크로마토그래피의 원리와 분석법

화합물의 UV absorbance의 이해

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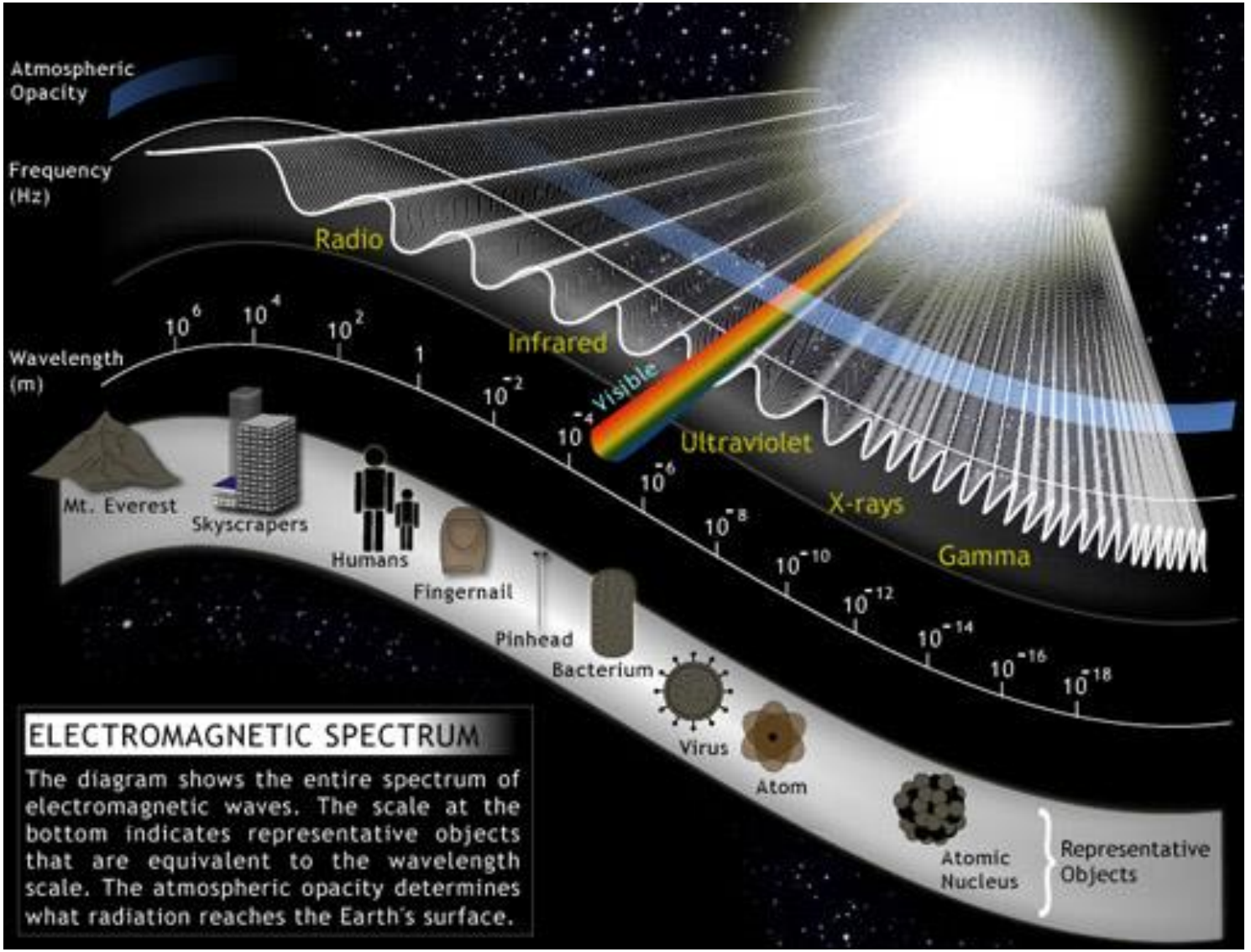
SCH 순천향대

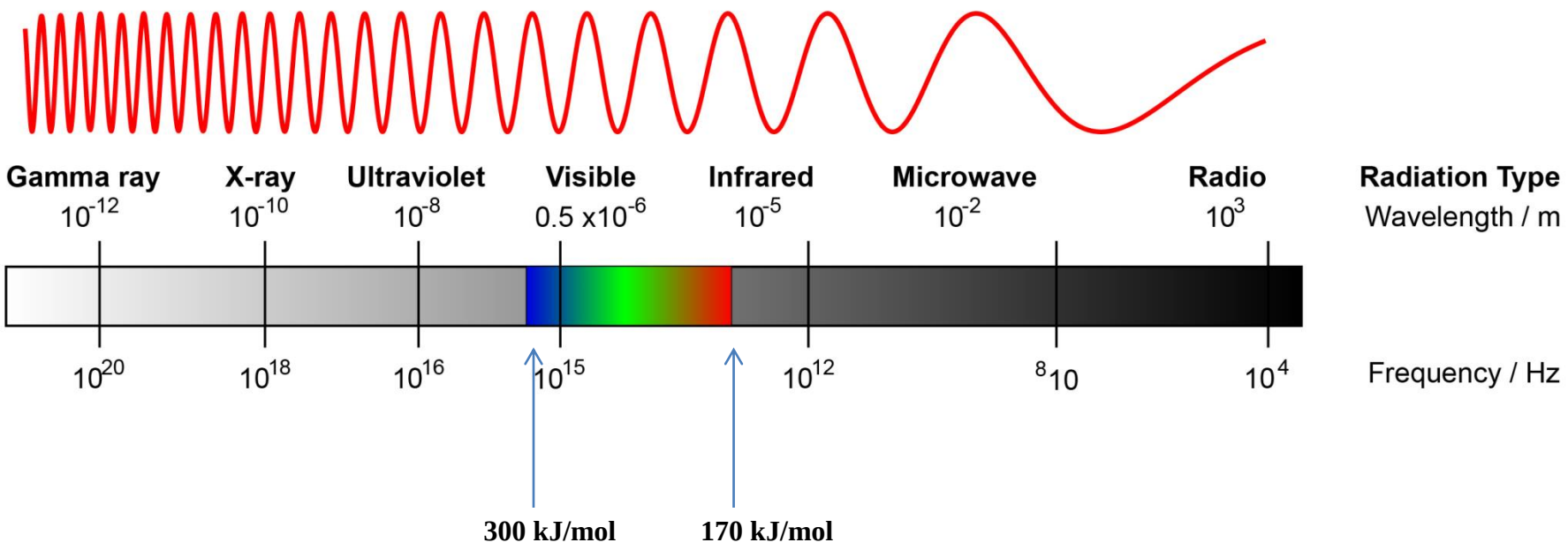
나노화학공학과

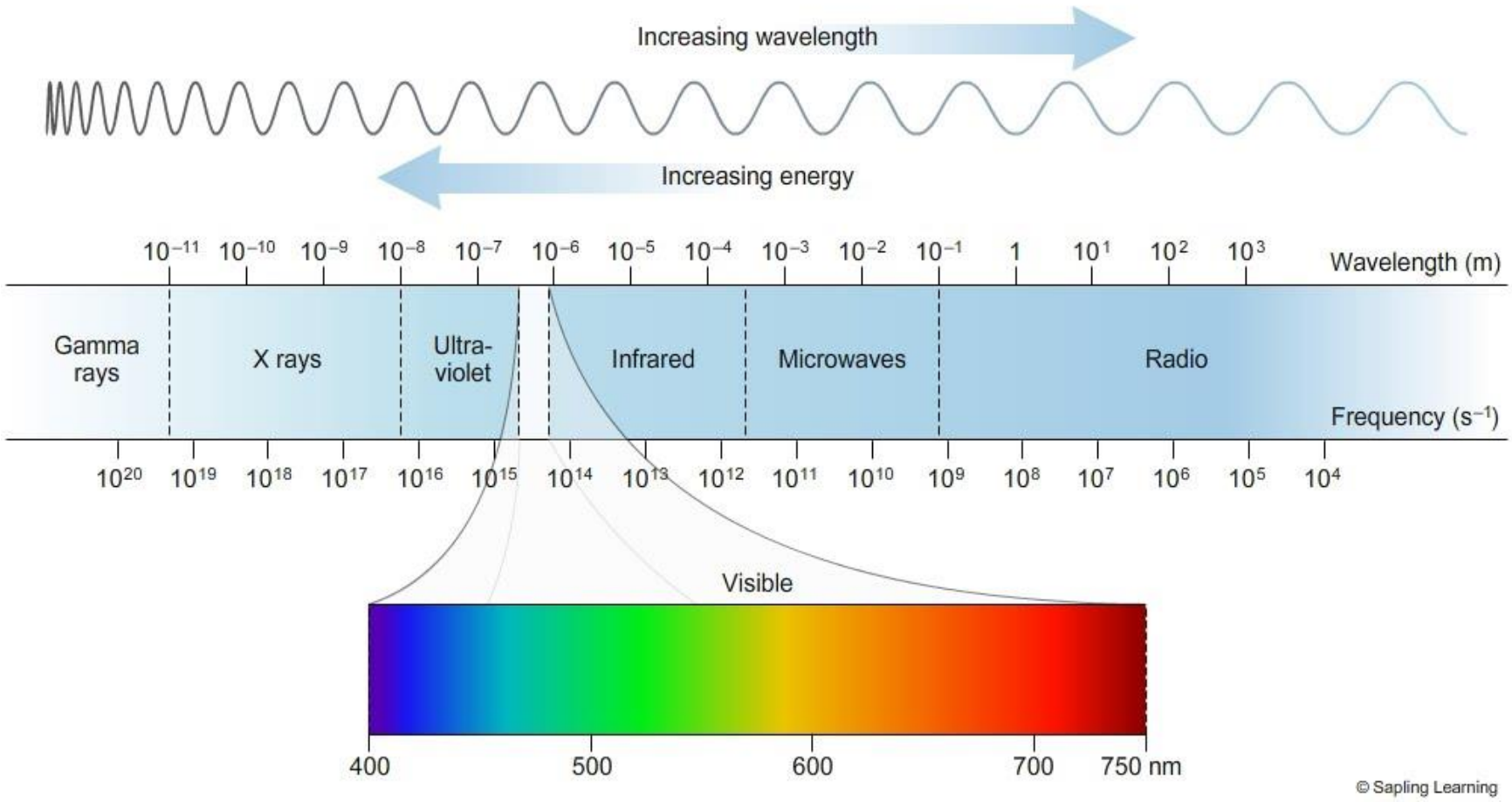
임 정 균 교수

빛의 스펙트럼

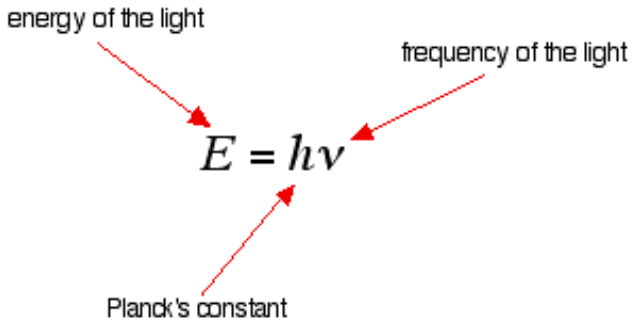

Atmospheric Opacity
Frequency (Hz)
Radio
Infrared
Visible
Ultraviolet
X-rays
Gamma
Wavelength (m)
10^{6} 10^{4} 10^{2} 1 10^{-2} 10^{-4} 10^{-6} 10^{-8} 10^{-10} 10^{-12} 10^{-14} 10^{-16} 10^{-18}
Mt. Everest
Skyscrapers
Humans
Fingernail
Pinhead
Bacterium
Virus
Atom
Atomic Nucleus
Representative Objects
ELECTROMAGNETIC SPECTRUM
The diagram shows the entire spectrum of electromagnetic waves. The scale at the bottom indicates representative objects that are equivalent to the wavelength scale. The atmospheric opacity determines what radiation reaches the Earth's surface.

