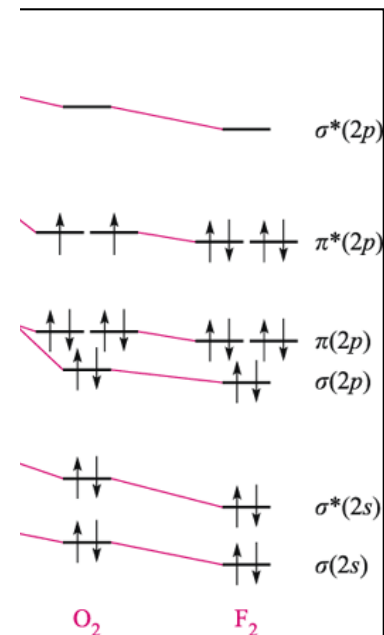
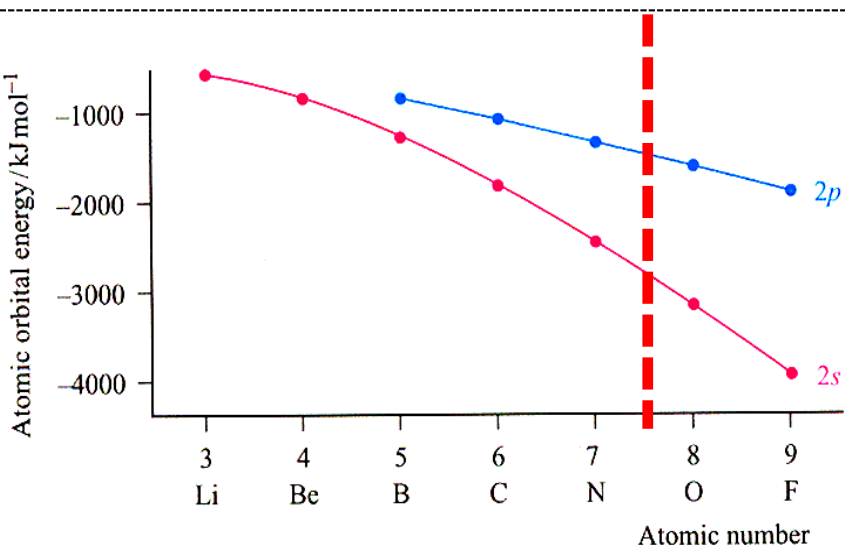
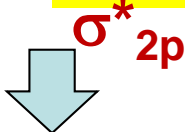


Review

Small S-P Energy Separation \rightarrow S-P orbital mixing



energy $\sigma_{2p} < 2\pi_{2p} < 2\pi^*_{2p} <$



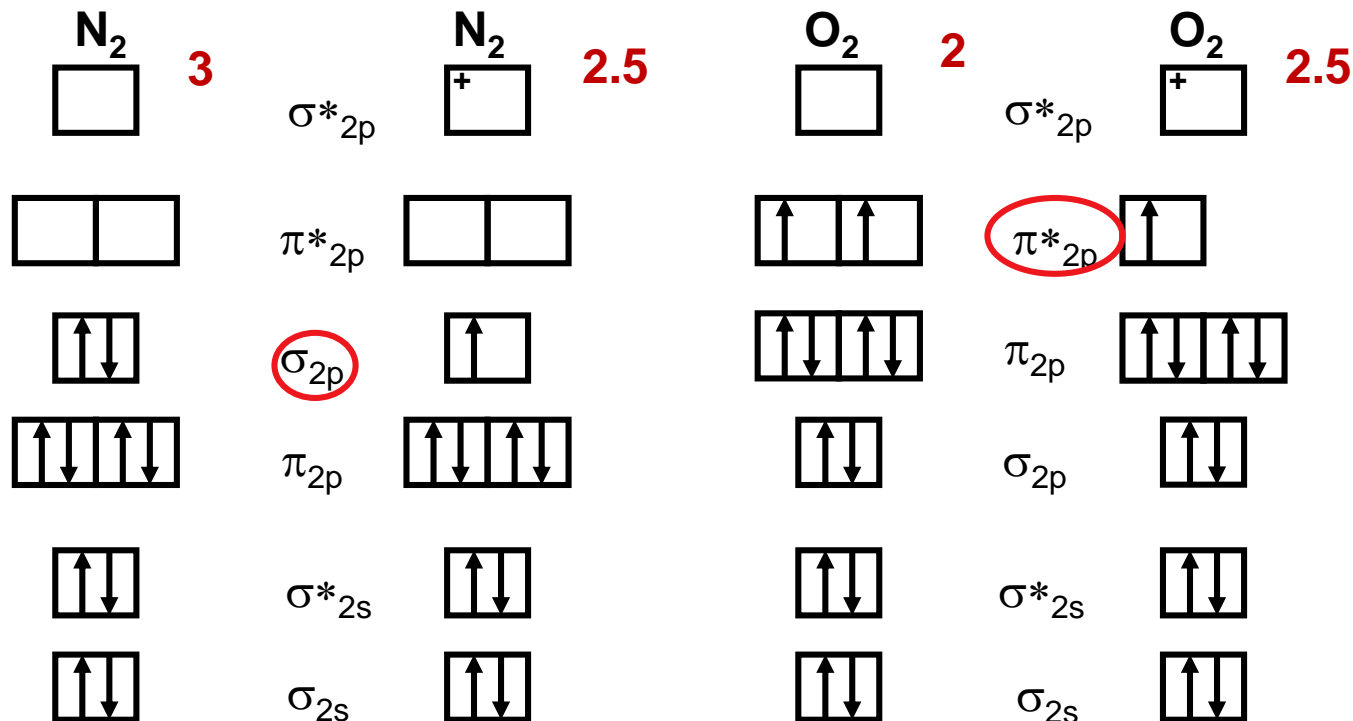
energy $2\pi_{2p} < \sigma_{2p} < 2\pi^*_{2p} < \sigma^*_{2p}$

\leq half filled *p* orbitals (B, C, N)

Review

MO Theory Explains Bonding

bond
order



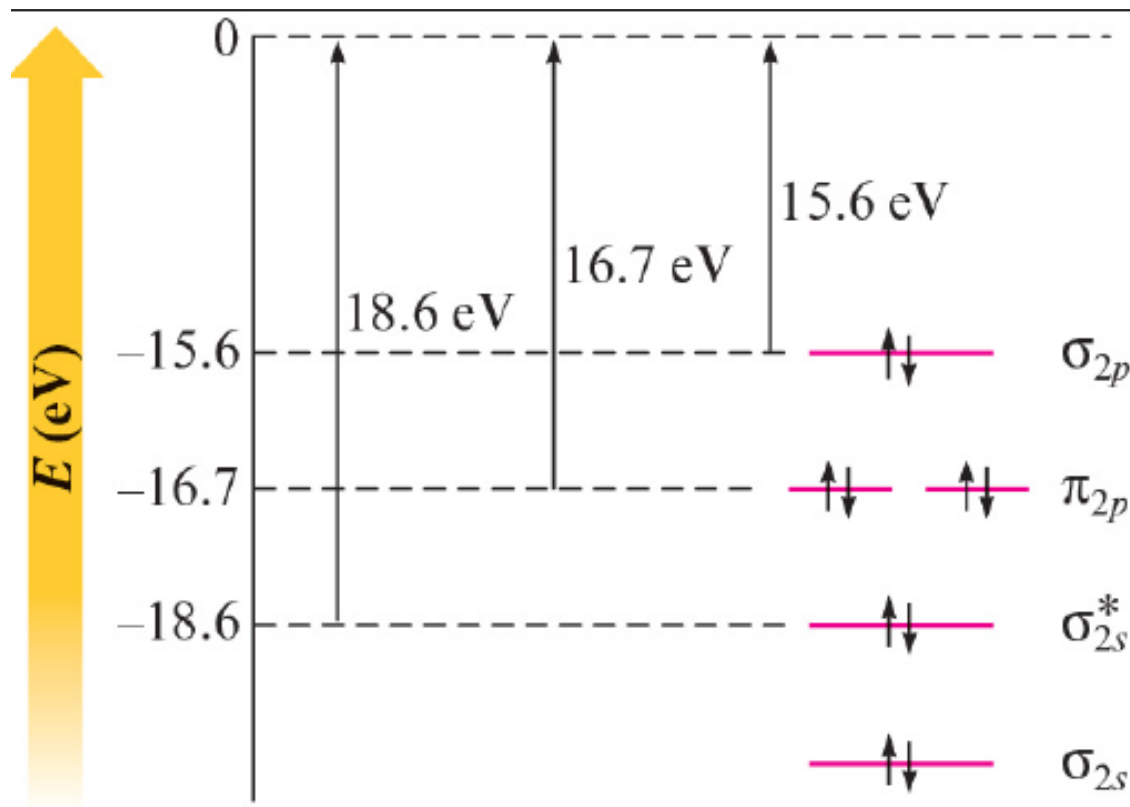
As the following data show, removing a **bonding electron** from N_2 forms an ion with a weaker, longer bond than in the parent molecules, whereas the ion formed from O_2 by removing an **antibonding electron** has a stronger, shorter bond:

	N_2	N_2^+	O_2	O_2^+
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

	B ₂	C ₂	N ₂	O ₂	F ₂
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Photoelectron Spectroscopy (PES) for Molecules

Additional

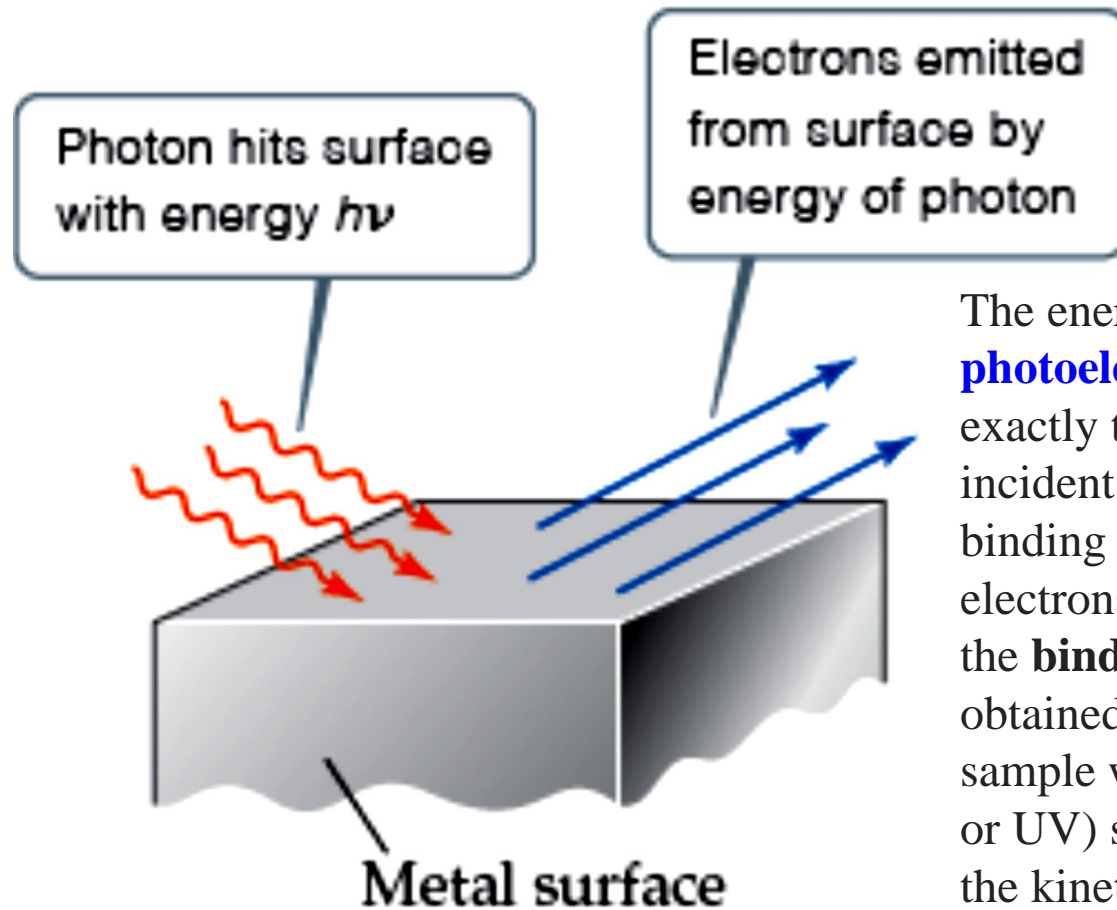


PES spectrum of N_2 : representation of the various electrons from nitrogen molecule.

no transition from σ_{2s} :
the electrons have such low
energy that they require
more than the **21.2 eV** that
can be furnished by the
helium source.

PES provides valuable information about **the energy levels of electrons in molecules**; a useful tool for characterizing and testing the theories of **bonding in molecules**

The incoming photon **must have enough E** to kick electrons off metal.



The energy of the **photoelectrons** emitted is exactly the energy of the incident photon minus the binding energy of the electrons of the material. Thus the **binding energy** can be obtained by bombarding the sample with a **photon** (X-rays or UV) source, and measuring the kinetic energy distribution of the electrons emitted.

▲ **Figure 6.7** The photoelectric effect.

