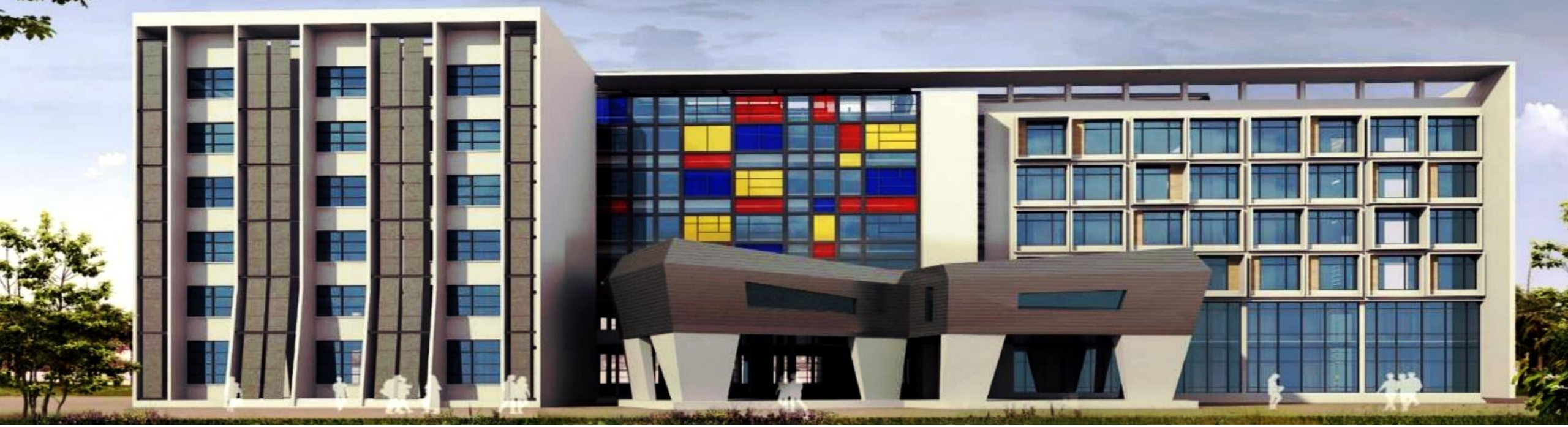

CY1018

भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

Department of Chemistry

Course Content

Know our environment (chemistry of lithosphere, energy balance, sustainability and recycle), Know about global warming (infrared absorption, molecular vibration, atmospheric window, residence time of greenhouse gases, evidences and effects of global warming)

Deeper analysis of atmospheric pollution (Chemistry of CO, NOx, VOCs, SO_2, Industrial smog, photochemical smog), Ozone depletion (production, catalytic destruction)

Organic Chemicals in the Environment, Insecticides, Pesticides, Herbicides and Insect Control, Soaps, Synthetic Surfactants, Polymers, and Haloorganics. Fate of organic/inorganic chemicals in natural and engineered systems (fate of polymers after use, detergents, synthetic surfactants insecticides, pesticides etc. after use)

Aspects of transformations in atmosphere (microbial degradation of organics-environmental degradation of polymers, atmospheric lifetime, toxicity). Green Chemistry and Industrial Ecology. **Future challenges (CO_2 sequestering, Nuclear energy)**. A project on environment related topic.