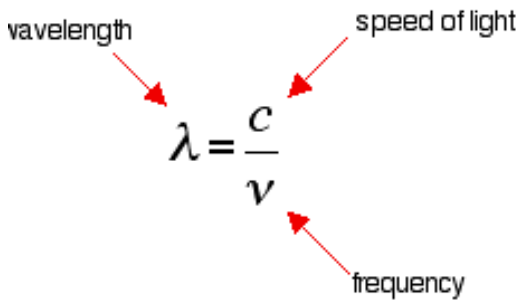
electromagentic spectrum





- 파장과 진동수는 반비례
- 파장과 에너지는 반비례
- 진동수와 에너지는 비례





$$E_{photon} = h\nu_{photon}$$

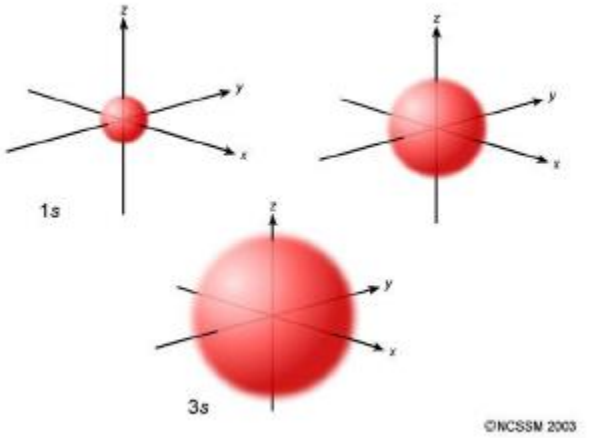
$$\nu = c/\lambda$$

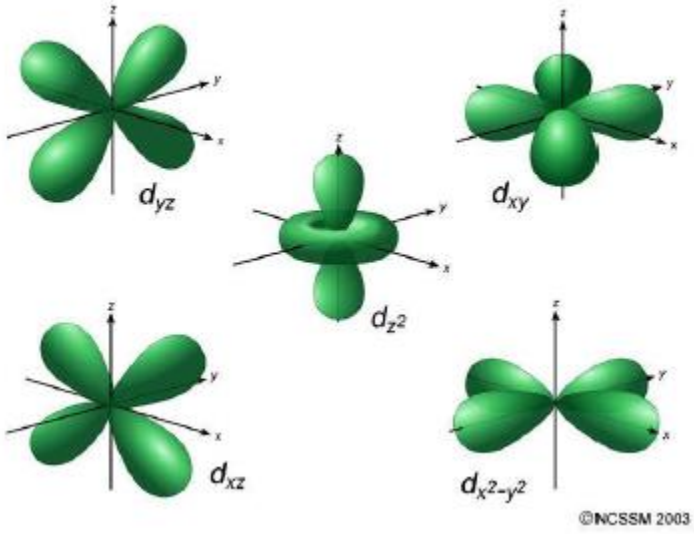
$h = 4.0 \times 10^{-13}$ kJ s/mol

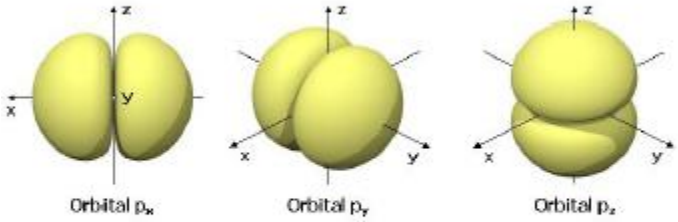
$c = 3.0 \times 10^{8}$ m/s

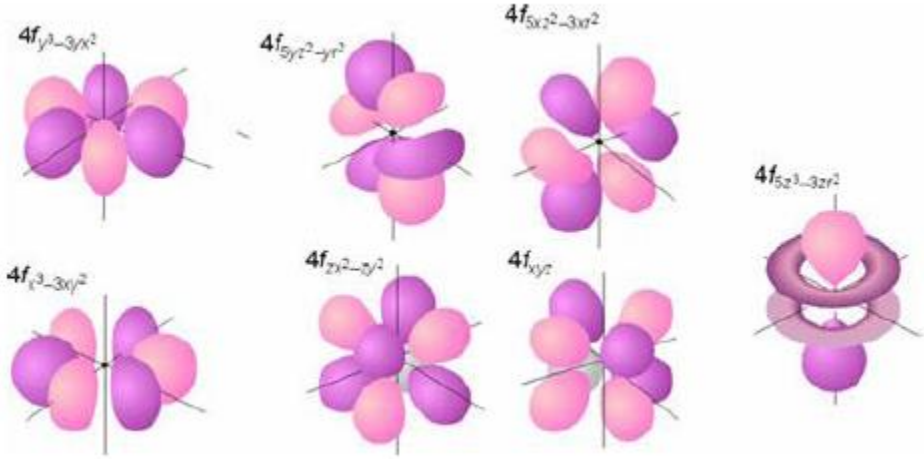
$$E = hc/\lambda = 1.2 \times 10^{-4} \text{ (kJ m/mol)} / \lambda$$

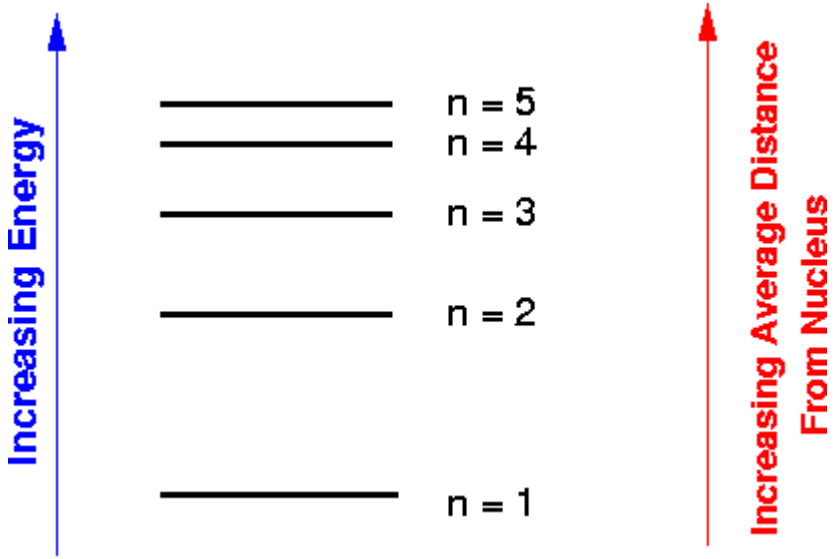
Atomic Orbital (AO)

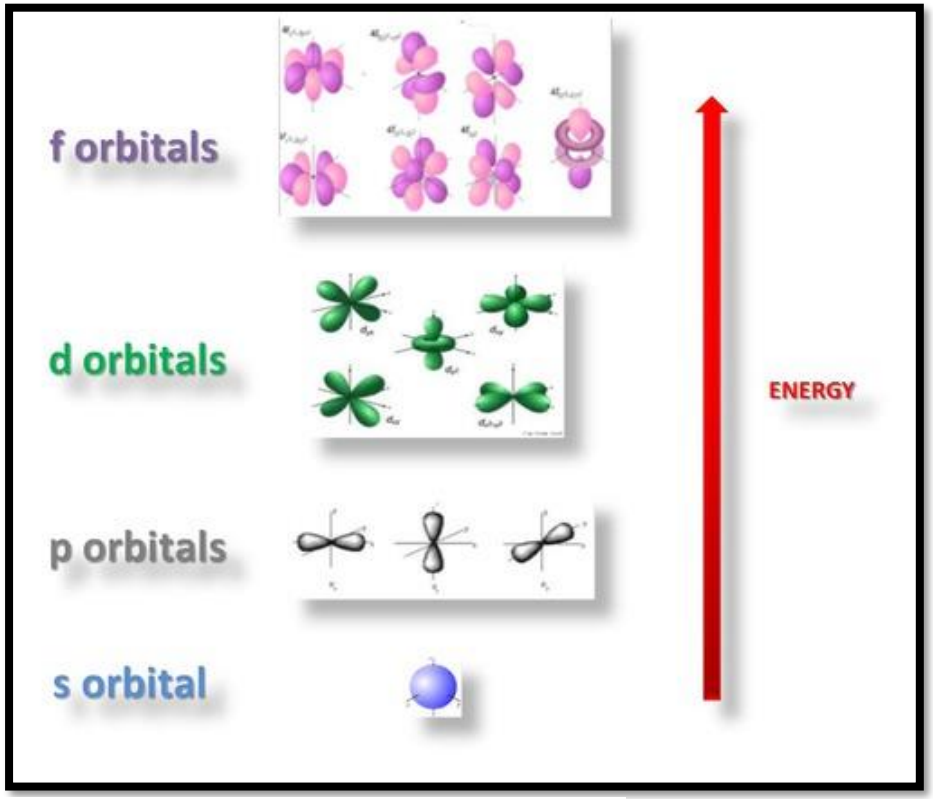




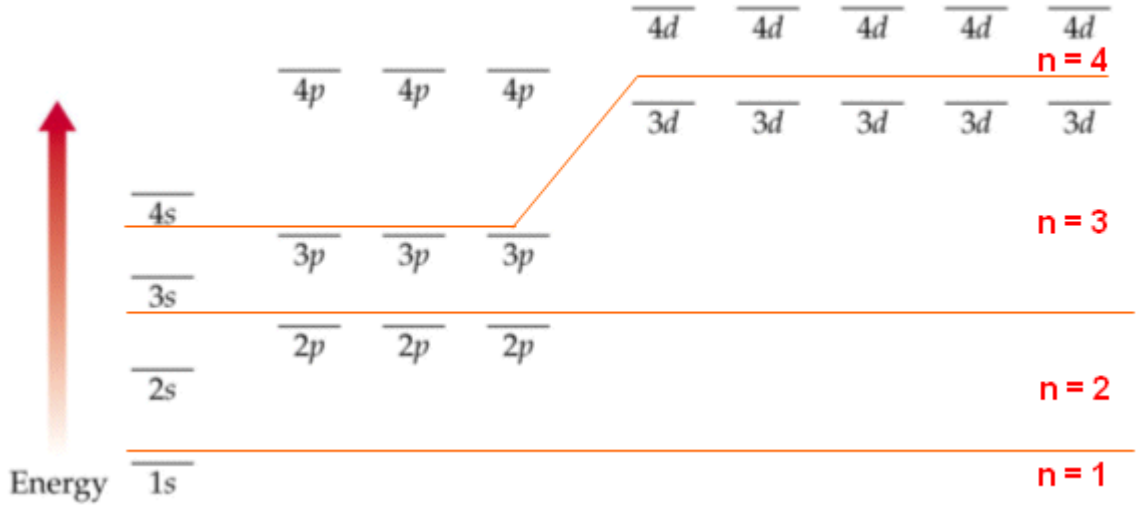




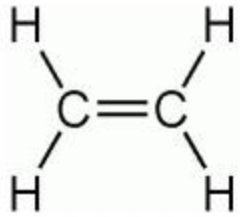




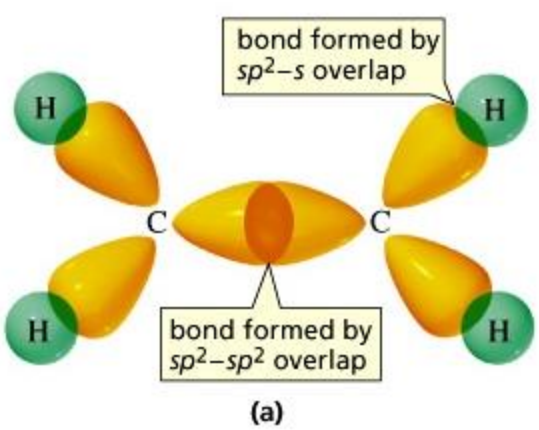
Energy ordering of orbitals for multi-electron atoms