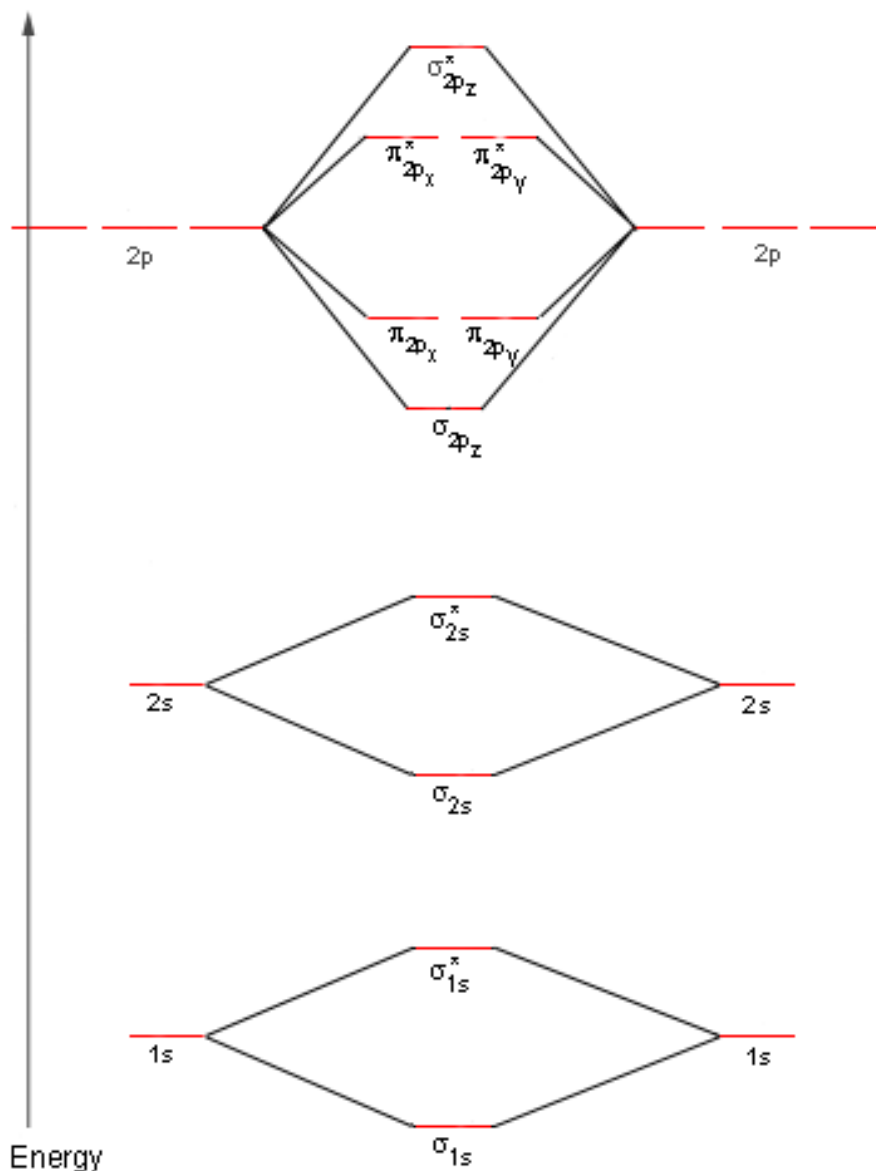
In PES, high-energy photons (the photon source is helium gas, photons emitted from excited helium atom are with a wavelength of 58.4 nm, high enough to eject electrons from any common atoms and molecules) are directed at the sample, and the KE of ejected electrons are measured.

$$\begin{aligned} \text{Energy of the electron} &= \text{Energy of photons used} \\ &\quad - \text{Kinetic energy of the electron} \end{aligned}$$

From this information, we can determine the **relative energies of electrons** in individual atoms/molecules or analyse for the presence of specific elements in samples by identifying known binding energies. For example, the O_{1s} electrons occur in the PES spectrum at 530 eV (using photon energy 640 eV or greater) and C_{1s} appears at 285 eV (using photon energy of 350 eV or greater).

MO Diagrams for O₂ and F₂

A full diagram of the energy level of molecular orbitals



Exercise: Write the electron configurations for O₂, O₂⁻, F₂, F₂⁻ & Ne₂.

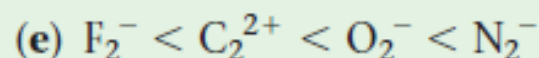
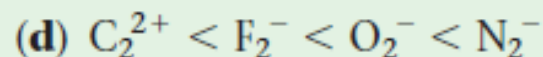
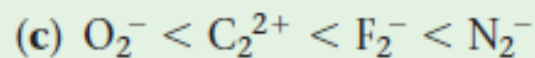
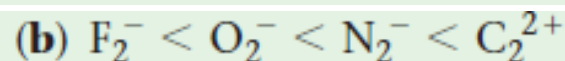
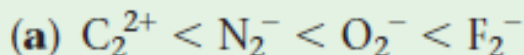
Sample Exercise 9.9

Molecular Orbitals of a Period 2 Diatomic Ion

For the O_2^+ ion predict **(a)** number of unpaired electrons, **(b)** bond order, **(c)** bond enthalpy and bond length.

Practice Exercise 1

Place the following molecular ions in order from smallest to largest bond order: C_2^{2+} , N_2^- , O_2^- , and F_2^- .



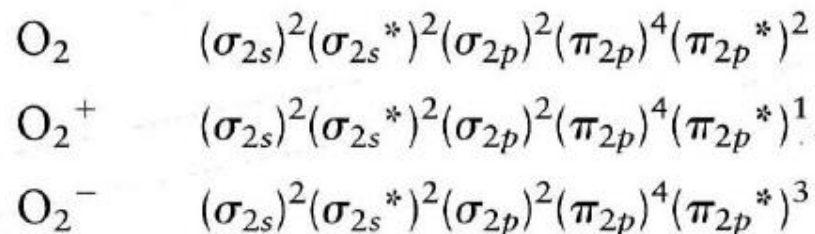
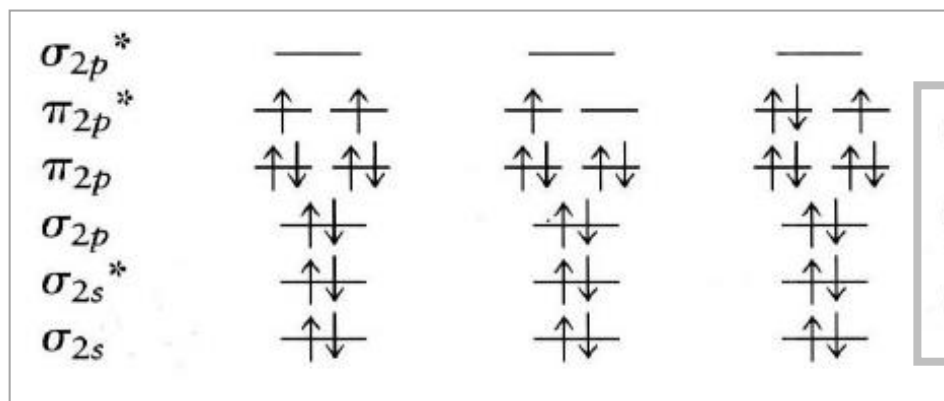
► Practice Exercise 2

Predict the magnetic properties and bond orders of **(a)** the peroxide ion, O_2^{2-} ; **(b)** the acetylide ion, C_2^{2-} .

Example

For the species O_2 , O_2^+ , and O_2^- , give the electron configuration and the bond order for each. Which has the strongest bond?

MO



The bond orders are as follows:

$$\text{For } O_2: \quad \frac{8 - 4}{2} = 2$$

$$\text{For } O_2^+: \quad \frac{8 - 3}{2} = 2.5$$

$$\text{For } O_2^-: \quad \frac{8 - 5}{2} = 1.5$$

Thus O_2^+ is expected to have the strongest bond of the three species.

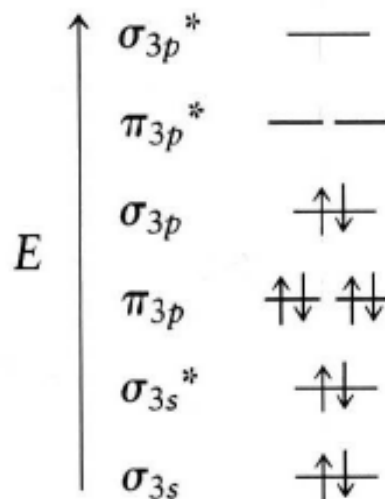
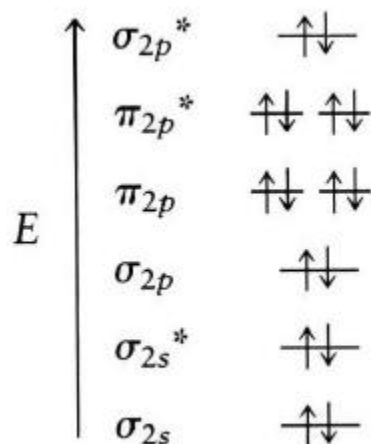
Experimental evidence supports these predictions. The bond energies for O_2^+ , O_2 , and O_2^- are 643, 495, and 395 kJ/mol, respectively.

Example

Use the MO model to predict the bond order and magnetism of each molecule.

a. Ne_2

b. P_2

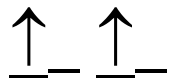


The bond order is $(8-8)/2 = 0$, so Ne_2 should not exist.

The molecule has a bond order of 3 and is expected to be diamagnetic. (It should be noted that phosphorus exists in nature as P_4 molecules)

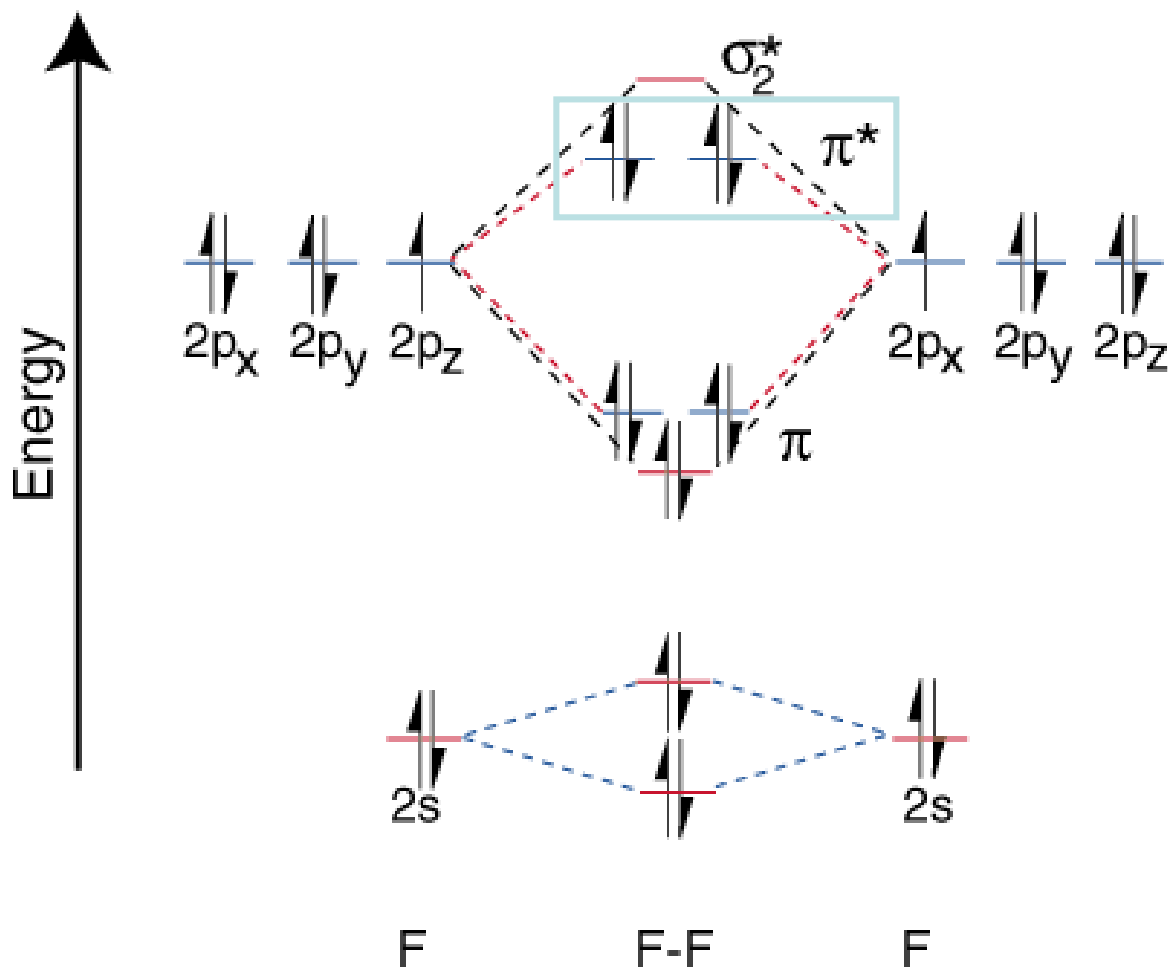
The O_2^+ , O_2 , O_2^- , & F_2^+ , F_2 , F_2^- Molecules

for $\bullet\text{O}=\text{O}\bullet$



O_2 : Paramagnetic ,
bond length indicates
double bond,
electronic
configuration agrees

**F_2 : electronic
configuration agree
with single bond.**



MO Theory Explains Bonding

As the following data show, removing an electron from N_2 forms an ion with a weaker, longer bond than in the parent molecules, whereas the ion formed from O_2 has a stronger, shorter bond:

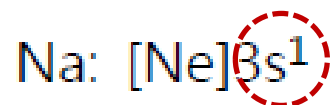
	N_2	N_2^+	O_2	O_2^+
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112

Give electronic configurations for

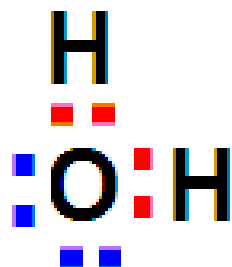
Be_2^+ , Be_2^- , B_2^+ , B_2 , B_2^- , C_2^+ , C_2 , C_2^- , N_2^+ , N_2 , N_2^- .