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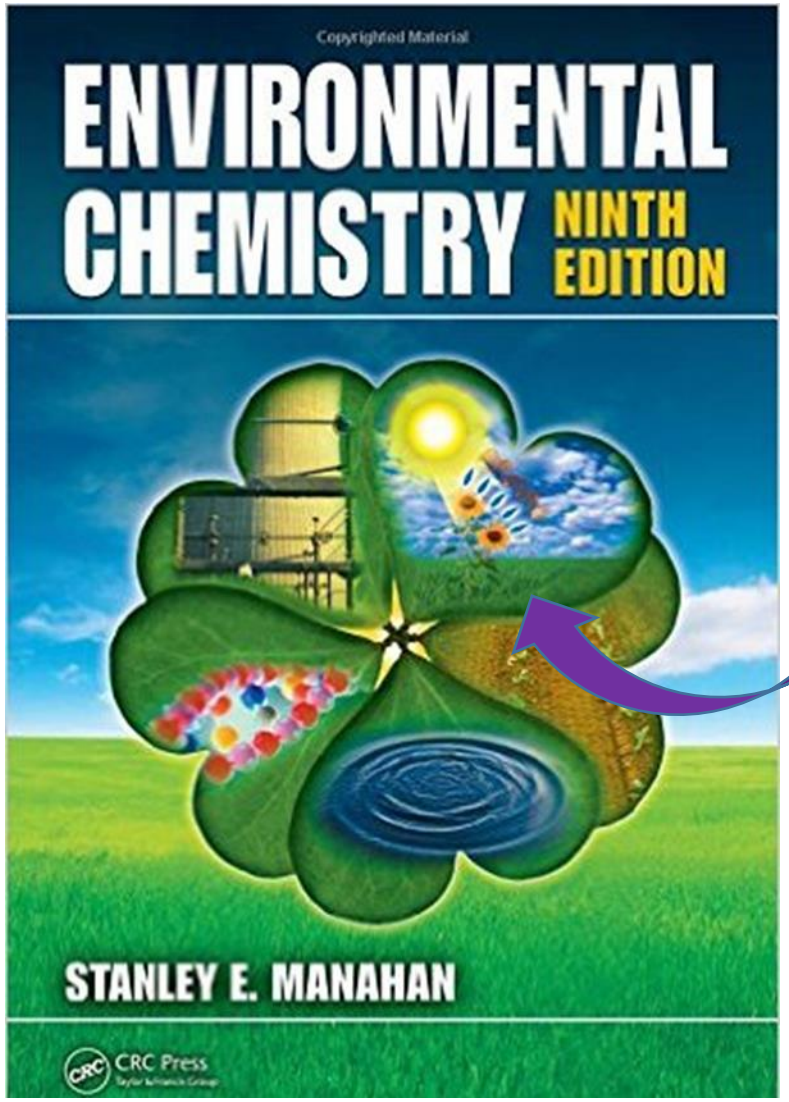
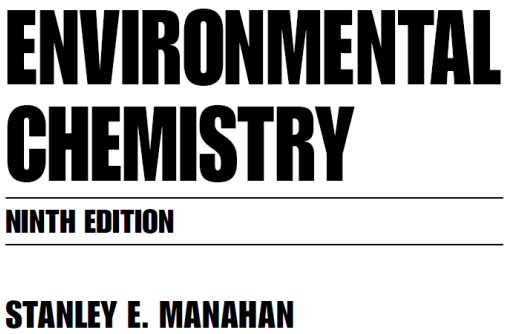
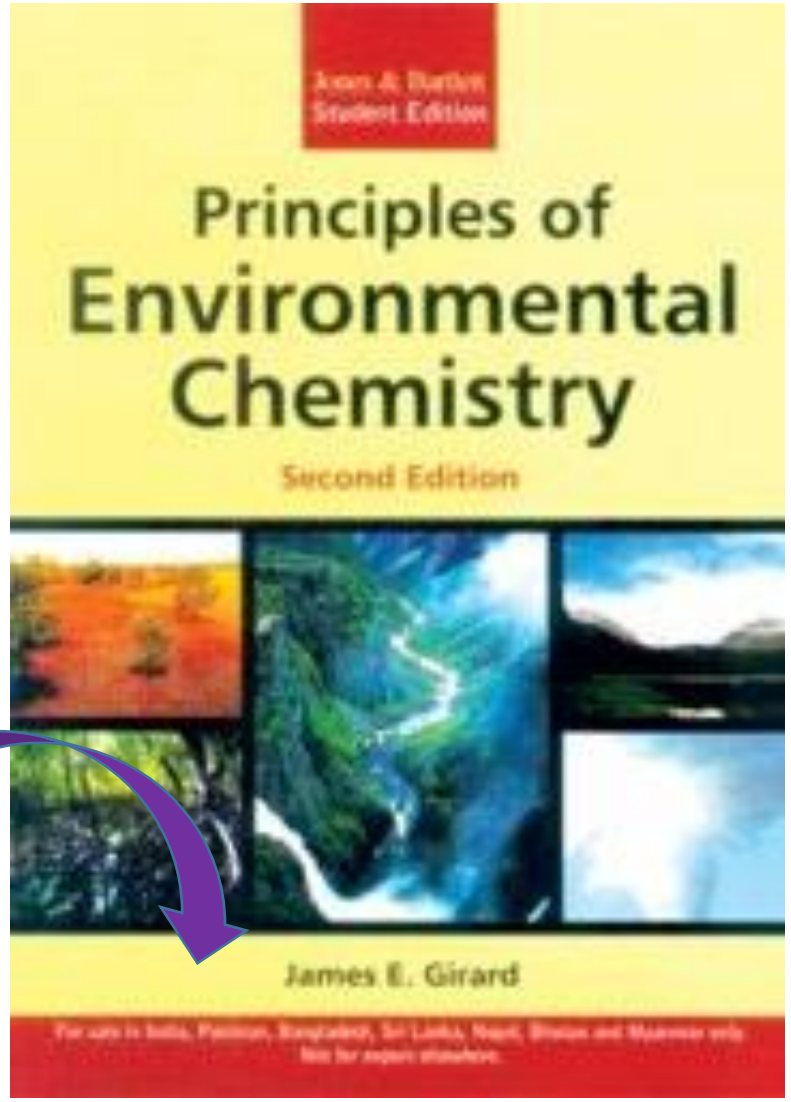
Reference books





Principles of Environmental Chemistry
By James E. Girard



Chemistry of Troposphere

- ❖ Carbon Monoxide
  - ➢ Source of Carbon monoxide
  - ➢ Main anthropogenic source of CO is the combustion of gasoline in automobile engines