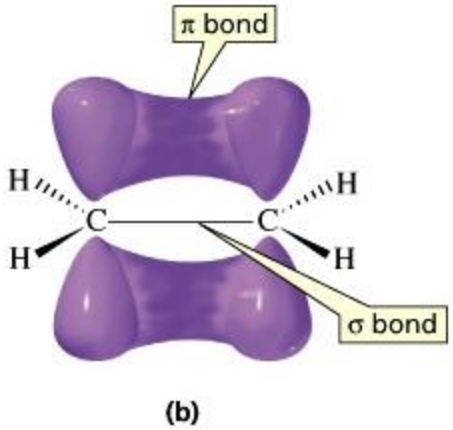


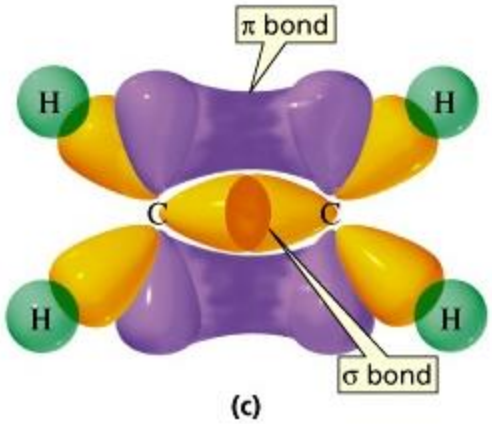
Molecular Orbital (MO)



Ethylene (Ethene)

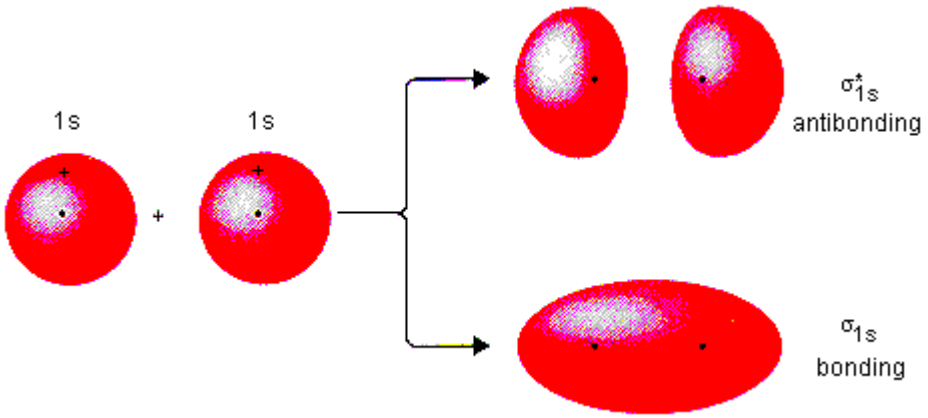


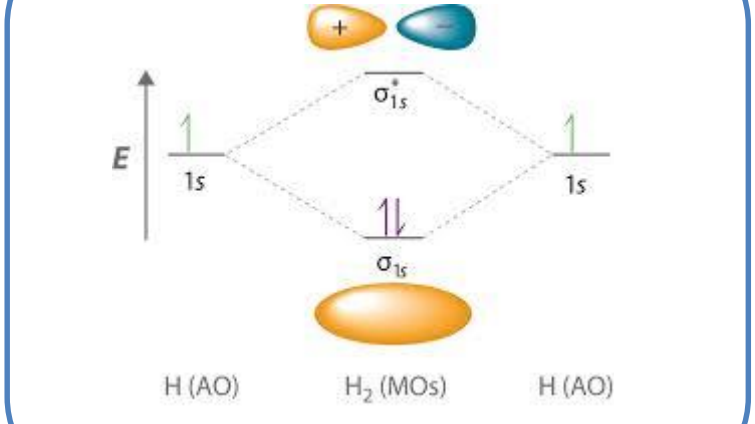


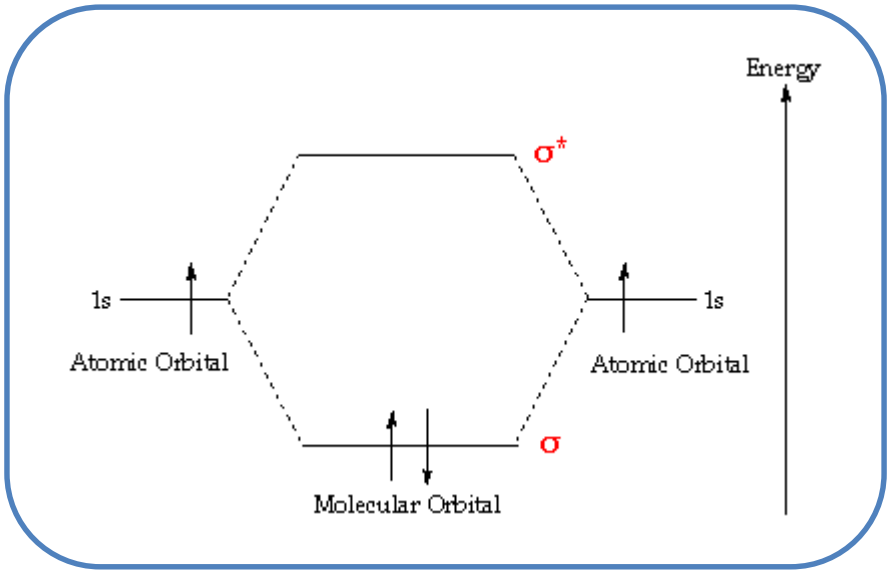


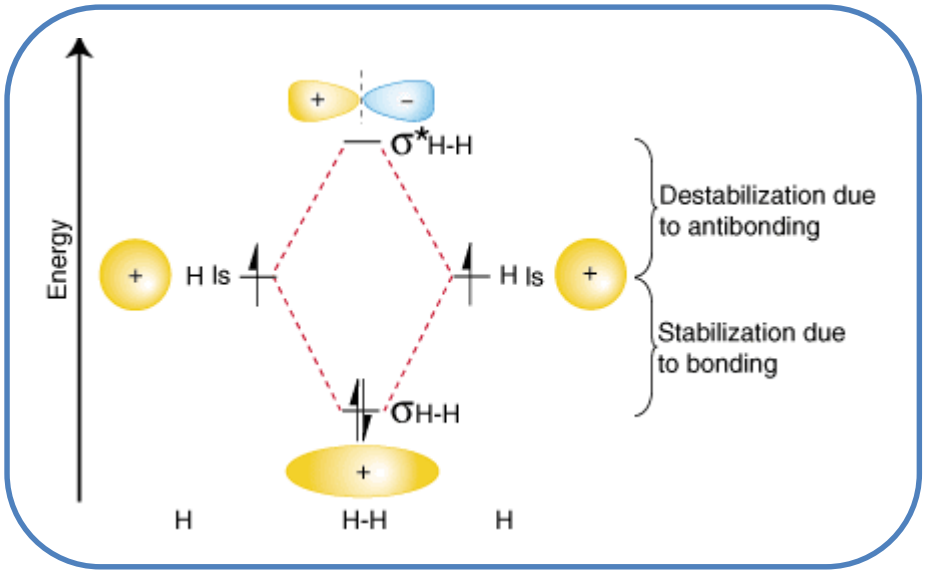
Molecular Orbital (MO) of Hydrogen

N개의 atomic orbital이 모이면 N개의 molecular orbital(MO)이 생긴다.