Valence electrons and Octet Rule

Electrons in the **highest (outer)** electron level



Electrons are lost, gained or shared to form **the most stable arrangement of electrons, an octet** (or **duet** for hydrogen only), in which all atoms have a "noble" gas configuration.



LEWIS STRUCTURES

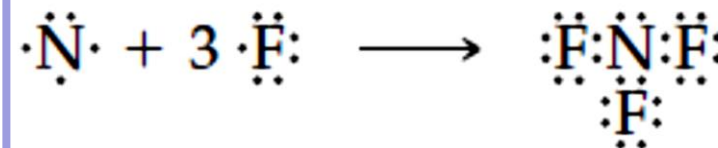
Using **dots** to represent **valence electrons (VEs)**

Building Lewis dot structures:

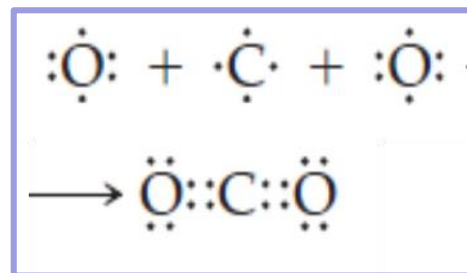
1. Sum the valence electrons for all atoms to determine **total number of VE**.
2. Use pairs of electrons to **form a bond** between each pair of atoms
3. Calculate **remaining electrons**
4. **Arrange** remaining electrons around atoms as bonding electrons (**BE**) and lone-pair electrons (**LE**) (assigning lone pairs to satisfy the "**octet rule**" or "**duet rule**"---for H only)



single bond



double bond

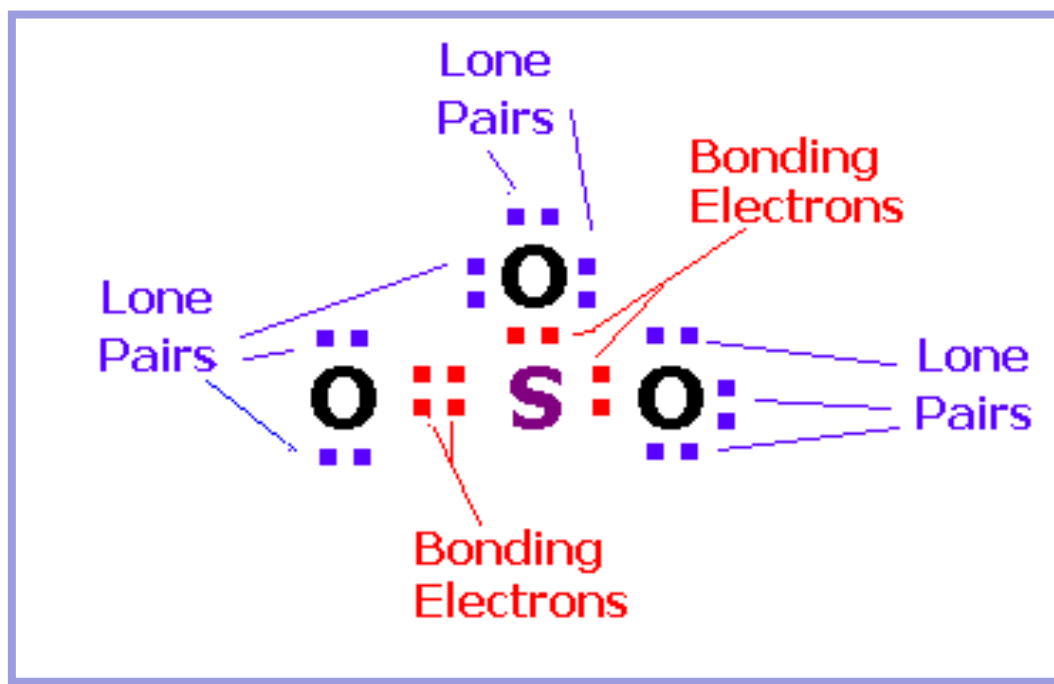


triple bond



Write Lewis dot structure for SO_3

1. total number of VE =
2. form a bond between each pair of atoms
3. no. remaining electrons =
4. Arrange remaining as BE and LE to satisfy the "octet rule"



	step 1 total # electrons	step 2 drawing bonds	step 3 remaining electrons	step 4	
HF	$1 + 7 = 8$	$\text{H} - \text{F}$	$8 - 2 = 6$	$\text{H} - \ddot{\text{F}}:$	H, 2 F, 8
N₂	$5 + 5 = 10$	$\text{N} - \text{N}$	$10 - 2 = 8$	$:\text{N} \equiv \text{N}:$	N, 8
NH₃	$5 + 3(1) = 8$	$\begin{array}{c} \text{H} - \text{N} - \text{H} \\ \\ \text{H} \end{array}$	$8 - 2(3) = 2$	$\begin{array}{c} \text{H} - \text{N} - \text{H} \\ \\ \text{H} \end{array}$	H, 2 N, 8
CH₄	$4 + 4(1) = 8$	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array}$	$8 - 4(2) = 0$	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \\ \\ \text{H} \end{array}$	H, 2 C, 8
CF₄	$4 + 4(7) = 32$	$\begin{array}{c} \text{F} \\ \\ \text{F} - \text{C} - \text{F} \\ \\ \text{F} \end{array}$	$32 - 4(2) = 24$	$\begin{array}{c} :\ddot{\text{F}}: \\ \\ :\ddot{\text{F}} - \text{C} - \ddot{\text{F}}: \\ \\ :\ddot{\text{F}}: \end{array}$	F, 8 C, 8
NO⁺	$5 + (6 - 1) = 10$	$\text{N} - \text{O}$	$10 - 2 = 8$	$[\text{N} \equiv \text{O}]^+$	O, 8 N, 8

Sample Exercise 8.7

Draw the Lewis structure for HCN

SOLUTION

Hydrogen has one valence electron, carbon (group 14) has four, and nitrogen (group 15) has five. The total number of valence electrons is, therefore, $1 + 4 + 5 = 10$. In principle, there are different ways in which we might choose to arrange the atoms. Because hydrogen can accommodate only one electron pair, it always has only one single bond associated with it. Therefore, **C—H—N is an impossible arrangement.** The remaining two possibilities are **H—C—N** and **H—N—C**. The first is the arrangement found experimentally. You might have guessed this because the formula is written with the atoms in this order, and **carbon is less electronegative than nitrogen.** Thus, we begin with the skeleton structure



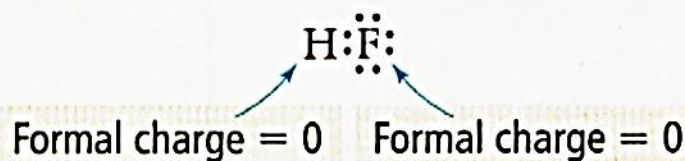
The octet rule is satisfied for the C and N atoms, and the H atom has two electrons around it. **This is a correct Lewis structure.**

Formal Charge and Alternative Lewis Structures

p. 361

When we draw a Lewis structure, we are describing how the electrons are distributed in a molecule or polyatomic ion. In some instances, we can draw two or more valid Lewis structures for a molecule that all obey the octet rule. All of these structures can be thought of as contributing to the *actual* arrangement of the electrons in the molecule, but not all of them will contribute to the same extent. How do we decide which one of several Lewis structures is the most important? One approach is to do some “bookkeeping” of the valence electrons to determine the *formal charge* of each atom in each Lewis structure.

Formal Charge is a fictitious charge assigned to each atom in a Lewis structure that helps us to distinguish among competing Lewis structures. The **formal charge** of an atom in a Lewis structure is *the charge it would have if all bonding electrons were shared equally between the bonded atoms*. In other words, formal charge is the calculated charge for an atom if we completely ignore the effects of electronegativity. For example, we know that because fluorine is more electronegative than hydrogen, HF has a dipole moment—the hydrogen atom has a slight positive charge and the fluorine atom has a slight negative charge. However, the *formal charges* of hydrogen and fluorine in HF (the calculated charges if we ignore their differences in electronegativity) are both zero.



Formal Charge

Formal charge = number of valence electrons –
(number of nonbonding electrons + $\frac{1}{2}$ number of bonding electrons)

So the formal charge of hydrogen in HF is 0:

$$\text{Formal charge} = 1 - \left[0 + \frac{1}{2}(2) \right] = 0$$

Number of valence

Number of electrons that H

Two possible Lewis structures. Which is better?



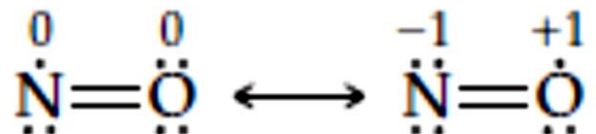
Heteronuclear Diatomic Molecule nitric oxide, NO

How many valence-shell electrons are there in NO?

The NO molecule controls several important human physiological functions. **Our bodies use it**, for example, **to relax muscles, kill foreign cells, and reinforce memory**. The 1998 Nobel Prize in Physiology or Medicine was awarded to three scientists for their research that uncovered the importance of NO as a “signaling” molecule in the cardiovascular system. **NO also functions as a neurotransmitter** and is implicated in many other biological pathways.

That NO plays such an important role in human metabolism was unsuspected before 1987 because NO has an odd number of electrons and is highly reactive.

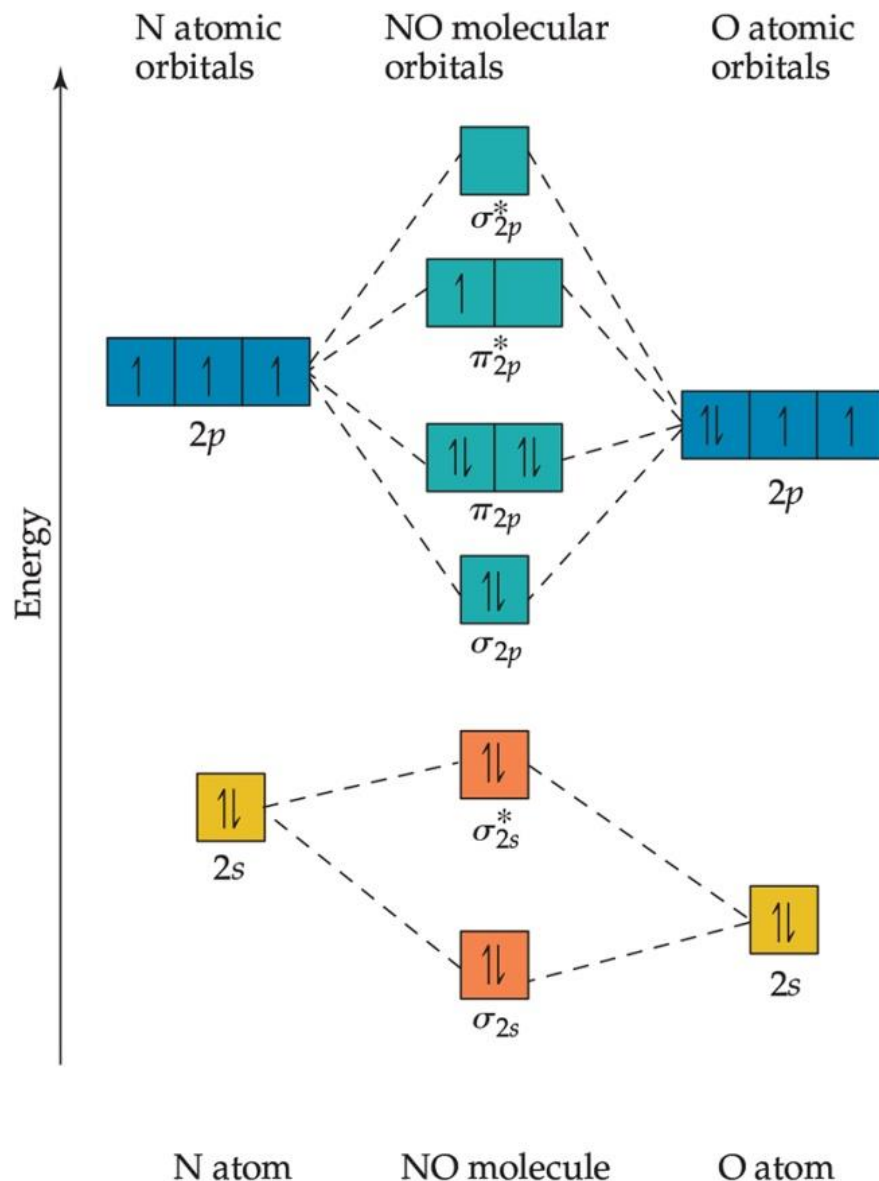
The molecule has two possible **Lewis structures** can be drawn. The Lewis structure with the lower **formal charges** places the odd electron on the N atom:



Both structures indicate the presence of a double bond, but the experimental bond length of NO (115 pm) suggests a bond order greater than 2.

