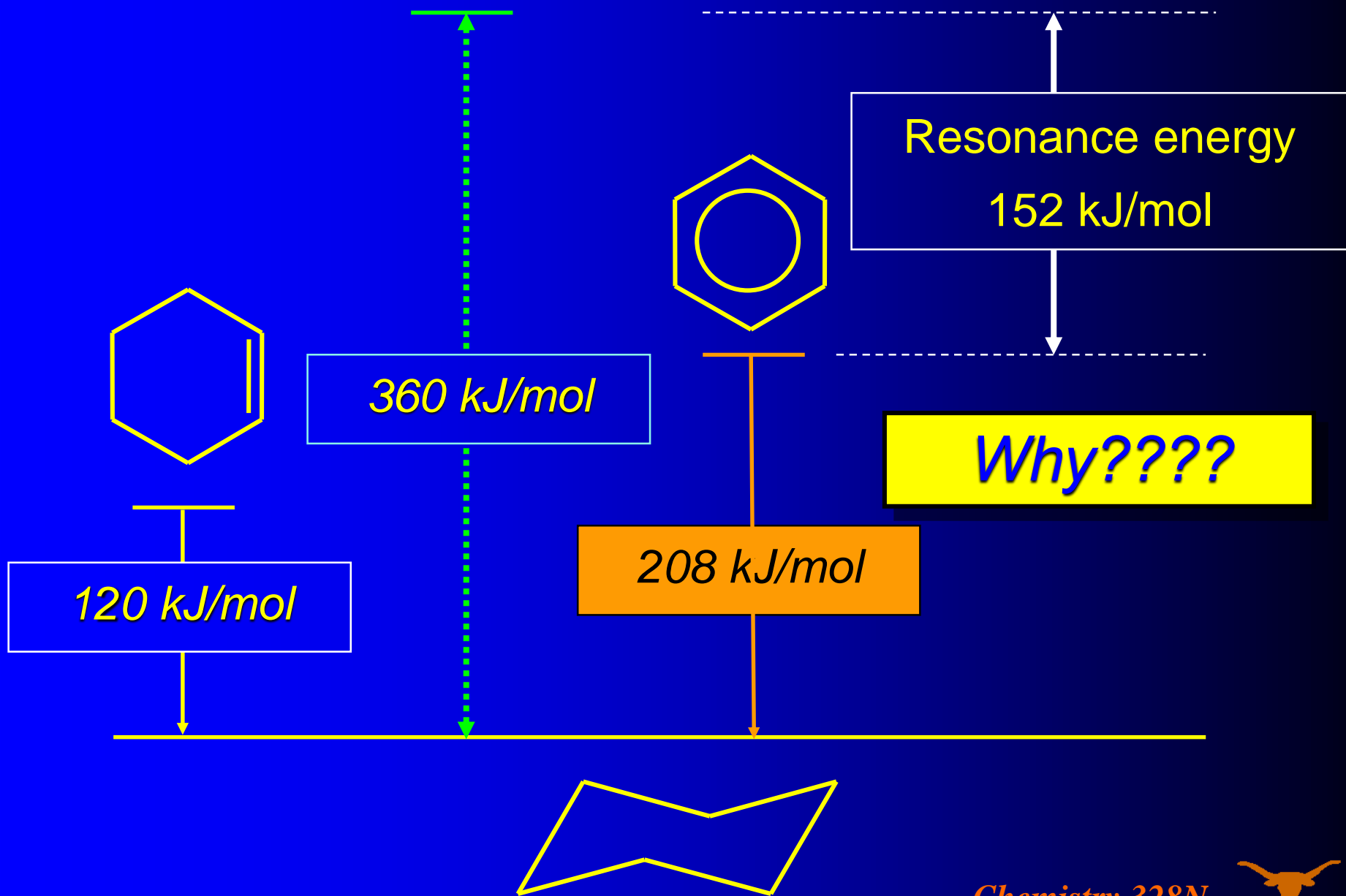


120 kJ/mol

360 kJ/mol



3 x cyclohexene



The answer comes from MO Theory

1. But I hate MO stuff ...it is confusing.....☹
2. How do you even know how many MOs there are??
3. How do you know the relative energies of these MO's???