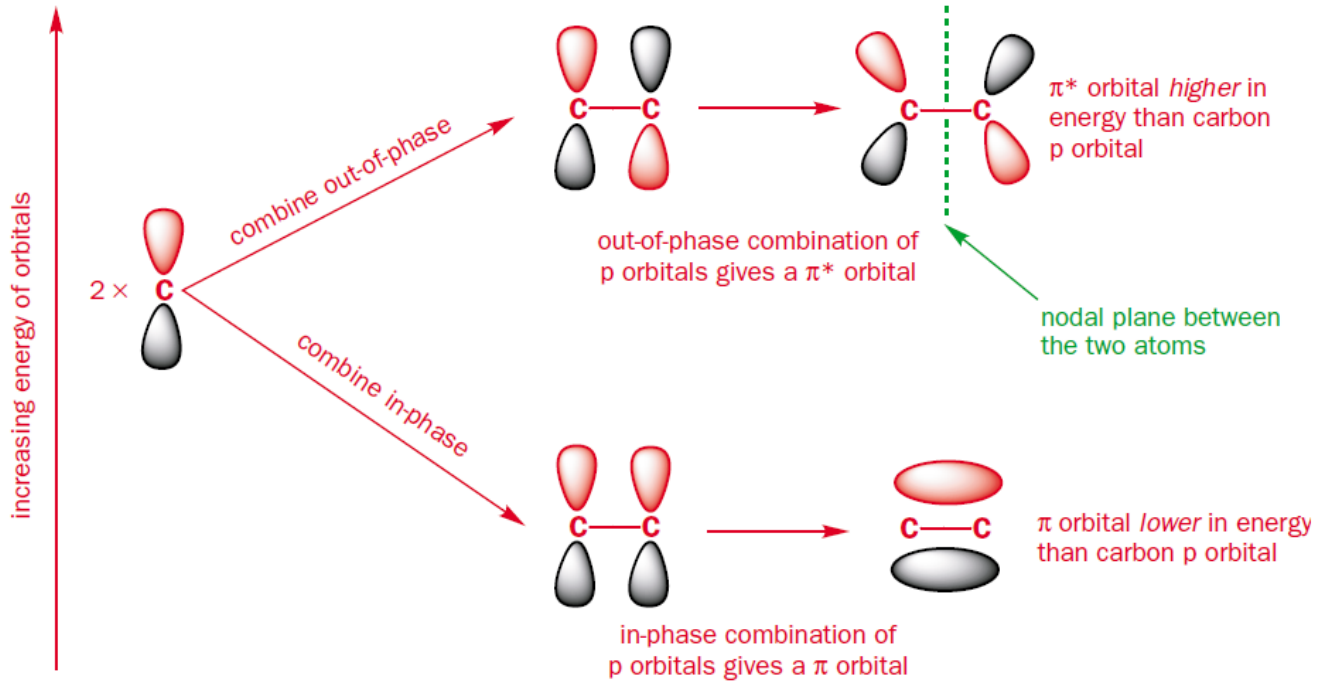


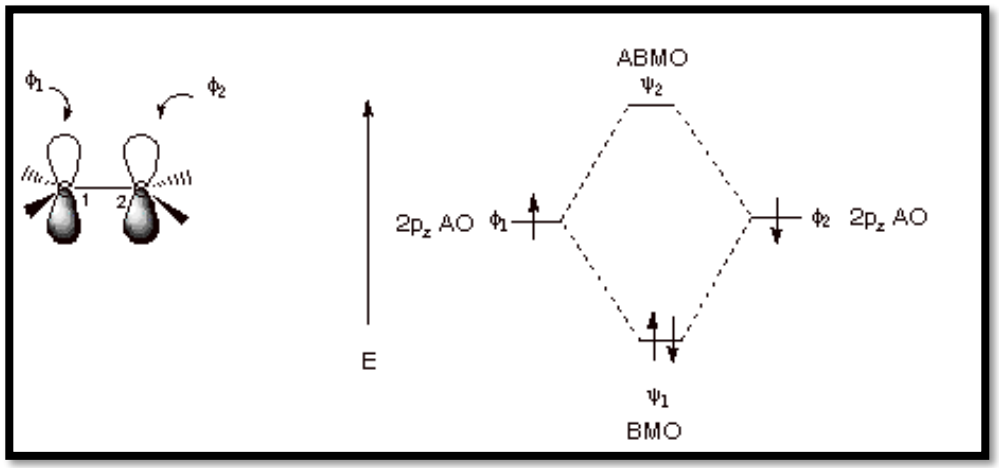


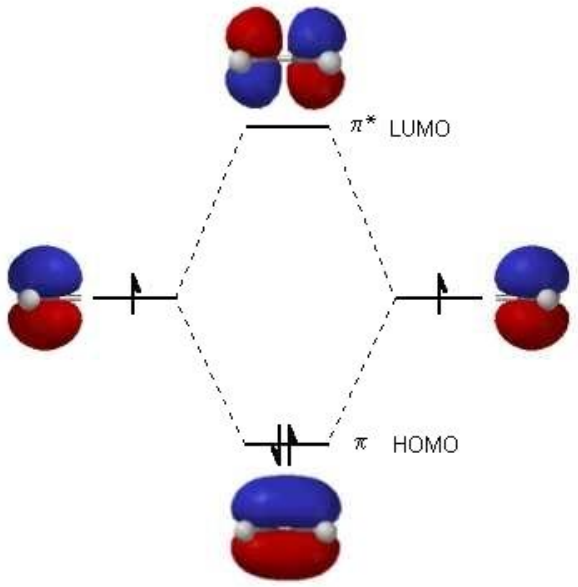




Molecular Orbital (MO) of a double bond







Molecular Orbital (MO) of a double bond

HOMO (Highest Occupied Molecular Orbital)

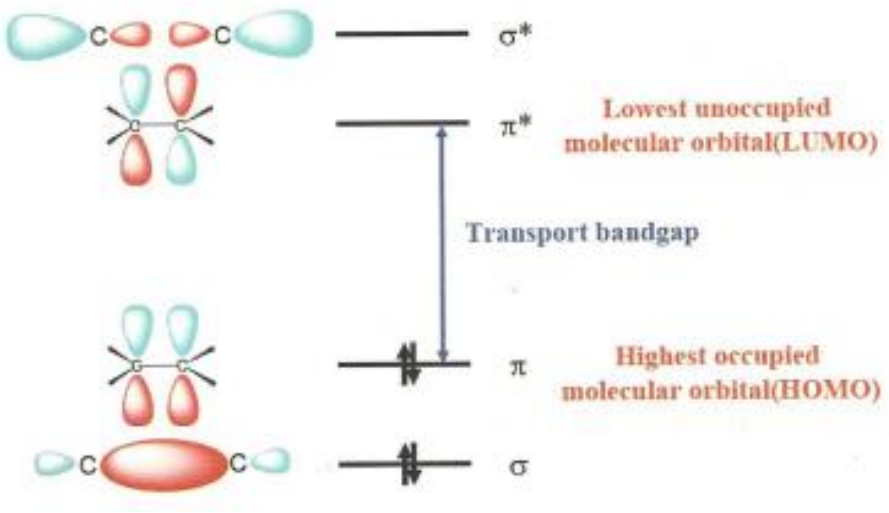
분자의 오비탈 다이어그램을 그리면, 전자는 낮은 에너지 준위부터 채우게 된다. 이때 전자가 찬 오비탈 중에서 에너지 준위가 가장 높은 오비탈을 말하며, 분자 내부에 속박되지만 가장 에너지가 작고 전자가 가장 움직이기 쉬운 곳을 'HOMO'라고 부른다. 이것은 최고 점유 분자 궤도(highest occupied molecular orbital)라는 의미를 나타낸다. 이것은 반도체의 가전자대(valence band)에 해당한다.

LUMO (Lowest Unoccupied Molecular Orbital)

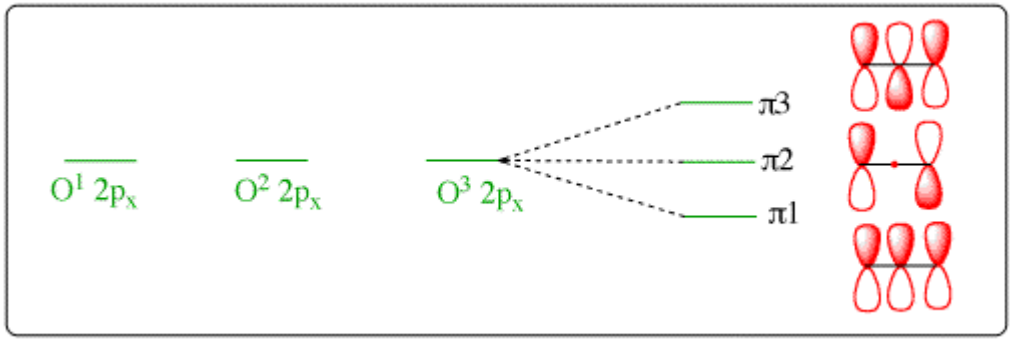
전자가 채워지지 않은 오비탈 중에서, 에너지 준위가 가장 낮은 오비탈을 말하며, 이 에너지 준위에 먼저 전자가 들어간다. 이것은 반도체의 전도대(conduction band)에 해당한다.

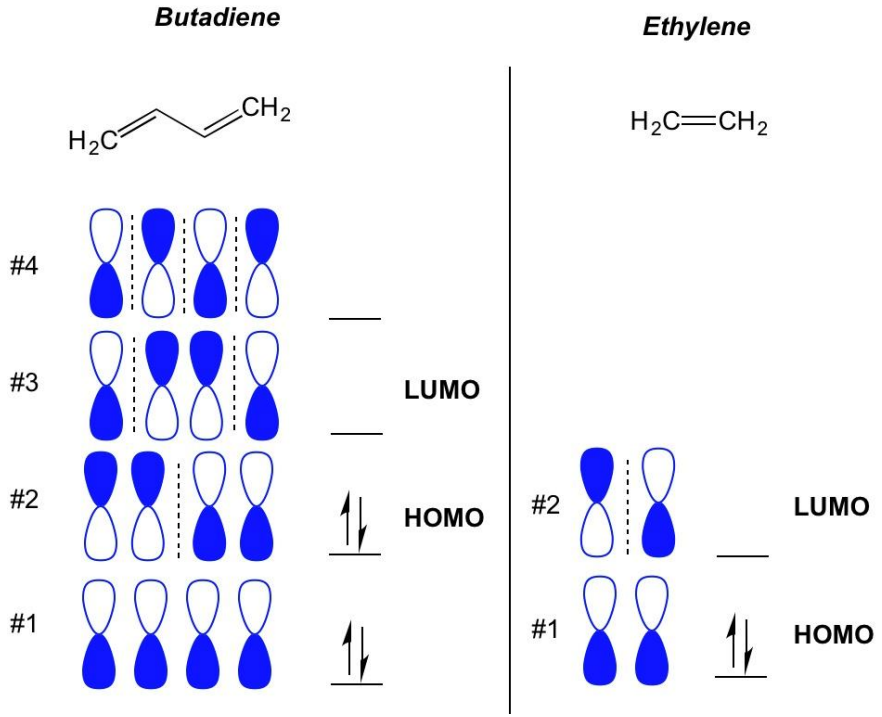
Band-gap

유기물, 반도체에서 band-gap은 HOMO와 LUMO의 에너지 차이에 해당되며 전자가 존재할 수 없는 영역이다. Band-gap 특성은 물질의 광학적 및

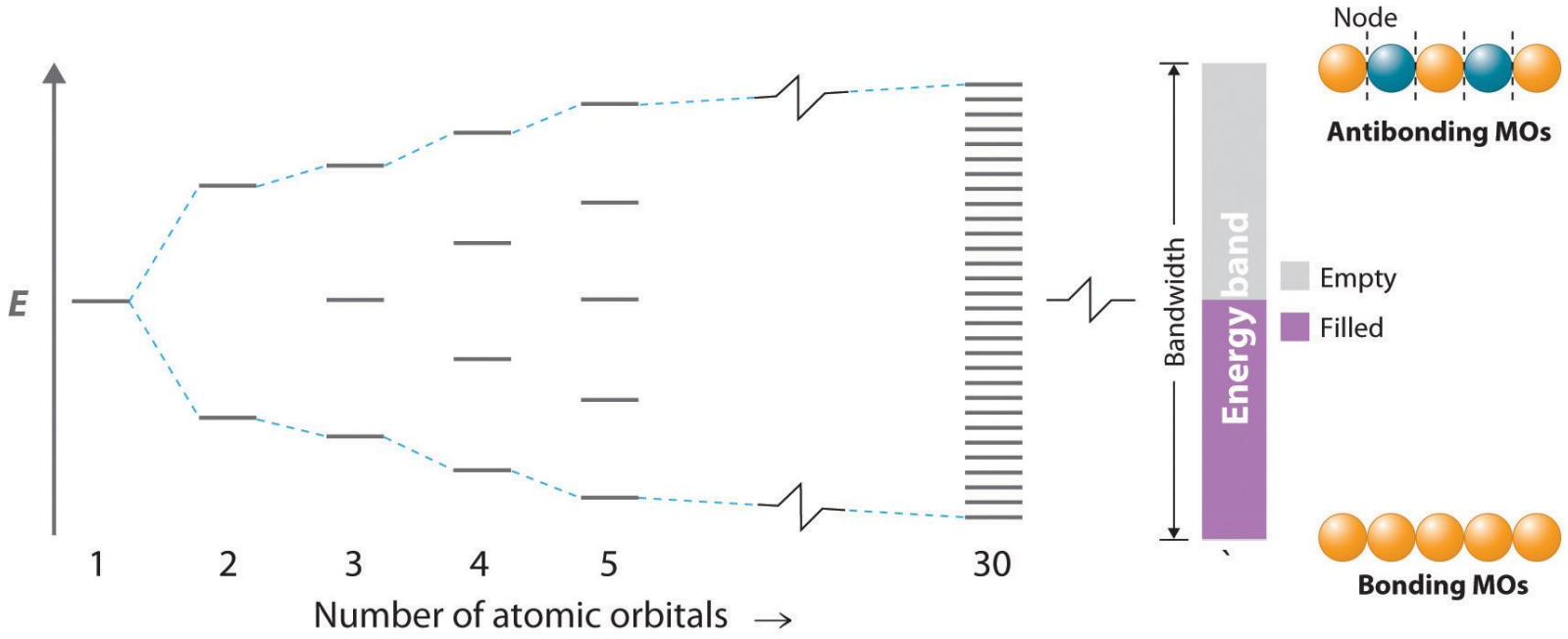


N개의 atomic orbital이 모이면 N개의 molecular orbital(MO)이 생긴다.