Treat NO using the MO model

MO for **Hetero**nuclear Diatomic Molecules



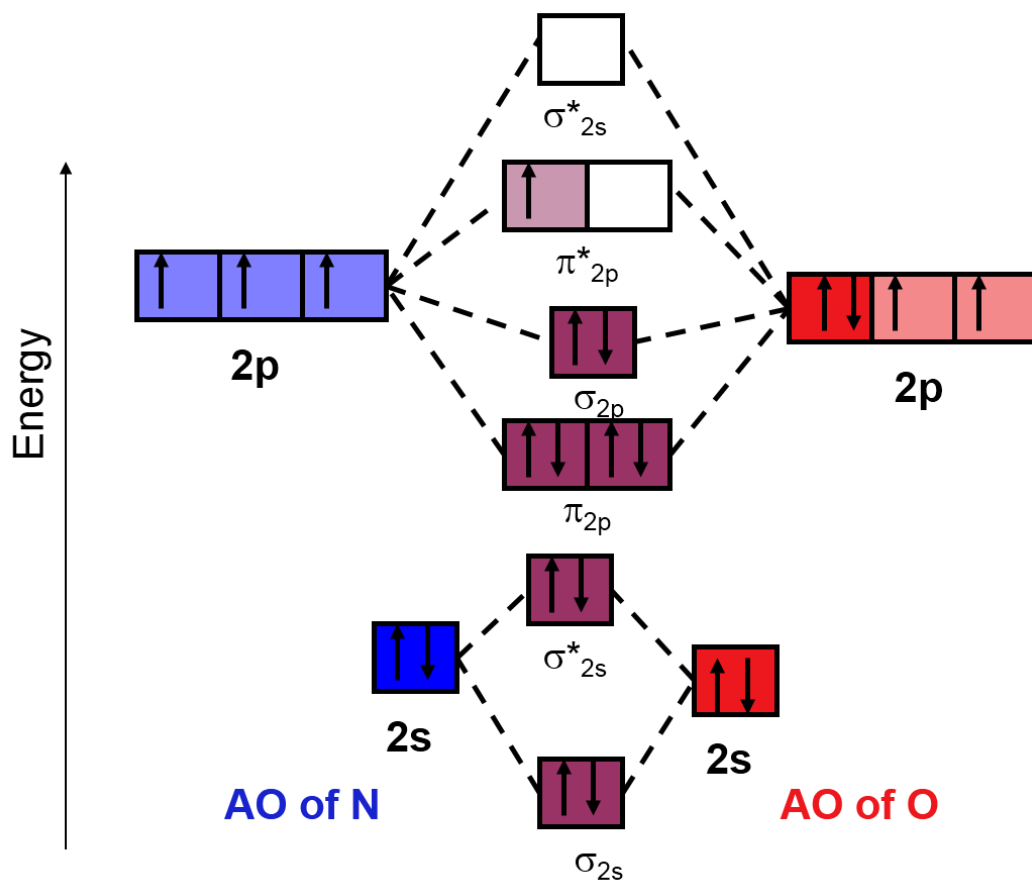
- Diatomic molecules can consist of atoms from different elements.
- How does a MO diagram reflect differences?
- The atomic orbitals have different energy, so the interactions change slightly.
- The more electronegative atom has orbitals lower in energy, so the bonding orbitals will more resemble them in energy.

Figure 9.46

Heteronuclear Diatomic Molecules

A special case (1) : when_ molecules containing **atoms adjacent to each other** in the periodic table; and MO diagram can be used for homonuclear molecules as atoms involved in such molecules are similar

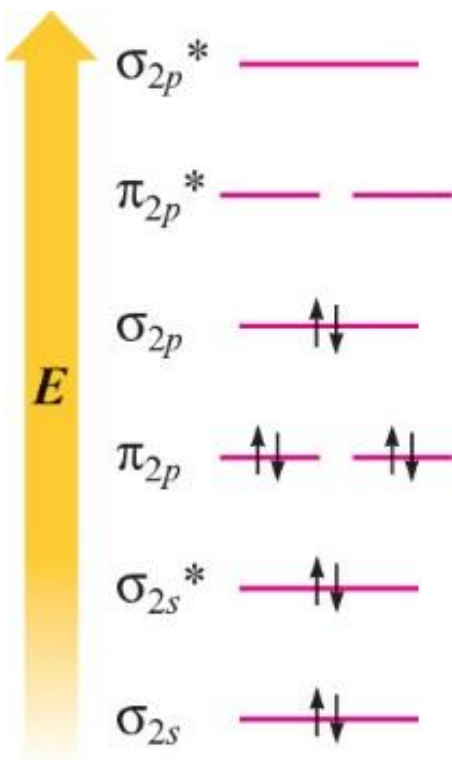
The MO diagram for NO



Bond order:

$$\frac{8 - 3}{2} = 2.5$$

Exercise: Use the molecular orbital model to predict the magnetism and bond order of the NO^+ and CN^- ions.



NO^+ ion has 10 valence electrons ($5 + 6 - 1$)

CN^- ion also has 10 valence electrons ($4 + 5 + 1$)

Both ions are diamagnetic

$$\text{Bond order} = \frac{8 - 2}{2} = 3$$

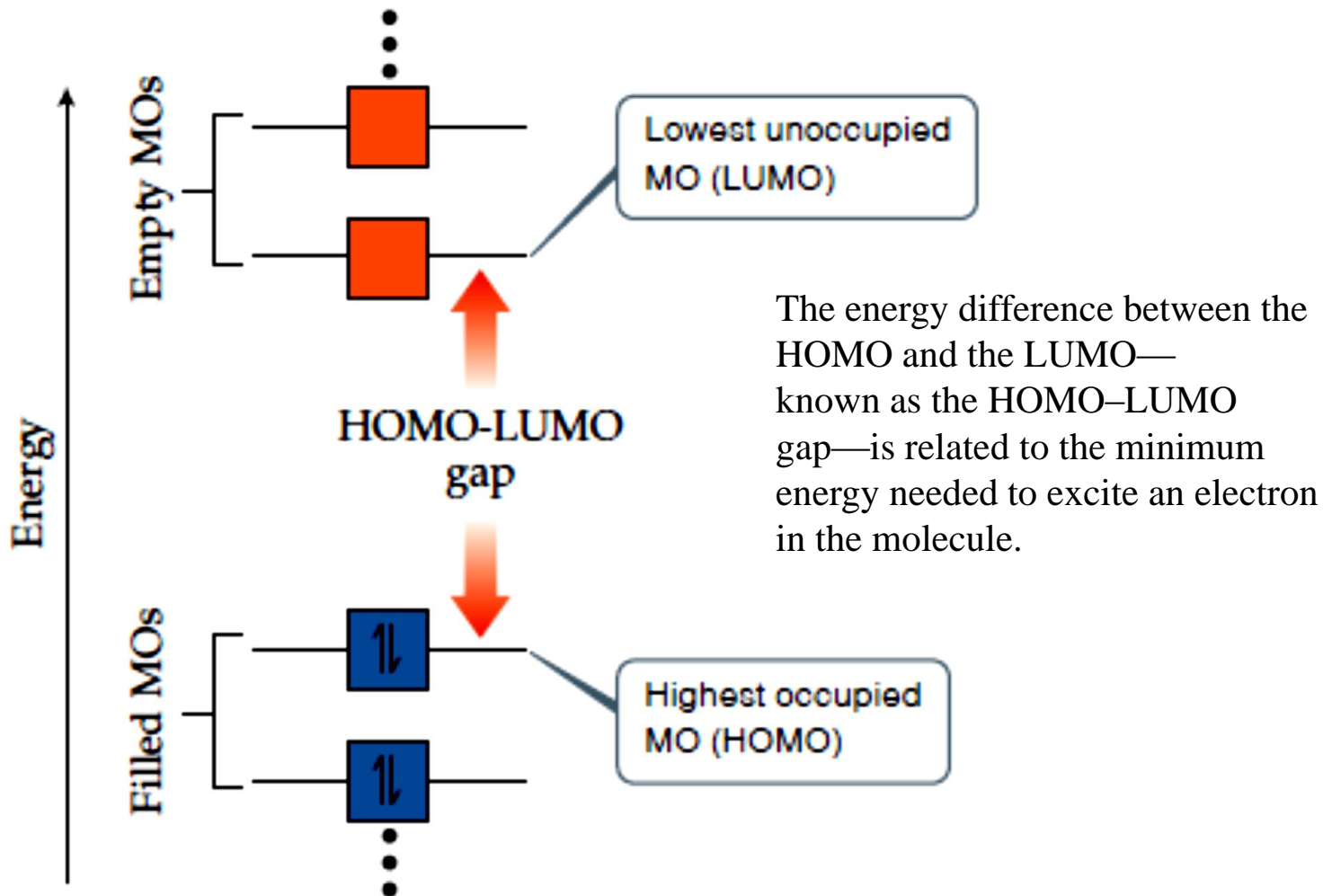


Figure 9.47 Definitions of the highest occupied and lowest unoccupied molecular orbitals. The energy difference between these is the HOMO-LUMO gap

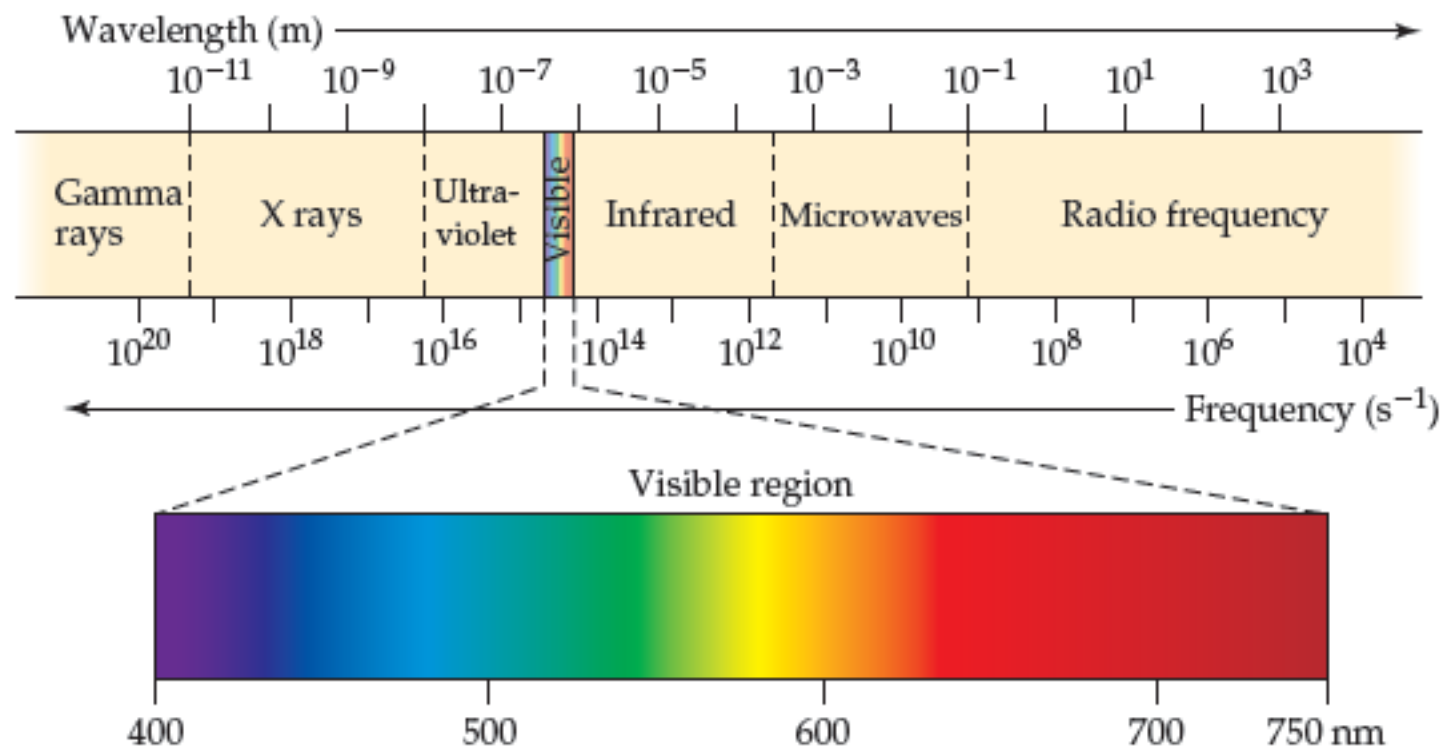
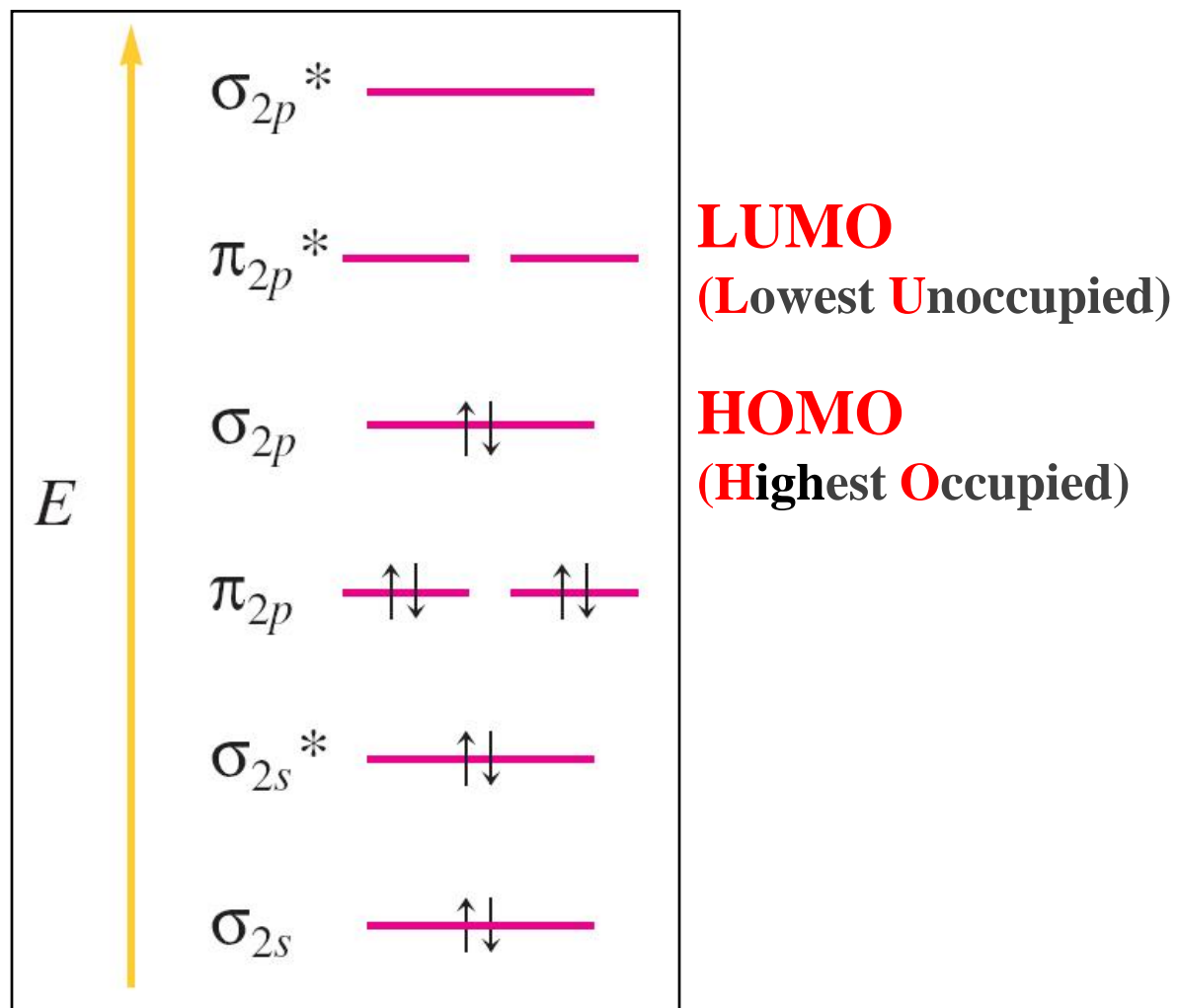