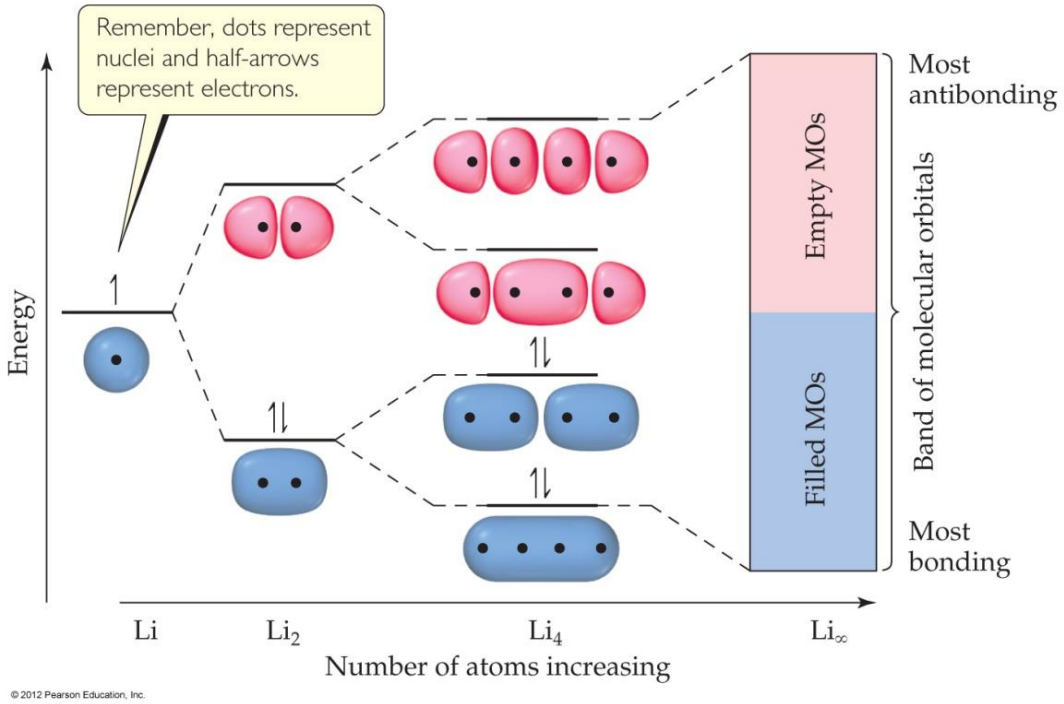
N개의 atomic orbital이 모이면 N개의 molecular orbital(MO)이 생긴다.



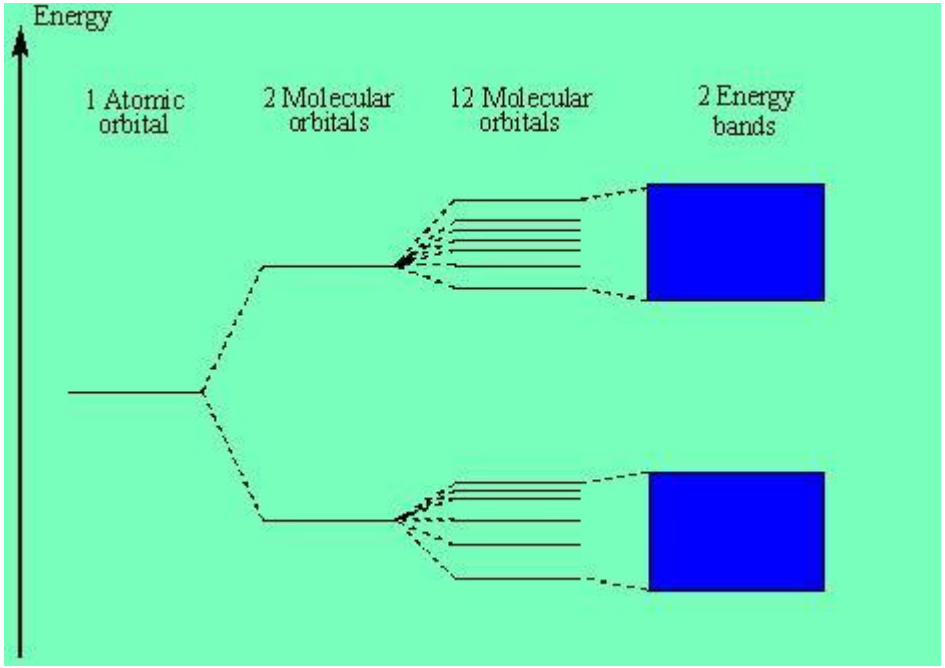
Bonding MO와 Antibonding MO간에 에너지 차이가 점점 작아진다.

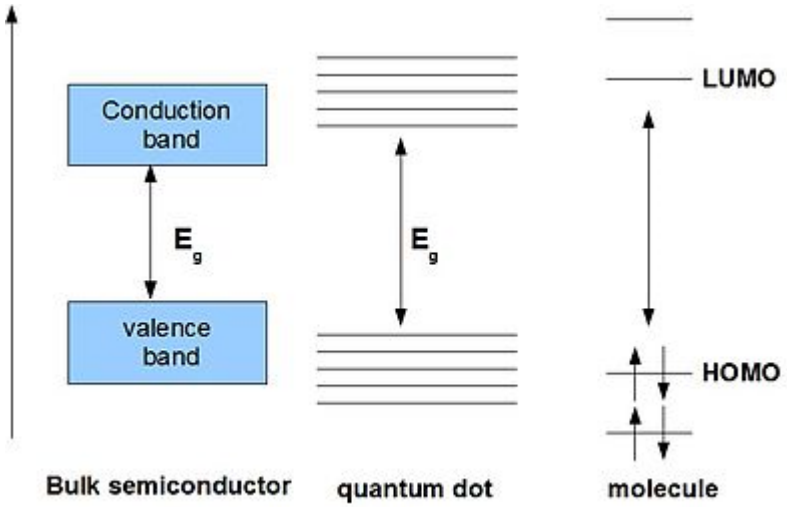
분자 오비탈적 접근
A Molecular-Orbital Approach

사슬의 길이가 길어짐에 따라 분자 오비탈들 간의 에너지 차이가 결국엔 없어지게 되어 연속적인 띠의 에너지 상태가 된다.



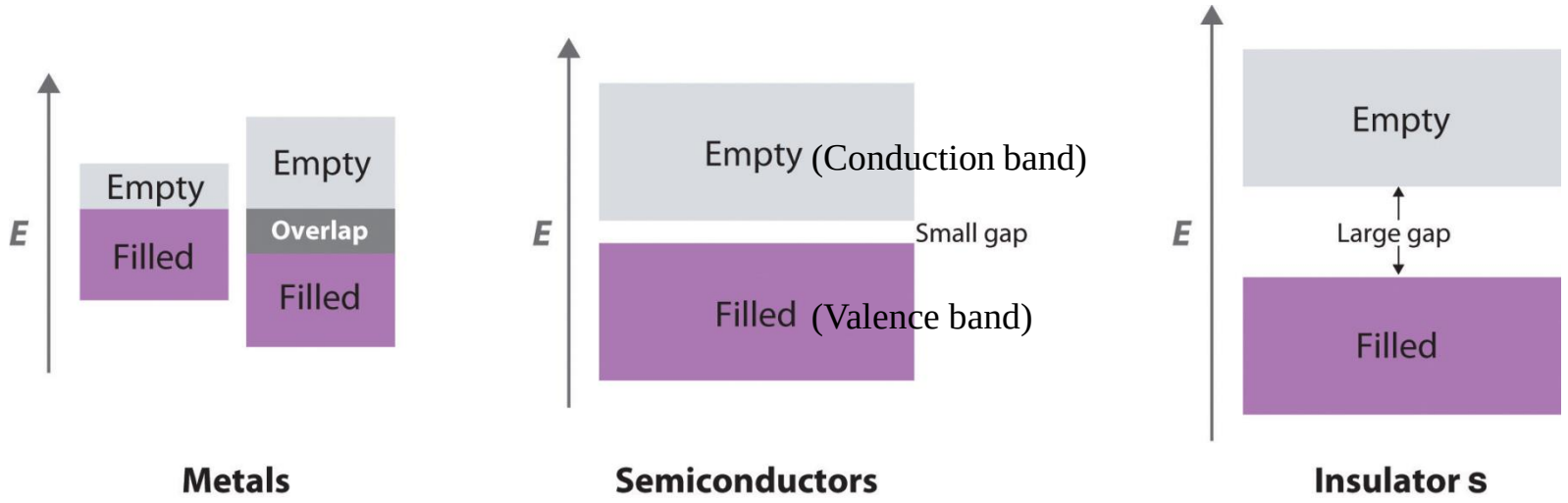
N개의 atomic orbital이 모이면 N개의 molecular orbital(MO)이 생긴다.