Figure 6.4 The electromagnetic spectrum.* Wavelengths in the spectrum range from very short gamma rays to very long radio waves.

The magnitude of the **energy gap** between filled and empty electronic states is critical for **solar energy conversion**. Ideally, we want a substance that absorbs as many solar photons as possible and then converts the energy of those photons into a useful form of energy. **Titanium dioxide** is a readily available material that can be **reasonably efficient at converting light directly into electricity**. However, **TiO₂ is white and absorbs only a small amount of the Sun's radiant energy**. Scientists are working to make solar cells in which **TiO₂ is mixed with highly colored molecules, whose HOMO–LUMO gaps correspond to visible and near-infrared light to absorb more of the solar spectrum**. If the HOMO of these molecules is higher in energy than the HOMO of TiO₂, the excited electrons will flow from the molecules into the TiO₂, thereby generating electricity when the device is illuminated with light and connected to an external circuit.

Efficient solar energy conversion promises to be one of the most interesting and important areas of both scientific and technological development in our future. Many of you may ultimately end up working in fields that have an impact on the world's energy portfolio.



The MO energy-level diagram for both the NO^+ and CN^- ions.

E

σ_{2p}^*

π_{2p}^*

σ_{2p}

π_{2p}

σ_{2s}^*

σ_{2s}

Absorbs

photon

σ_{2p}^*

π_{2p}^*

σ_{2p}

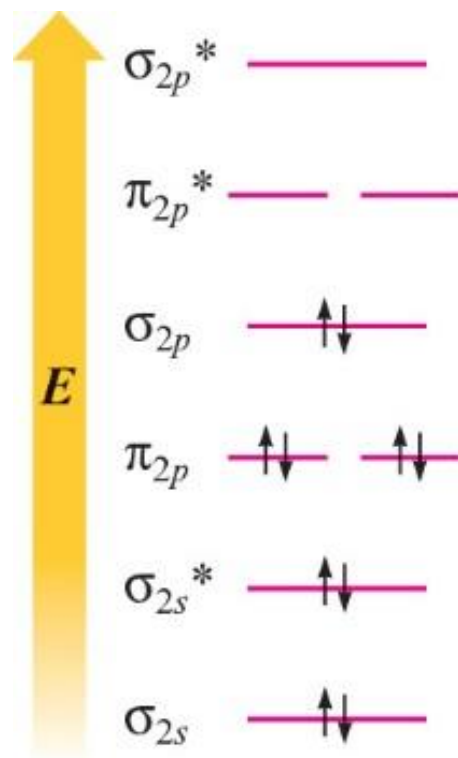
π_{2p}

σ_{2s}^*

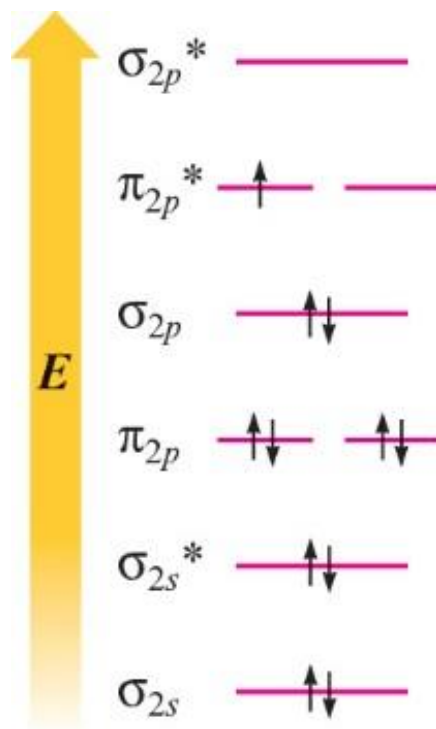
σ_{2s}

The molecular orbital diagram for the ground state of NO (on the left) and the first excited state of NO⁺ (on the right). This transition involves a bonding electron being transferred to an antibonding orbital.

NO⁺



NO



NO⁻

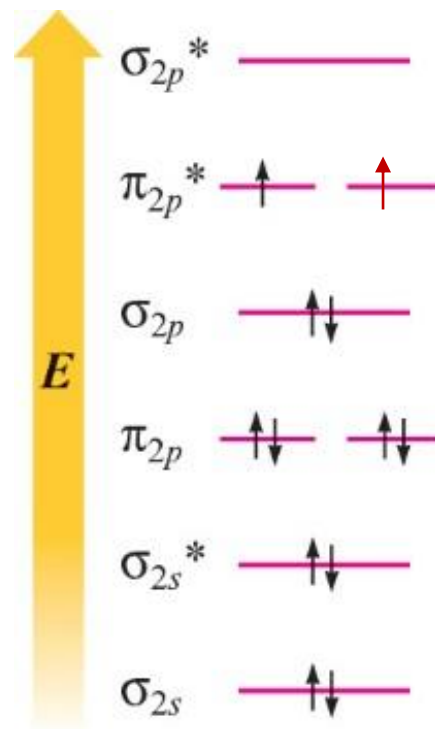


FIGURE 9.42

Both ions are paramagnetic

Heteronuclear Diatomic Molecules

A special case (2) : when the **two atoms** of a diatomic molecules are **very different**, the MO for homonuclear molecules cannot be used

Consider the hydrogen fluoride (HF) molecule:

- **Valence electrons:**
 - H – $1s^1$
 - F – $1s^2 2s^2 2p^5$
- **Accommodate for differences in electronegativity**
- **Allow mixing between symmetry-allowed states**

As you go from HF to HI, does the H—X bond become more or less polar?

TABLE 8.2 Bond Lengths, Electronegativity Differences, Moments of the Hydrogen Halides

Compound	Bond Length (pm)	Electronegativity Difference
HF	92	1.9
HCl	127	0.9
HBr	141	0.7
HI	161	0.4

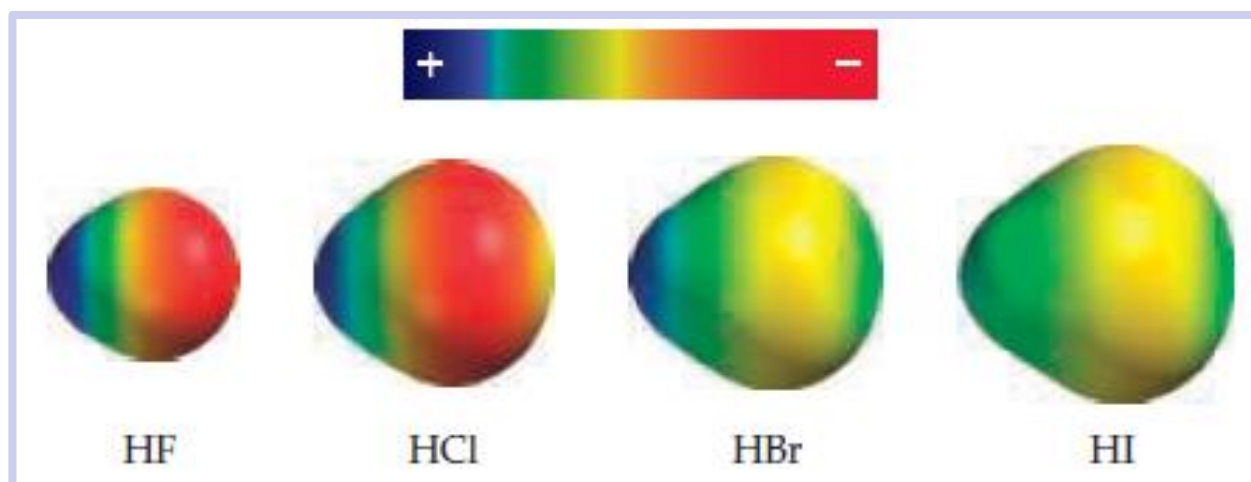
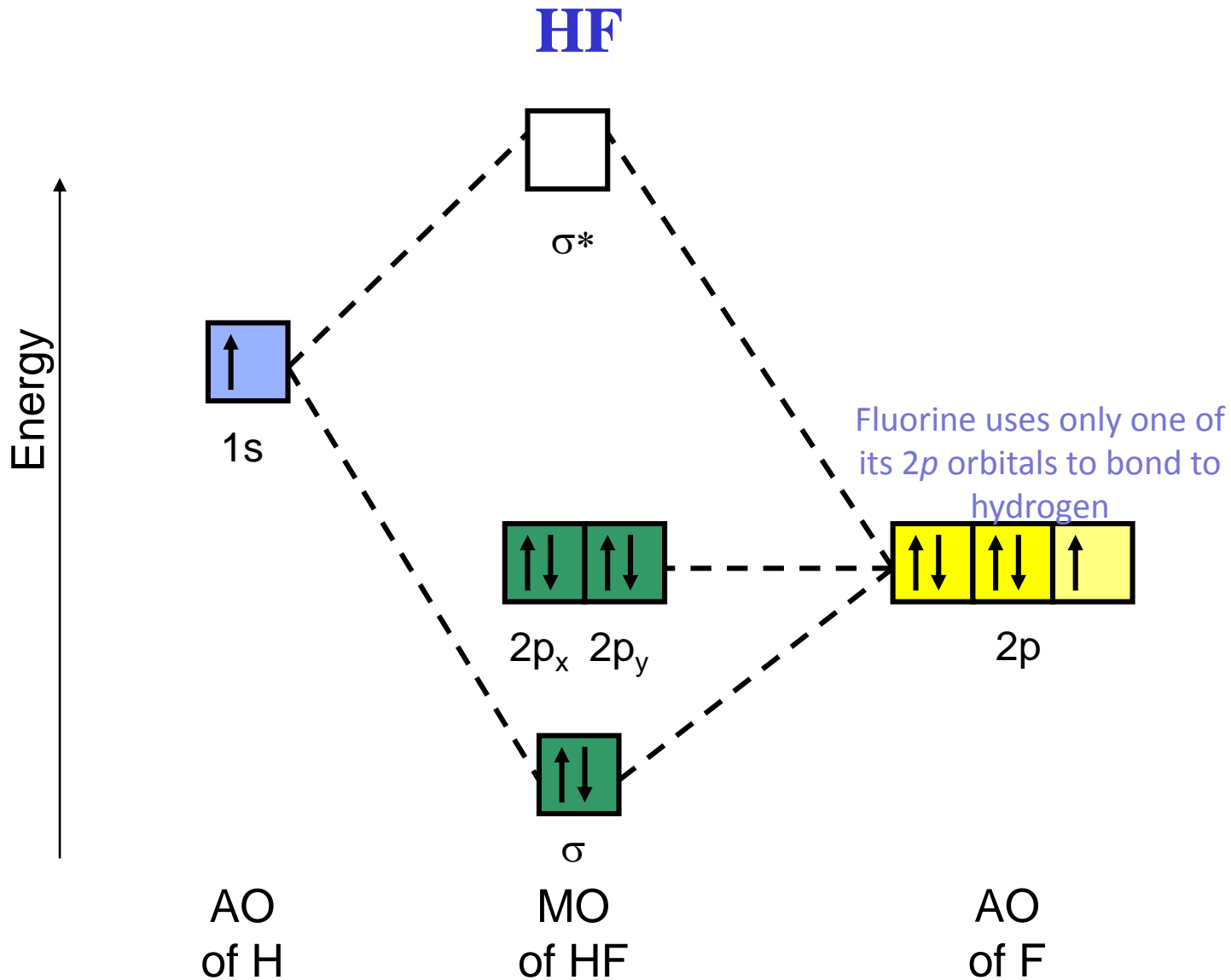


Figure 8.11 Charge separation in the hydrogen halides.

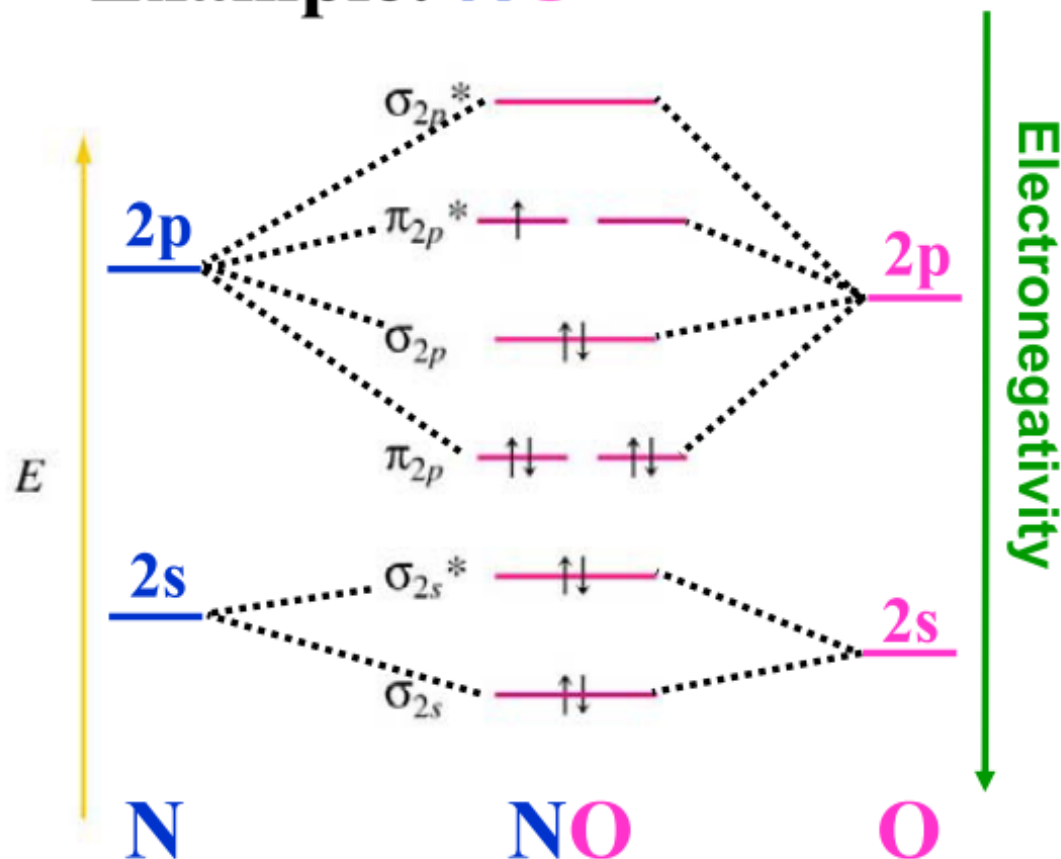


Electron configuration: H - $1s^1$

F - $1s^2 2s^2 2p^5$

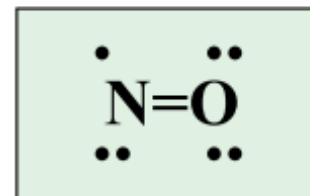
When the electronegativities of the 2 atoms are more similar, the bonding becomes less polar.

Example: **NO**

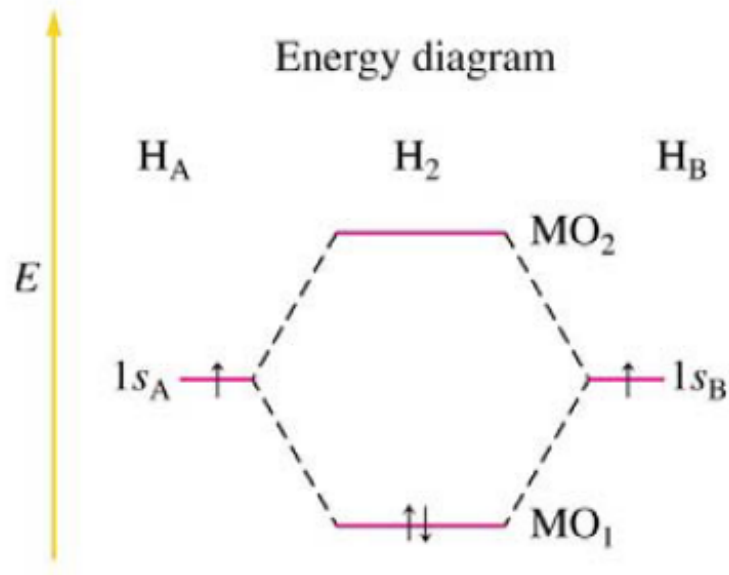


$$\chi(\text{N}) = 3.0$$

$$\chi(\text{O}) = 3.4$$



Homonuclear:



Nonpolar covalent bond
(450 kJ/mol bond)

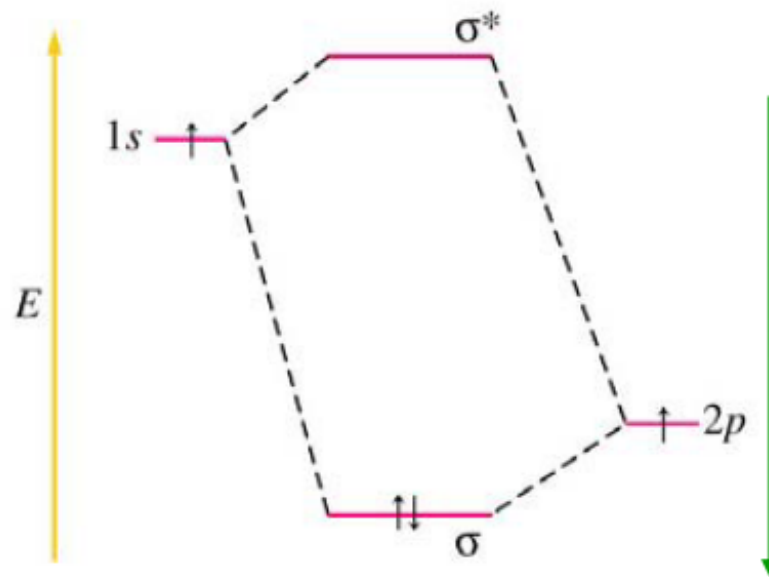
Heteronuclear:



H
atom

HF
molecule

F
atom

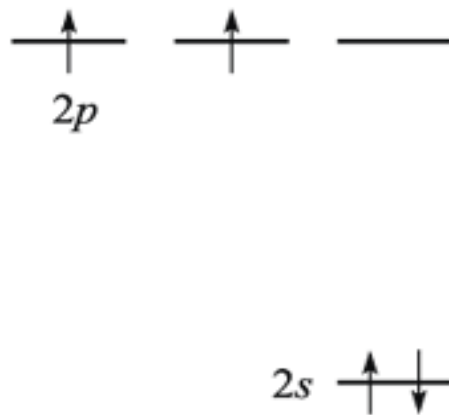


Electronegativity

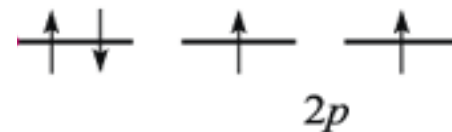
Polar covalent bond
(565 kJ/mol bond)