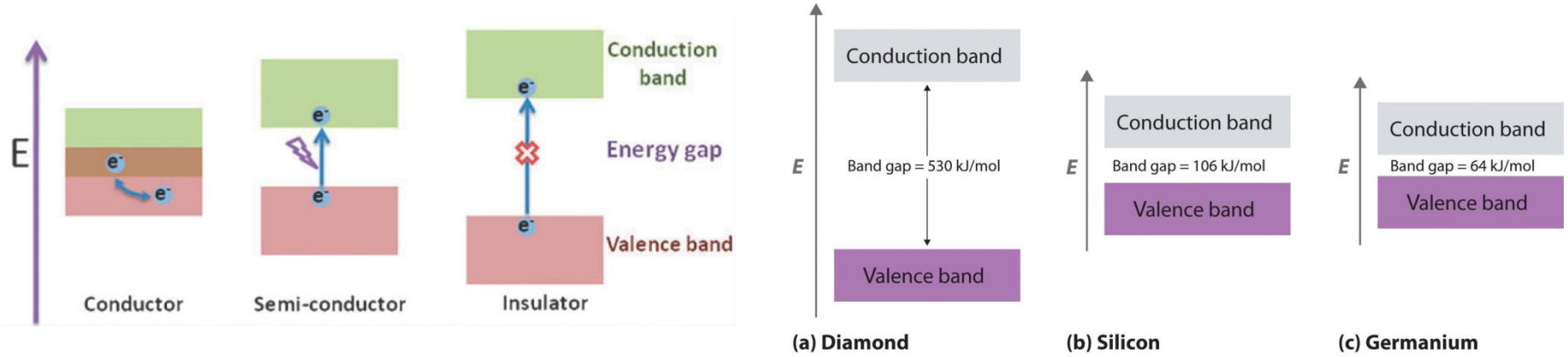




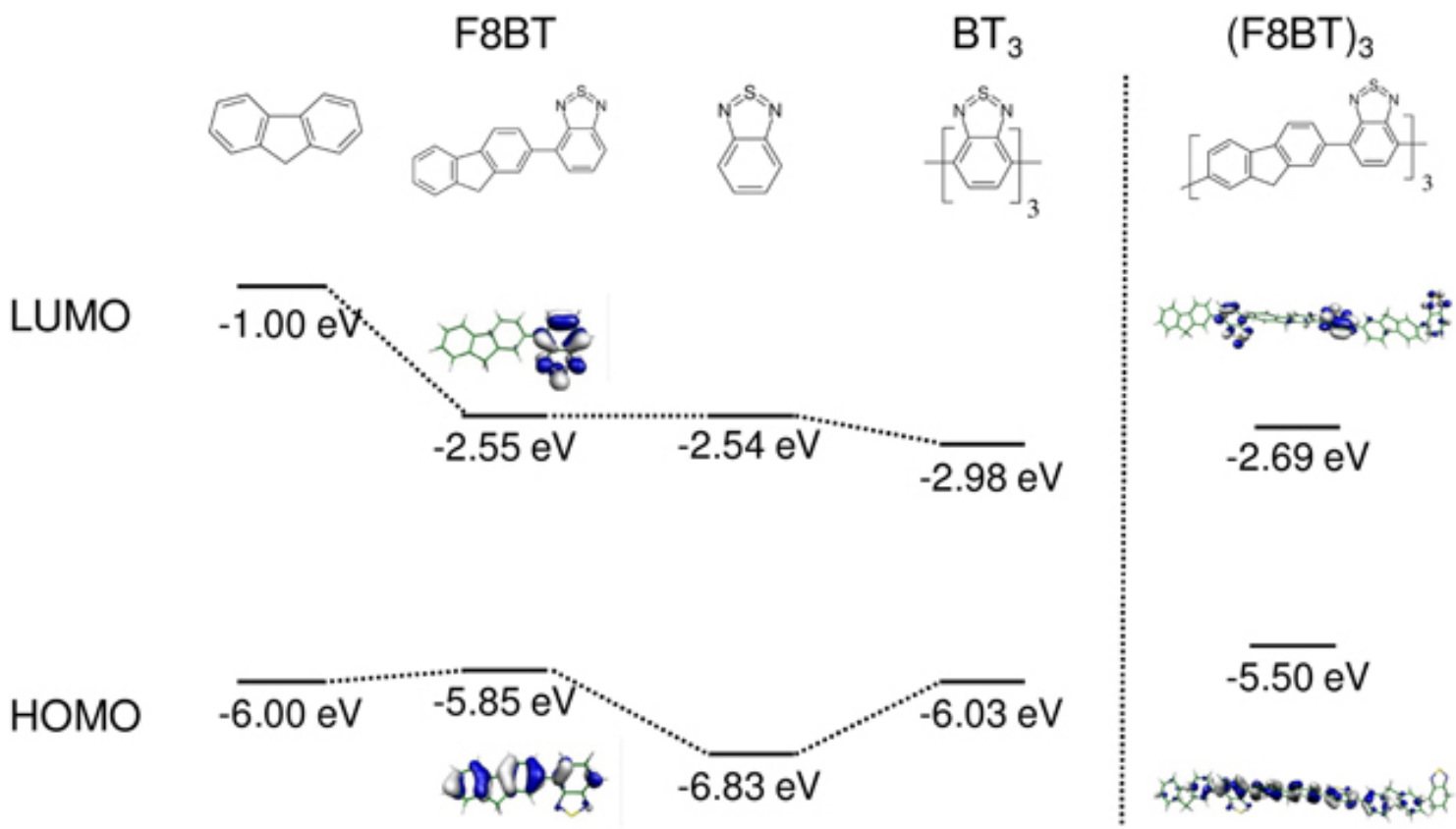
Bonding MO와 Antibonding MO간에 에너지 차이가 점점 작아진다.

Band gap



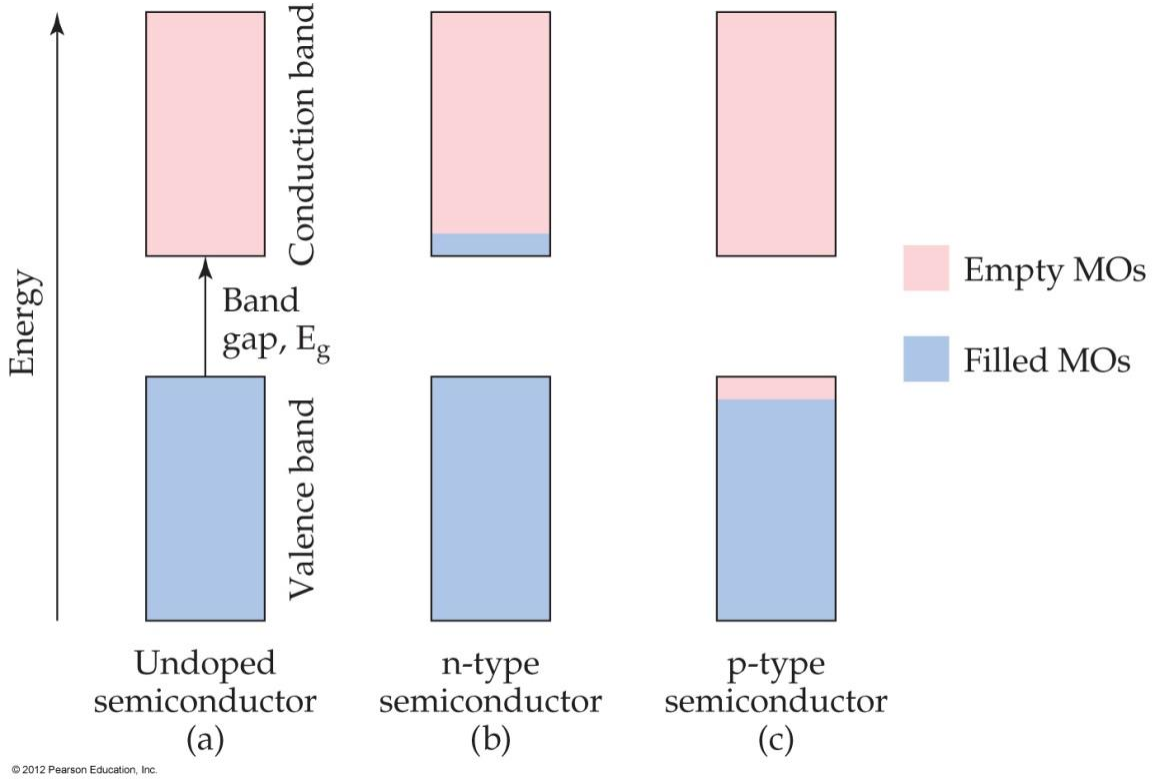


Group IVA 원소들은 원자가띠와 전도띠 사이에 에너지 차이가 0.08 부터 3.05 eV 만큼 난다(7 에서 300 kJ/mol).

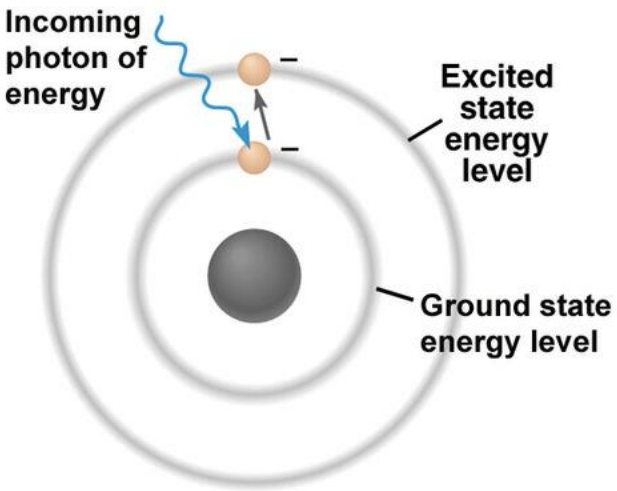

F8BT
BT3
(F8BT)3
LUMO
-1.00 eV
-2.55 eV
-2.54 eV
-2.98 eV
-2.69 eV
HOMO
-6.00 eV
-5.85 eV
-6.83 eV
-6.03 eV
-5.50 eV

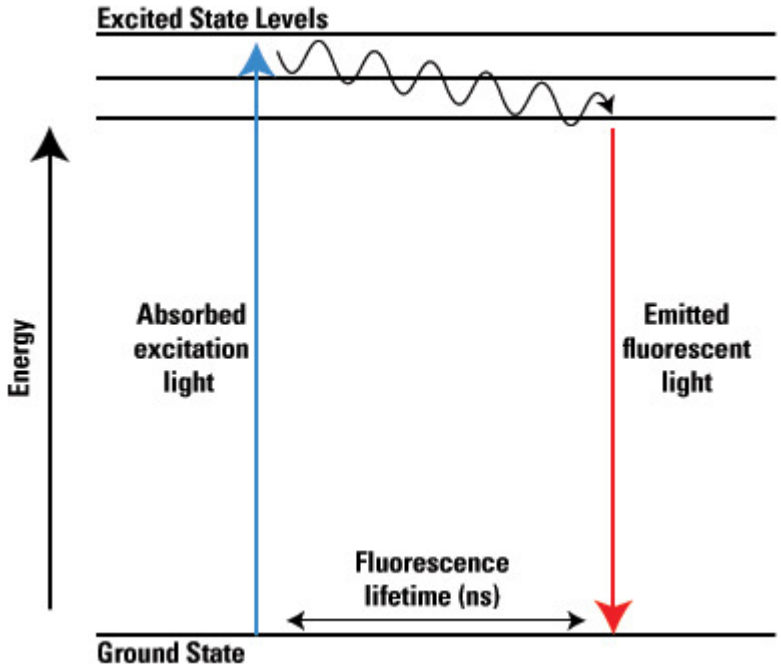
도핑
Doping

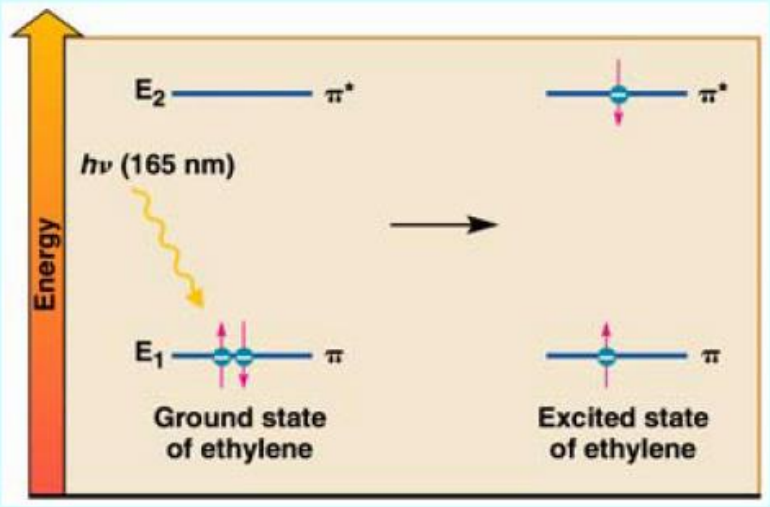
반도체에 원자가전자보다 많거나 (*n*-type) 적은(*p*-type) 불순물 원자를 소량 포함시키면 전기 전도도가 달라진다.



Absorption and Emission



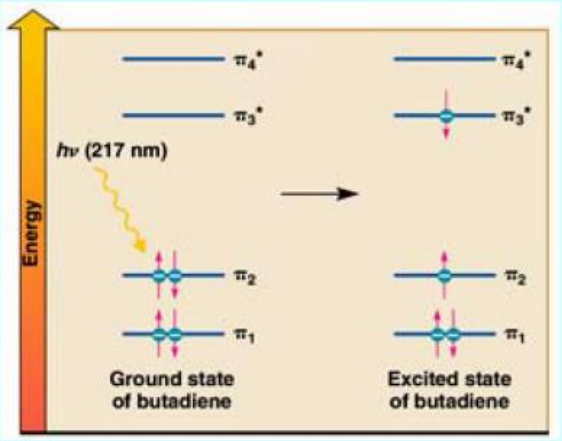




$$E = hc/\lambda = 1.2 \times 10^{-4} \text{ (kJ m/mol)} / \lambda$$

$$E = 1.2 \times 10^{-4} \text{ (kJ m/mol)} / 165 \times 10^{-9} \text{ m}$$

$$E = 724 \text{ kJ/mol}$$



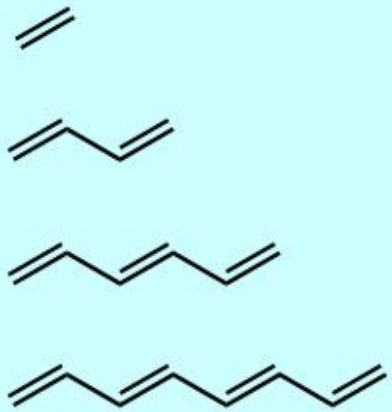
$$E = hc/\lambda = 1.2 \times 10^{-4} \text{ (kJ m/mol)} / \lambda$$