Atom Orbitals of C and O

Energy

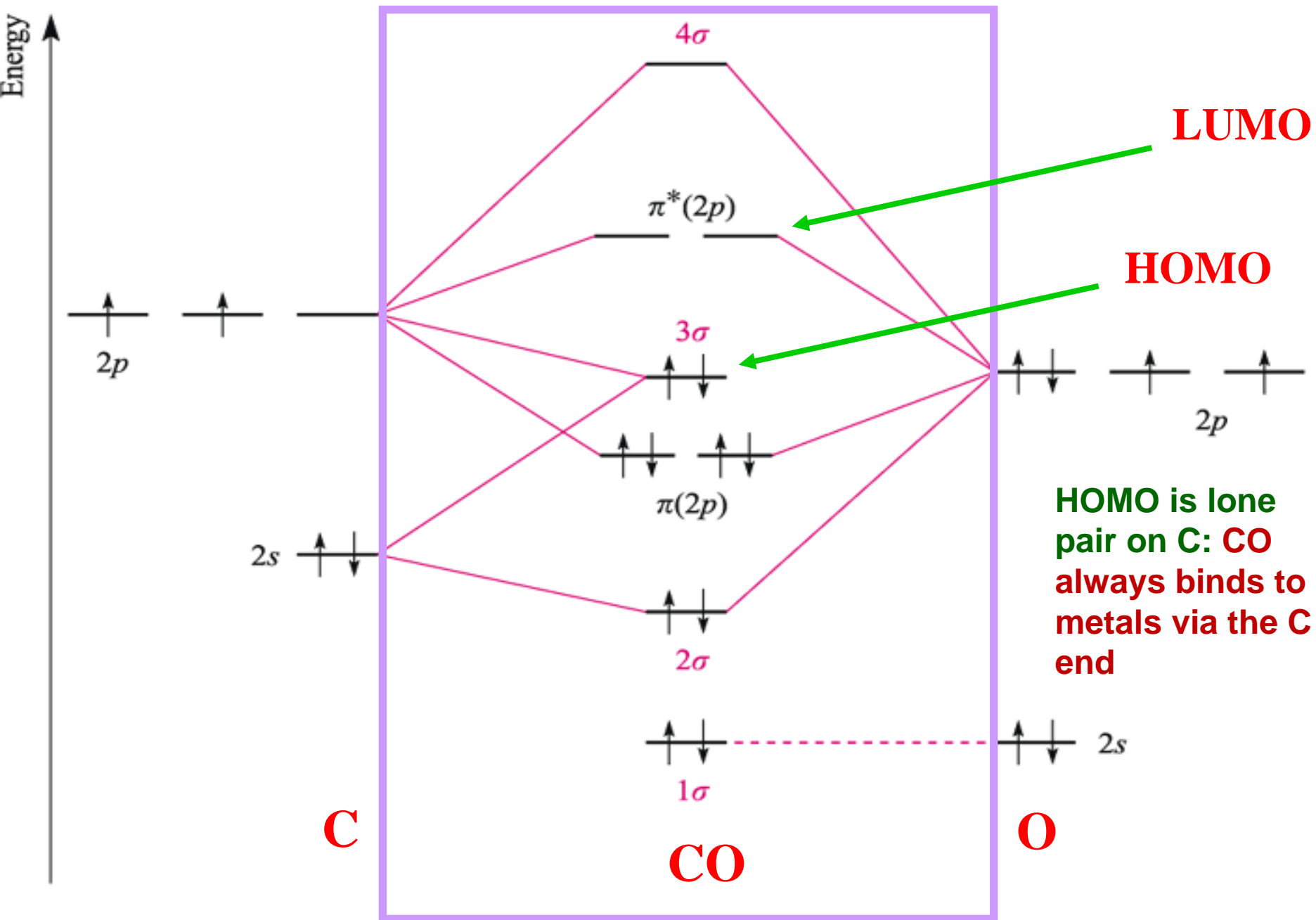


C



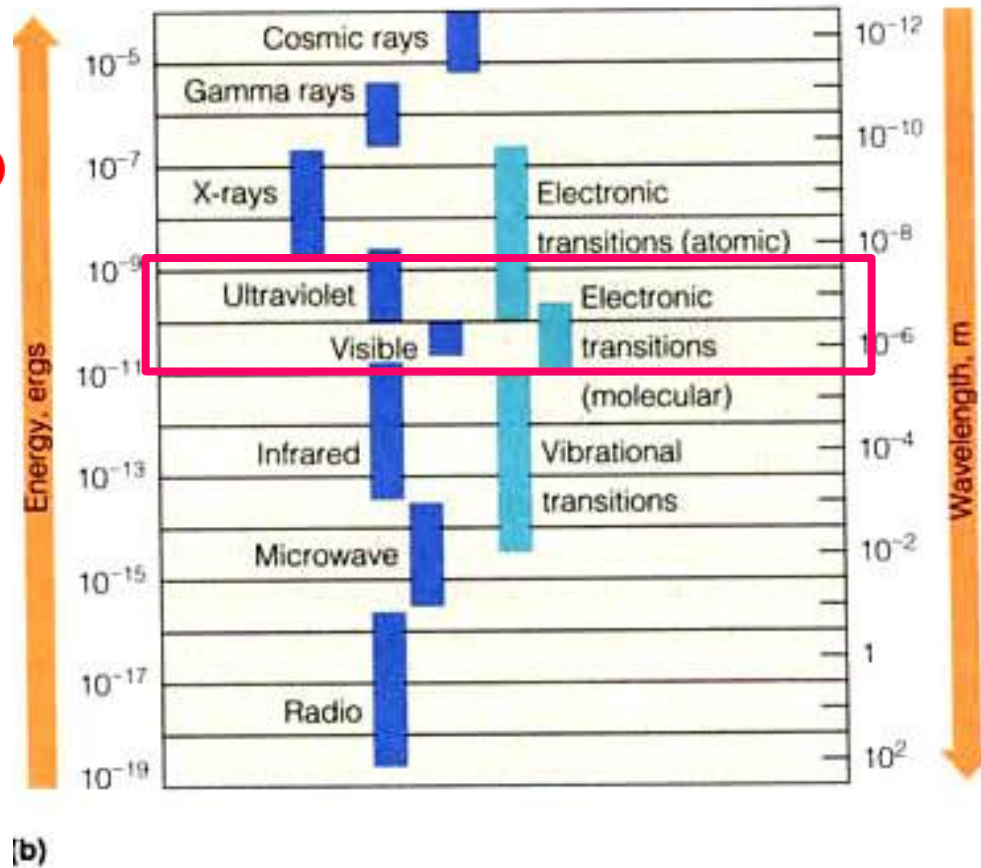
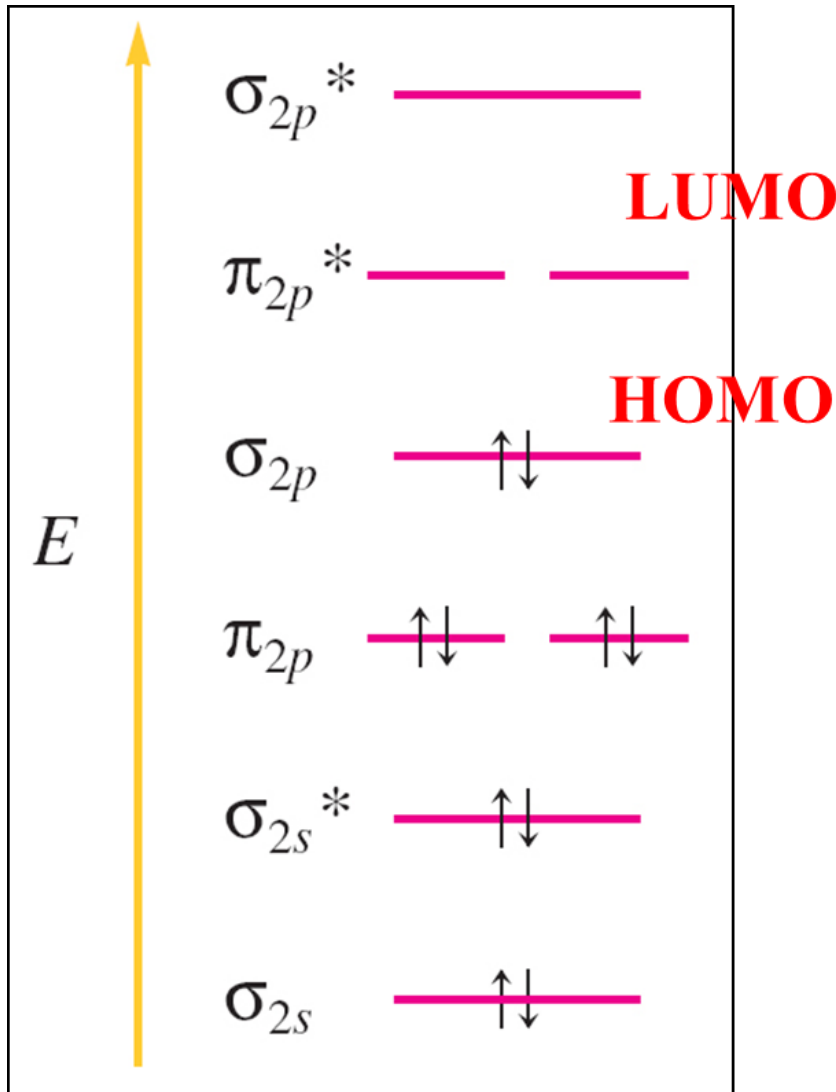
O

Molecular Orbital of CO

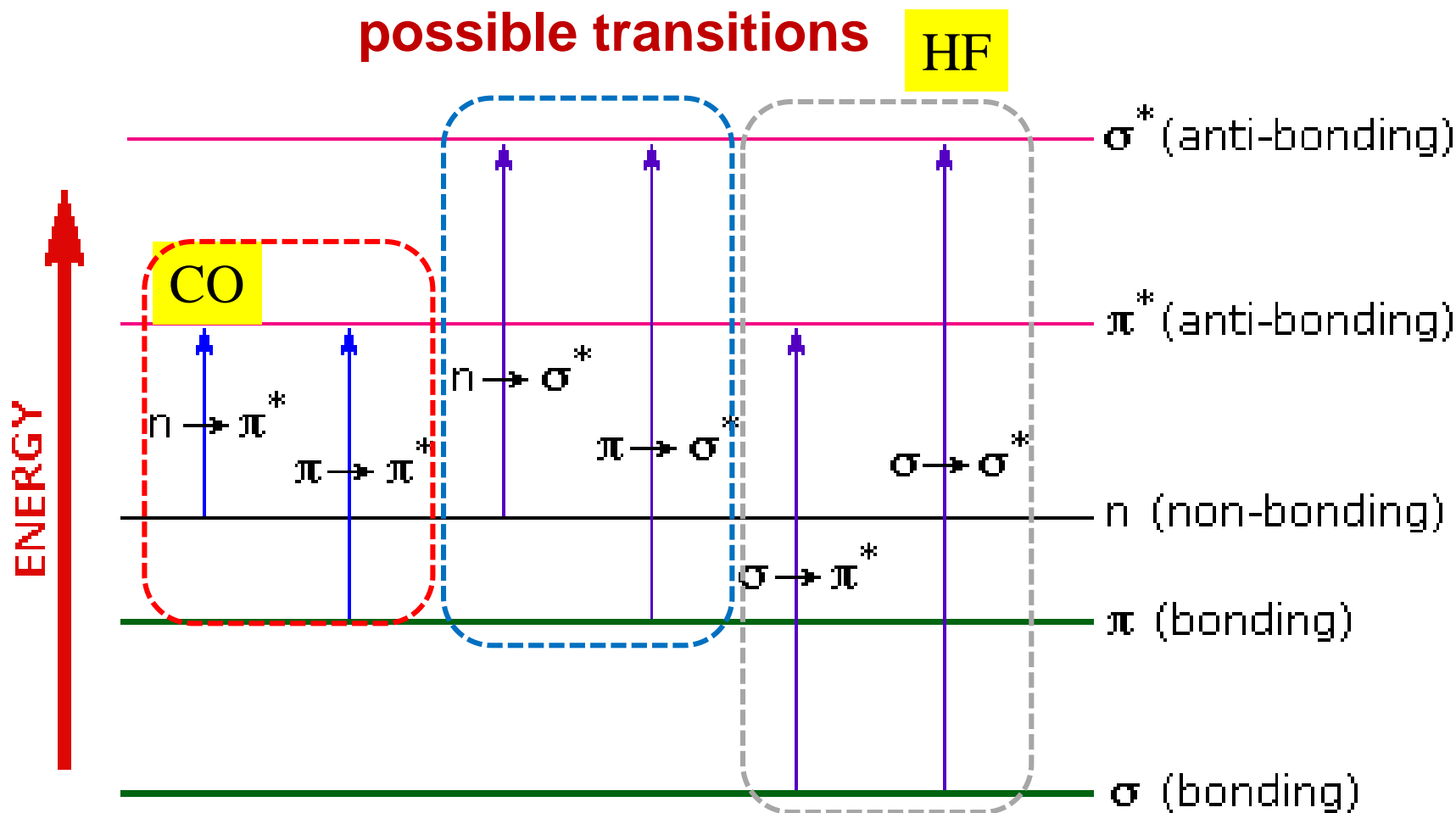


Molecular/Electronic Spectroscopy

- **Spectroscopy** can be defined as the study of the **interaction of electromagnetic radiation with matter**.
- Spectroscopy provides **a nondestructive and highly sensitive** method for obtaining information about the identity, structure, and properties of substances.
- This so-called **electronic transition** can be described approximately as a **change** from one **electron arrangement** to another.



The UV Absorption Process



•most common transitions observed in organic molecular UV-Vis, observed in compounds with lone pairs and multiple bonds with $\lambda_{\max} = 200\text{-}600\text{ nm}$.

wavelength (λ_{\max}) in the 150-250 nm region.
non-bonding electrons (lone pairs)

high-energy, accessible in vacuum UV ($\lambda_{\max} < 150\text{ nm}$).
Not usually observed in molecular UV-Vis spectroscopy

The UV Absorption Process

- $\sigma \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions:

high-energy, accessible in vacuum UV ($\lambda_{\text{max}} < 150$ nm).

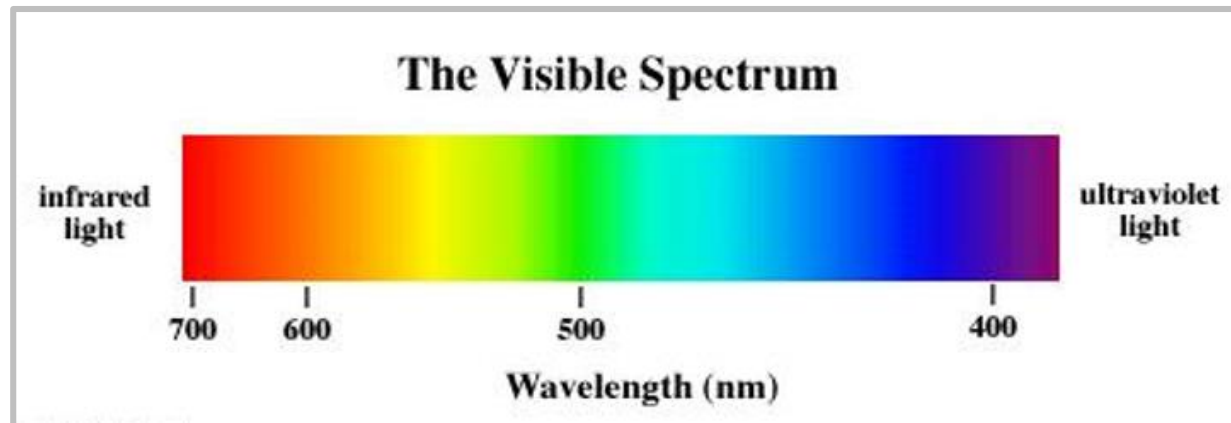
Not usually observed in molecular UV-Vis.

- $n \rightarrow \sigma^*$ and $\pi \rightarrow \sigma^*$ transitions:

wavelength (λ_{max}) in the 150-250 nm region.

non-bonding electrons (lone pairs)

- $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions: most common transitions observed in **organic molecular UV-Vis**, observed in compounds with lone pairs and multiple bonds with $\lambda_{\text{max}} = 200\text{-}600$ nm.



UV Regions

Name	Abbreviation	Wavelength range (in nanometres)	Energy per photon (in electronvolts)
visible to birds, insects and fish Near Ultraviolet	NUV	400 – 300 nm	3.10 – 4.13 eV
Ultraviolet A	UVA	400 – 315 nm	3.10 – 3.94 eV
Ultraviolet B	UVB	315 – 280 nm	3.94 – 4.43 eV
Ultraviolet C	UVC	280 – 100 nm	4.43 – 12.4 eV
Vacuum Ultraviolet	VUV	200 – 10 nm	6.20 – 124 eV
Extreme Ultraviolet	EUV	121 – 10 nm	10.25 – 124 eV

"SPF 15" means that 1/15th of the burning radiation will reach the skin (sunscreens with higher SPF do not last or remain effective on the skin any longer than lower SPF and must be continually reapplied).

The principal ingredients in sunscreens are usually aromatic molecules conjugated with carbonyl groups.

long wave, not absorbed by ozone layer, not cause sunburn but can increase the rate of melanoma and photodermatitis

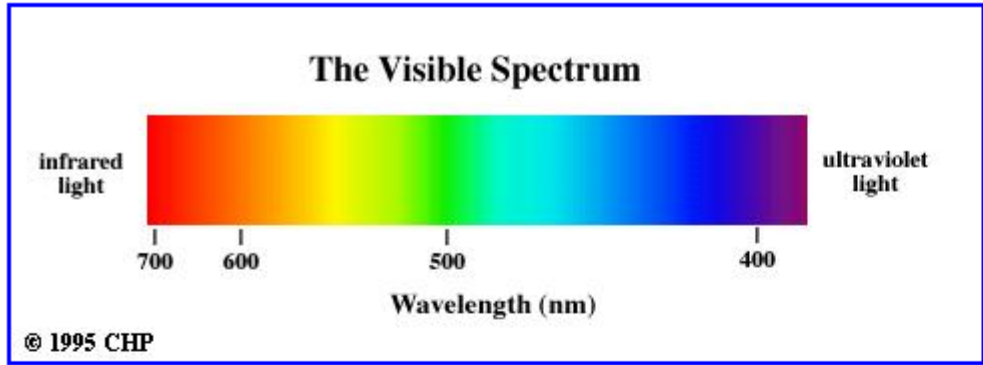
medium wave,
mostly absorbed by ozone layer
short wave, completely
absorbed by O₃ layer

strongly absorbed by atmospheric O₂, though 150-200 nm wavelength can propagate through N₂.

ionizing radiation, completely absorbed by the atmosphere

Molecular/Electronic Spectroscopy

- **Spectroscopy** can be defined as the study of the **interaction of electromagnetic radiation with matter**.
- Spectroscopy provides **a nondestructive and highly sensitive** method for obtaining information about the identity, structure, and properties of substances.
- This so-called **electronic transition** can be described approximately as a **change** from one **electron arrangement** to another.