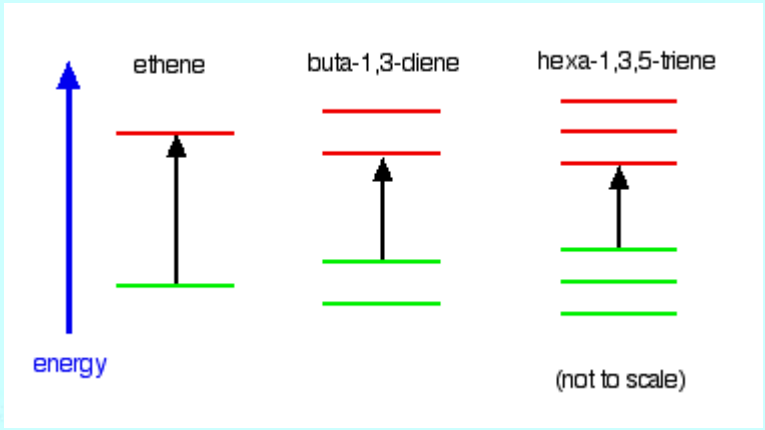
$$E = 1.2 \times 10^{-4} \text{ (kJ m/mol)} / 217 \times 10^{-9} \text{ m}$$

$$E = 552 \text{ kJ/mol}$$

Table 23.5 Wavelengths and Energies Required for $\pi \rightarrow \pi^*$ Transitions of Ethylene and Three Conjugated Polyenes

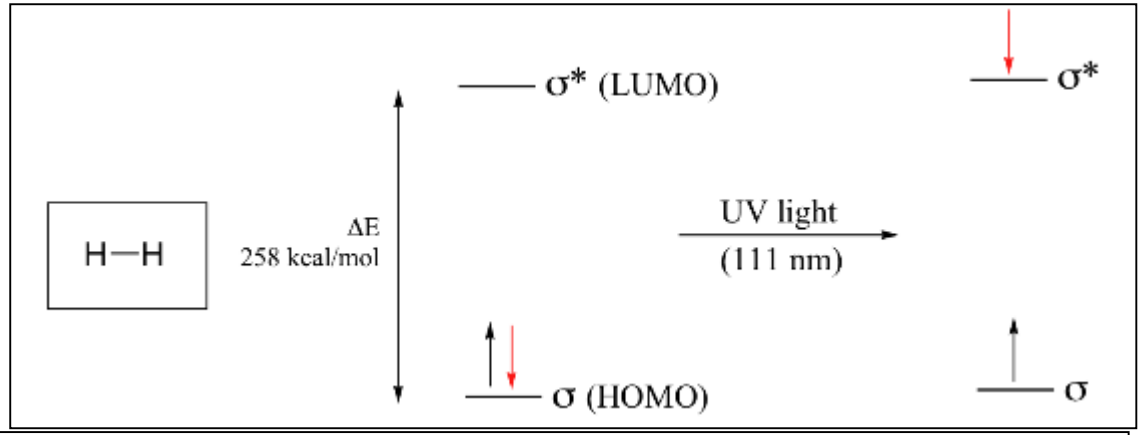
Name	Structural Formula	λ_{max} (nm)	Energy in kJ (kcal)/mol
Ethylene	$CH_2{=}CH_2$	165	724 (173)
1,3-Butadiene	$CH_2{=}CHCH{=}CH_2$	217	552 (132)
(3*E*)-1,3,5-Hexatriene	$CH_2{=}CHCH{=}CHCH{=}CH_2$	268	448 (107)
(3*E*,5*E*)-1,3,5,7-Octatetraene	$CH_2{=}CH(CH{=}CH)_2CH{=}CH_2$	290	385 (92)

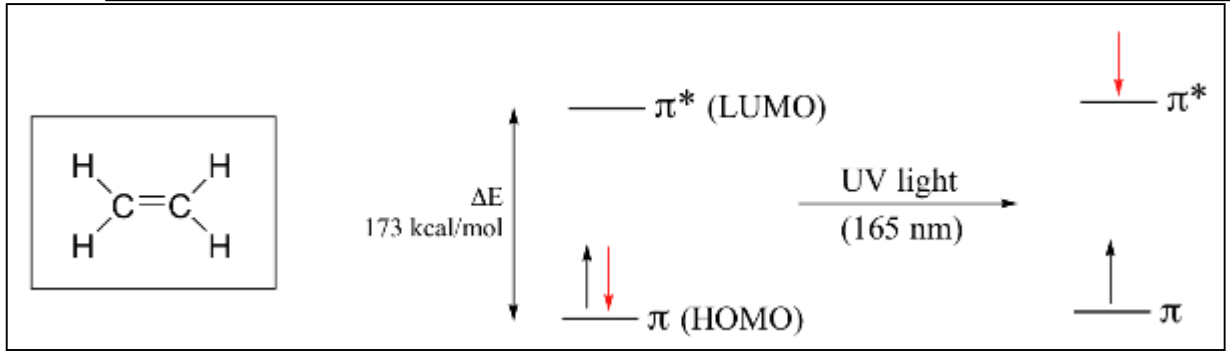


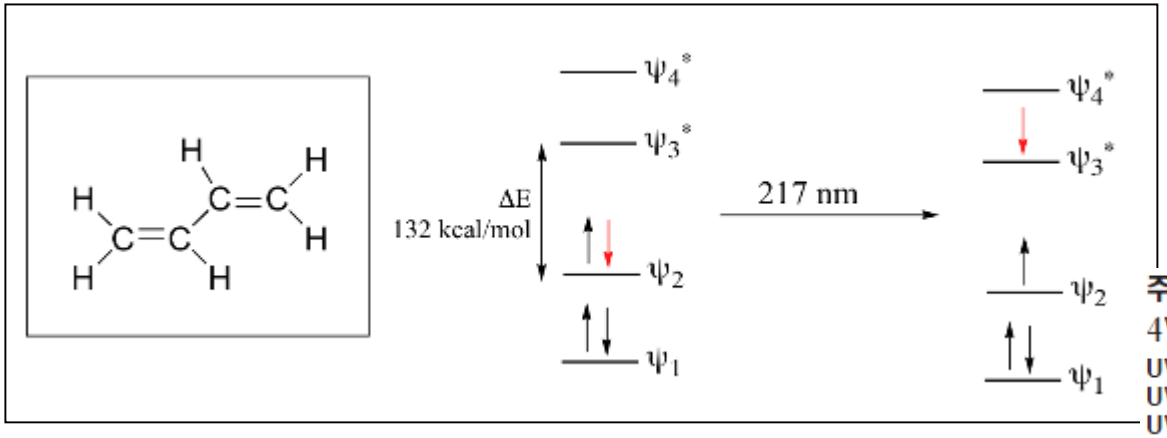


결론: double bond가 많고 conjugation이 많을 수록 energy gap이 작아진다.

- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm





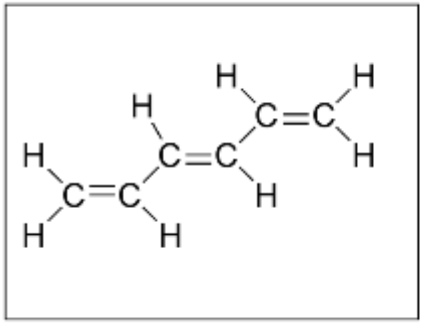


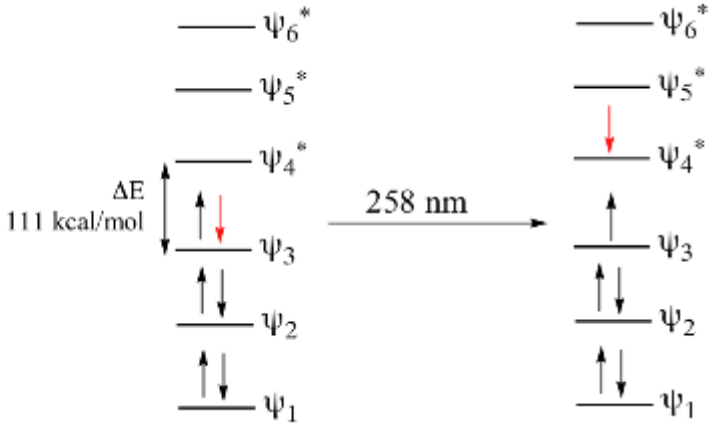
주문 (Ordering)

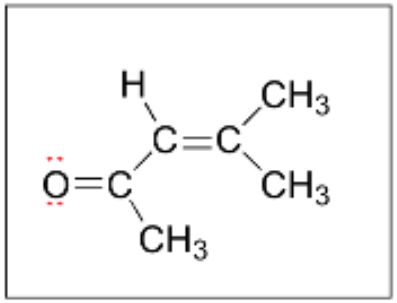
4W Tubes (Filter Size 50× 75 mm)

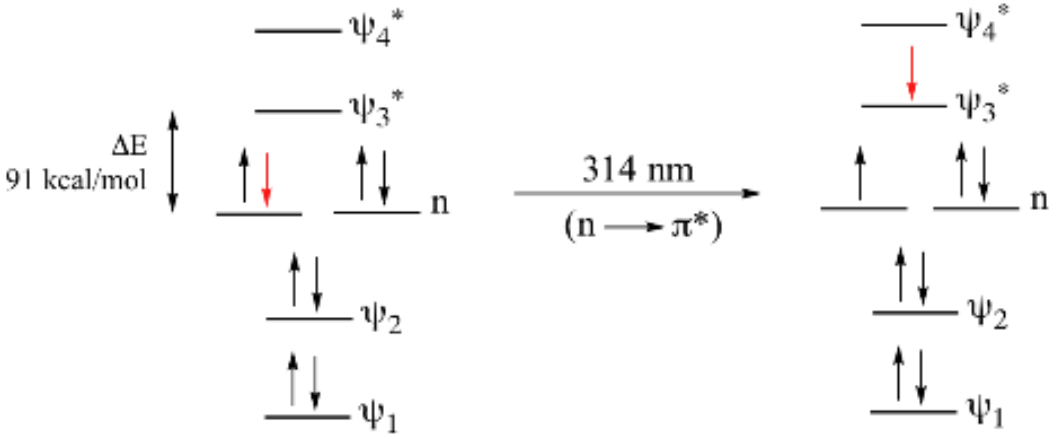
UV.LF104L	UV Lamp, 1×4W Tube, 365 nm
UV.LF104S	1×4W Tube, 254 nm
UV.LF204LS	1×4W / 1×4W Tube, 365 / 254 nm

- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

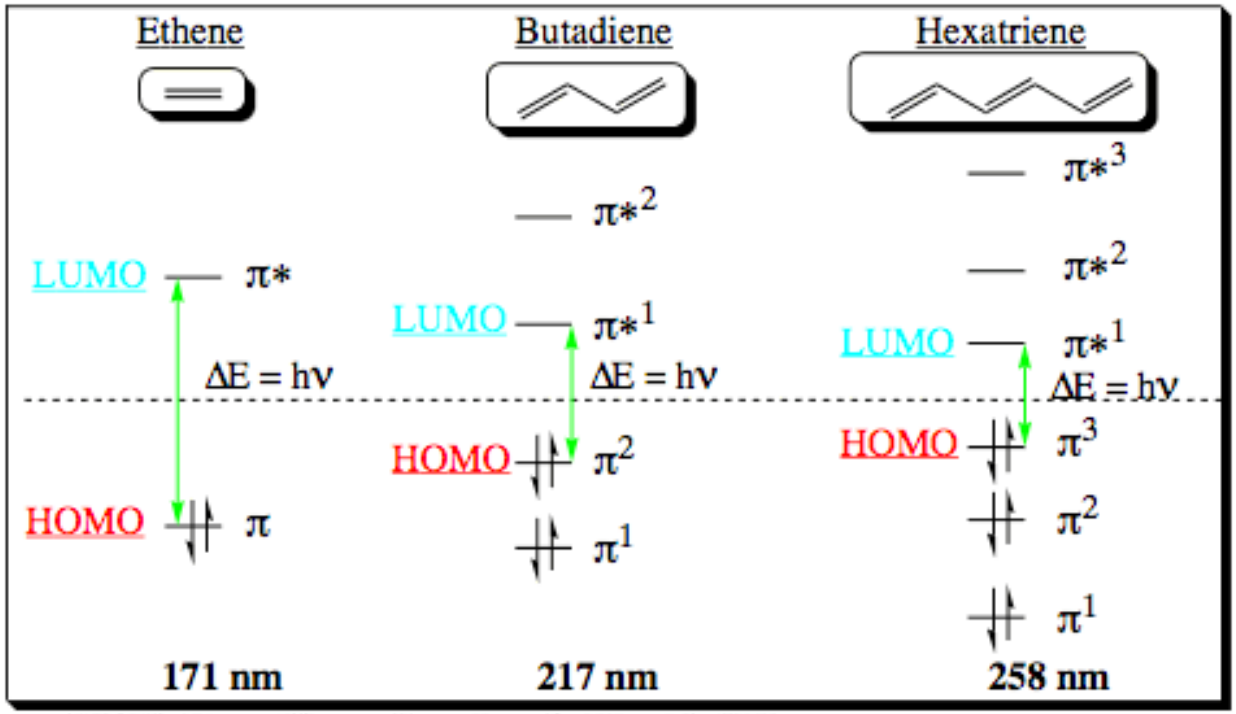




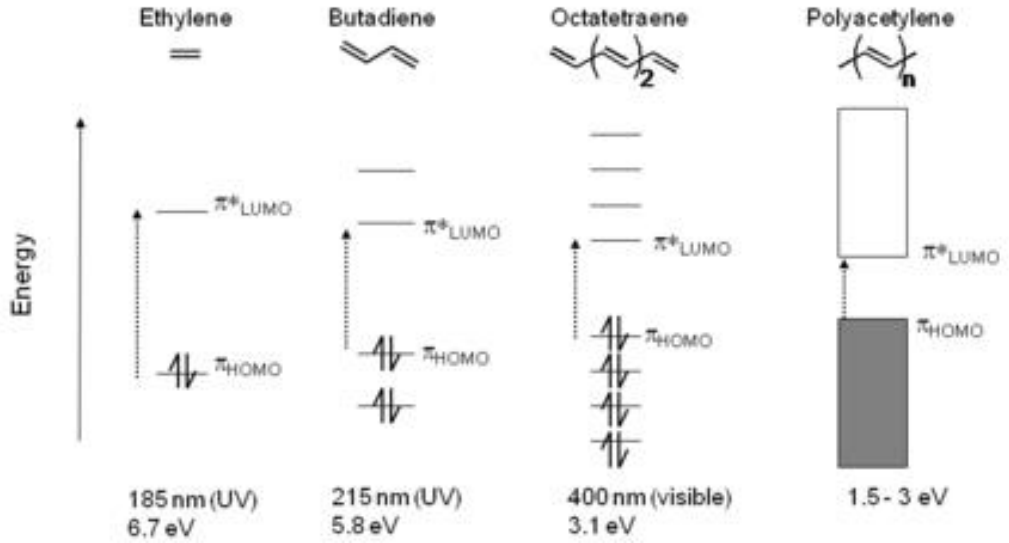




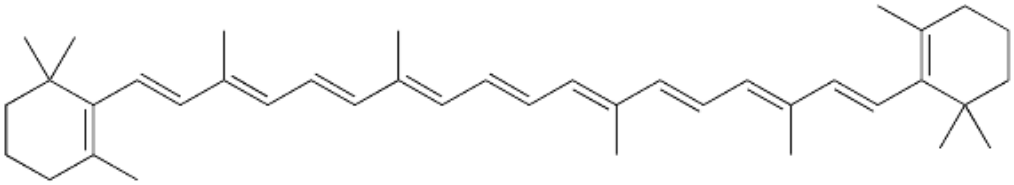
결론: double bond가 많아지고, energy gap이 작아지면서 UV 흡수가 가능하게 된다.



Light absoprtion of conjugated materials



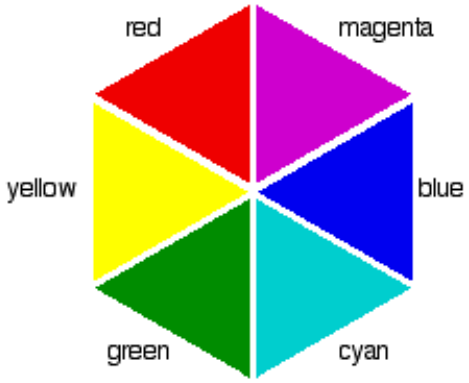
Complementary colors (보색)



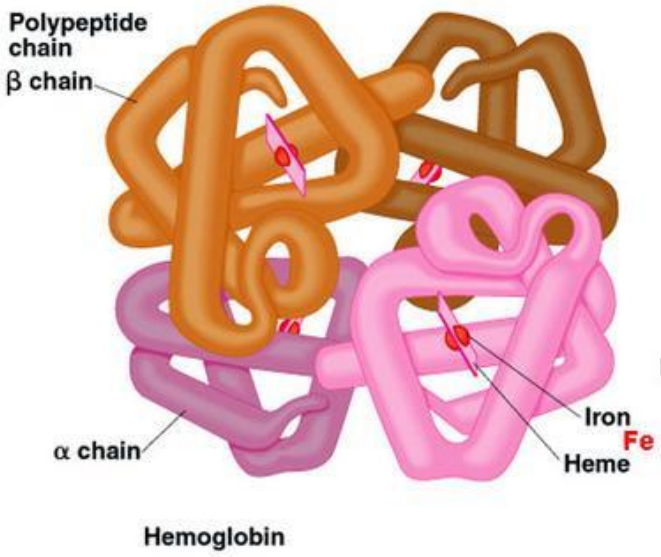
β-carotene

가시광선(파란색) 흡수

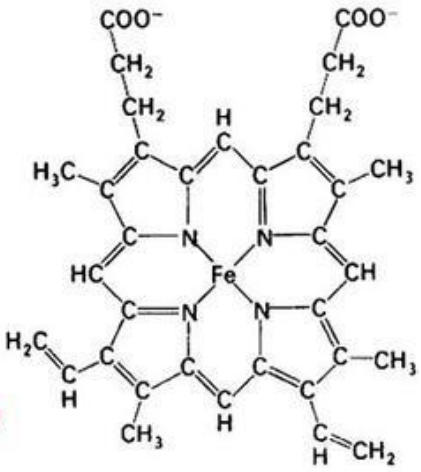
우리눈에는 빨노색으로 보임



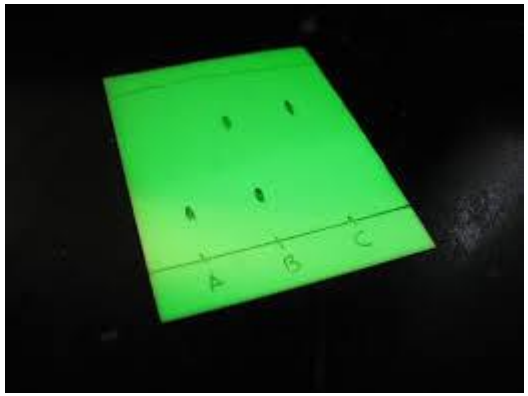
a color wheel

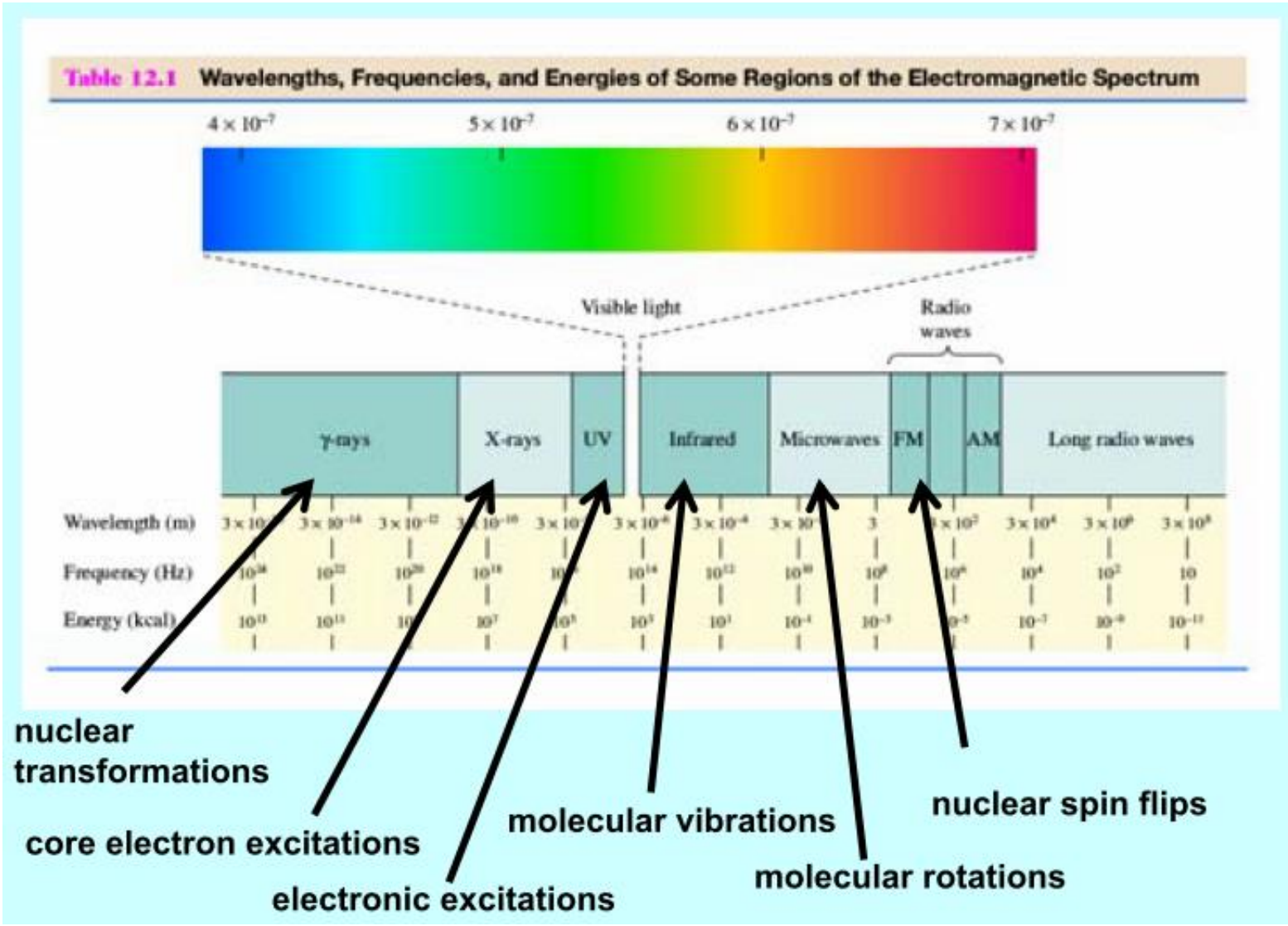


Hemoglobin



Heme
(Fe-protoporphyrin IX)





각각의 EM wave의 영역에 따라 에너지가 다르므로, 분자 및 원자에 끼치는 영향이 다르다.