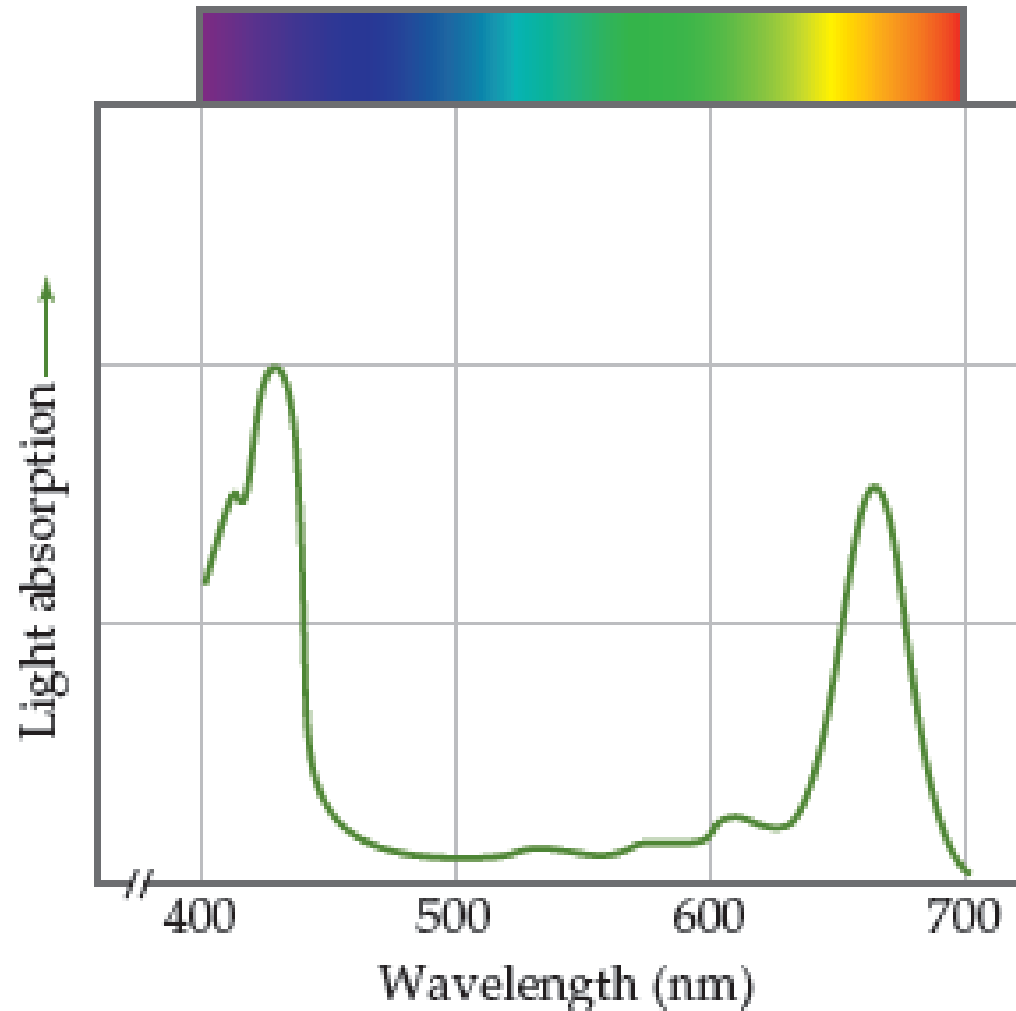
Electromagnetic Spectrum

The following table lists the names of different spectral regions, the range of frequencies and wavelengths in the transition that can occur when a photon in these spectral ranges interacts with matter.

Type of Radiation	Frequency Range (Hz)	Wavelength Range	Type of Transition
gamma-rays	10^{20} - 10^{24}	<1 pm	nuclear
X-rays	10^{17} - 10^{20}	1 nm-1 pm	inner electron
ultraviolet	10^{15} - 10^{17}	400 nm-1 nm	outer electron
visible	4 - 7.5×10^{14}	750 nm-400 nm	outer electron
near-infrared	1×10^{14} - 4×10^{14}	2.5 μ m-750 nm	outer electron molecular vibrations
infrared	10^{13} - 10^{14}	25 μ m-2.5 μ m	molecular vibrations
microwaves	3×10^{11} - 10^{13}	1 mm-25 μ m	molecular rotations, electron spin flips*
radio waves	$<3 \times 10^{11}$	>1 mm	nuclear spin flips*

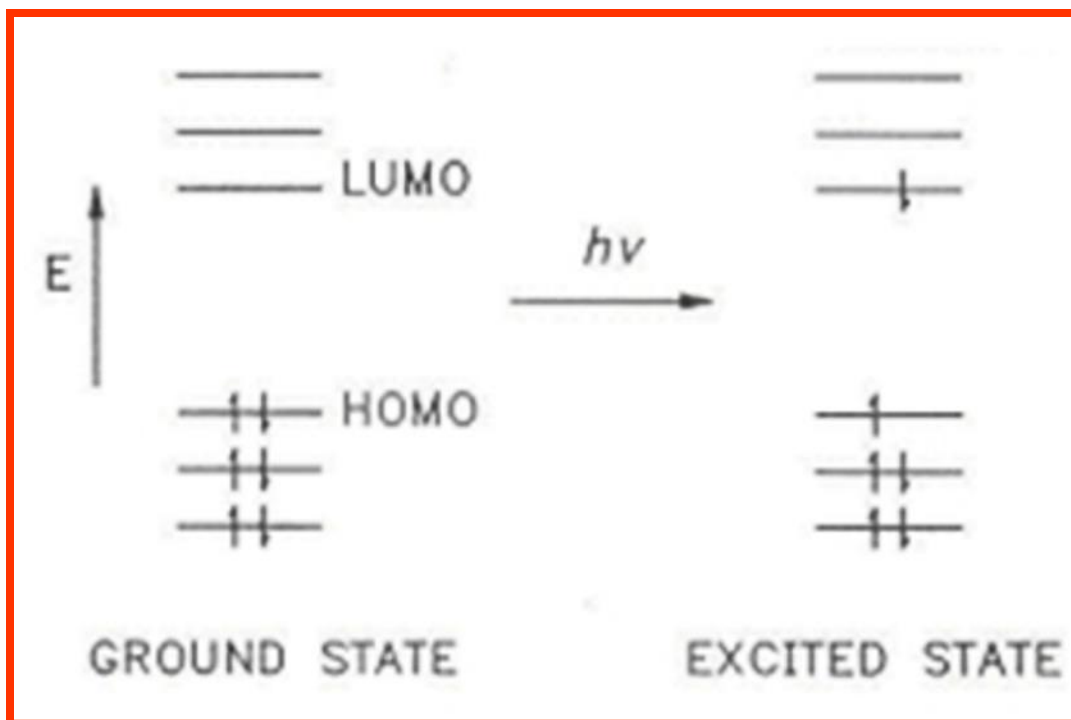
*for energy levels split by a magnetic field

Which peak in this curve corresponds to the lowest-energy transition by an electron in a chlorophyll molecule?

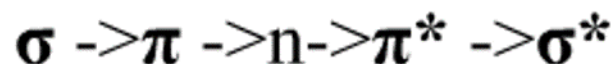


▲ **Figure 23.16** The absorption of sunlight by chlorophyll.

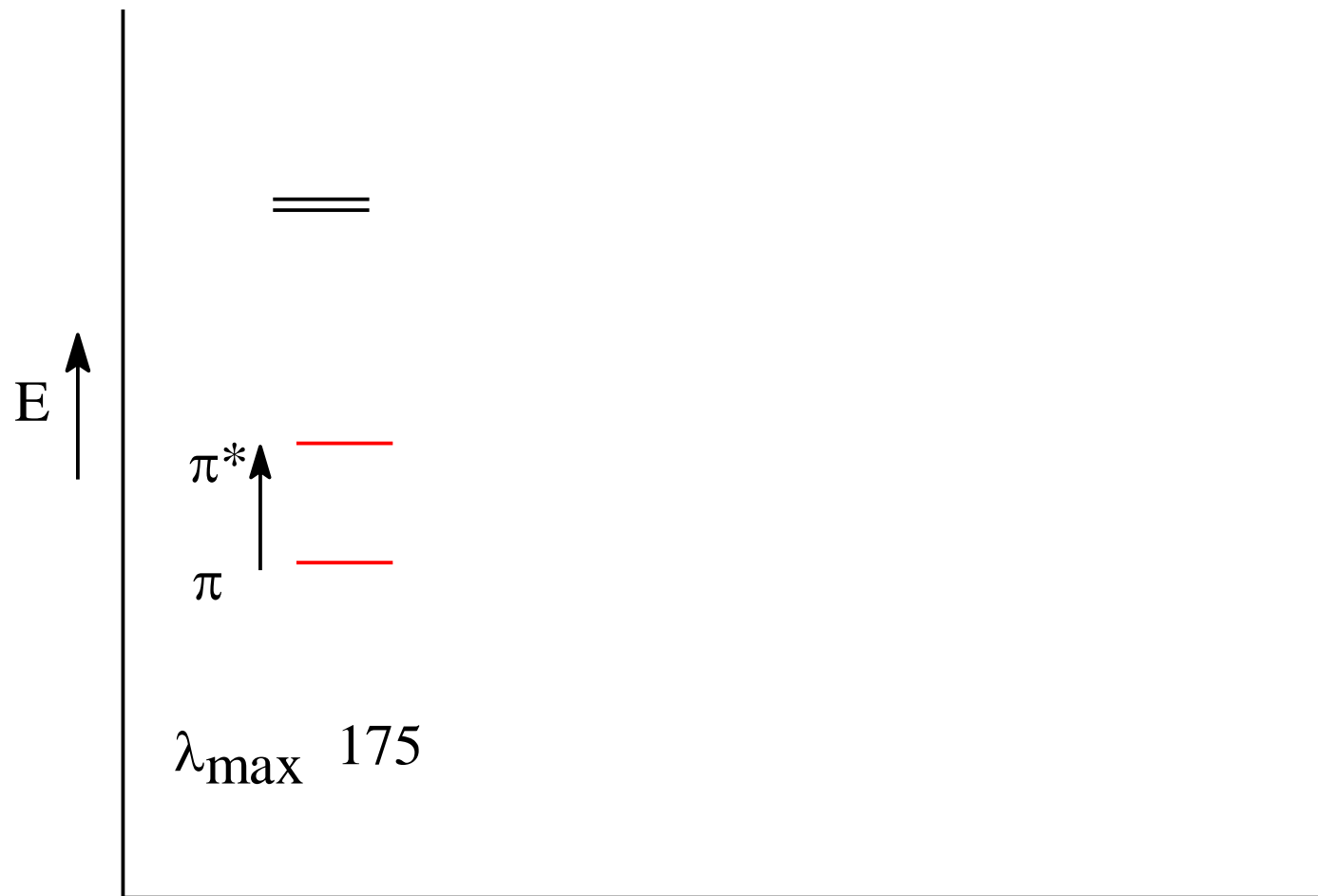
Transition of an electron from HOMO to LUMO by light photon.



The wavelength of an electronic transition depends on the energy difference between the ground state and the excited state. The order is



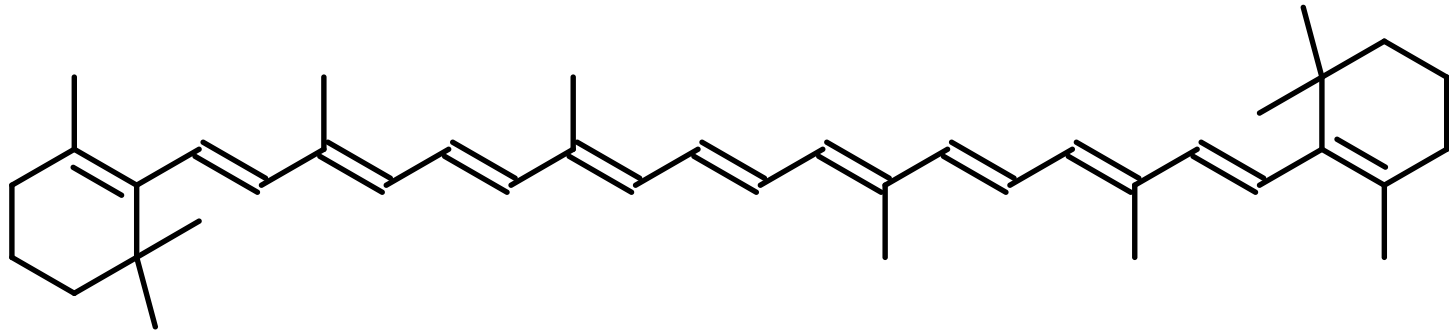
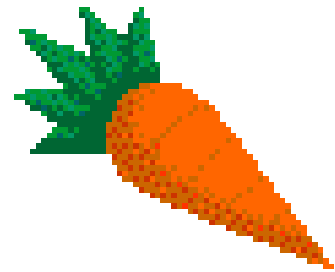
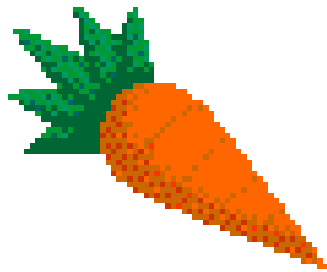
UV Absorption of Conjugated Alkenes



Increasing conjugation gives:

- longer wavelength absorption
- more intense absorption

b-Carotene



11 double bonds

$$\lambda_{\text{max}} = 460 \text{ nm}$$