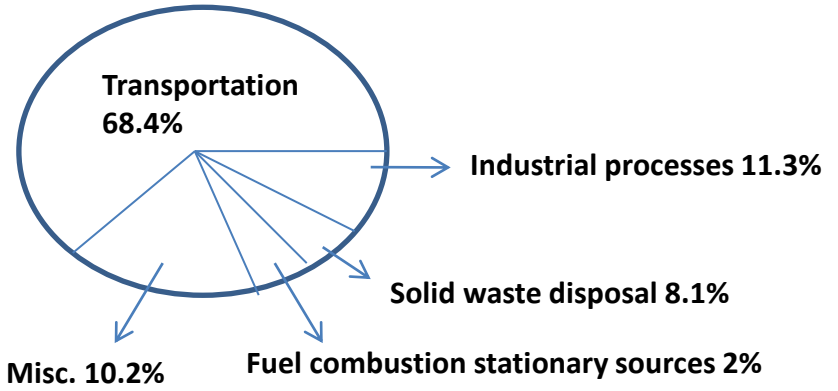
1. Gasoline is a complex mixture of hydrocarbons (HCs)
2. If this is ignited in an adequate supply of oxygen; the products are CO_2 and H_2O

$$2\ C_8H_{18} + 25\ O_2 \longrightarrow 18\ H_2O + 16 CO_2$$

1. In the confined space of the internal combustion of engine O_2 supply is limited and combustion is incomplete. Thus CO is formed and released to the atmosphere in auto mobile exhaust
2. $2\ C_8H_{18} + 17\ O_2 \longrightarrow 18\ H_2O + 16\ CO$

❖ However, the introduction of catalyst converter reduce the CO emissions

❖ Natural source of CO into the atmosphere is CH_4 gas



$$2\ CH_4 + 3\ O_2 \longrightarrow 2\ CO + 4\ H_2O$$

Methane is also produced in the stomach in the cattle and sheep and finally released into the atmosphere

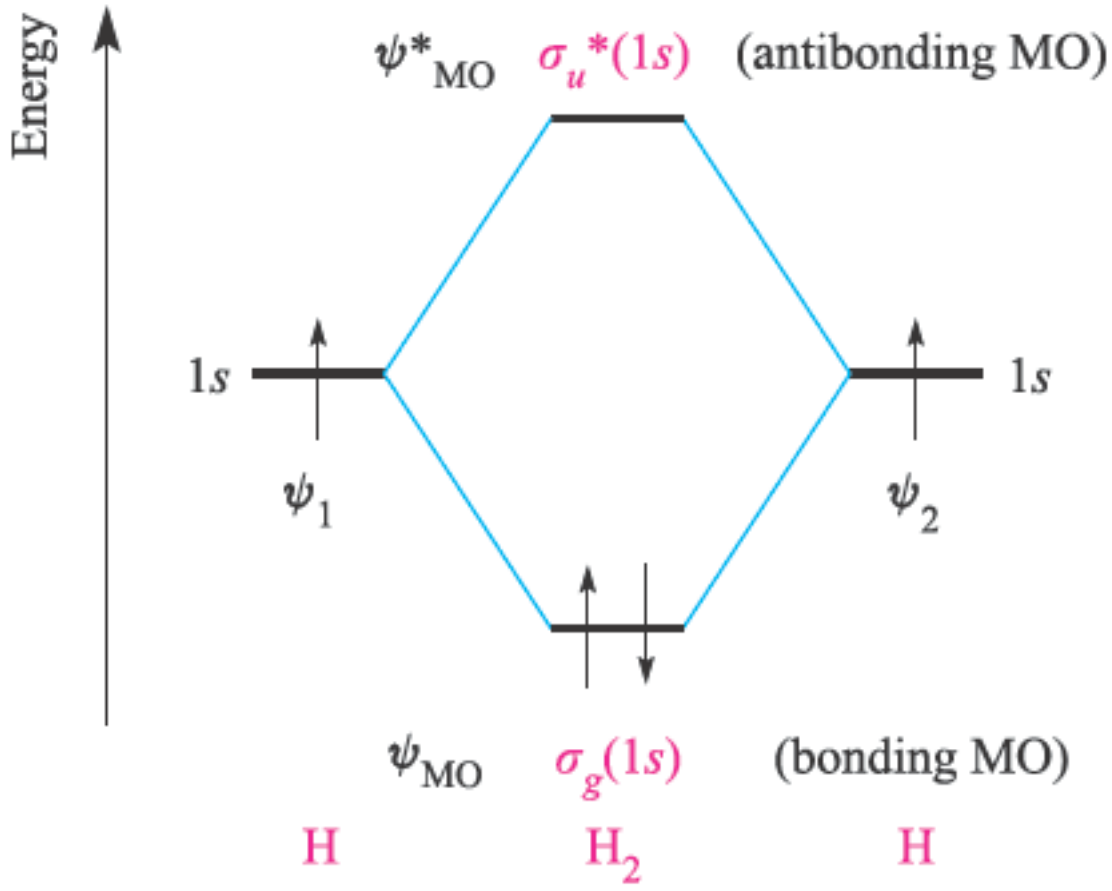
Carbon Monoxide

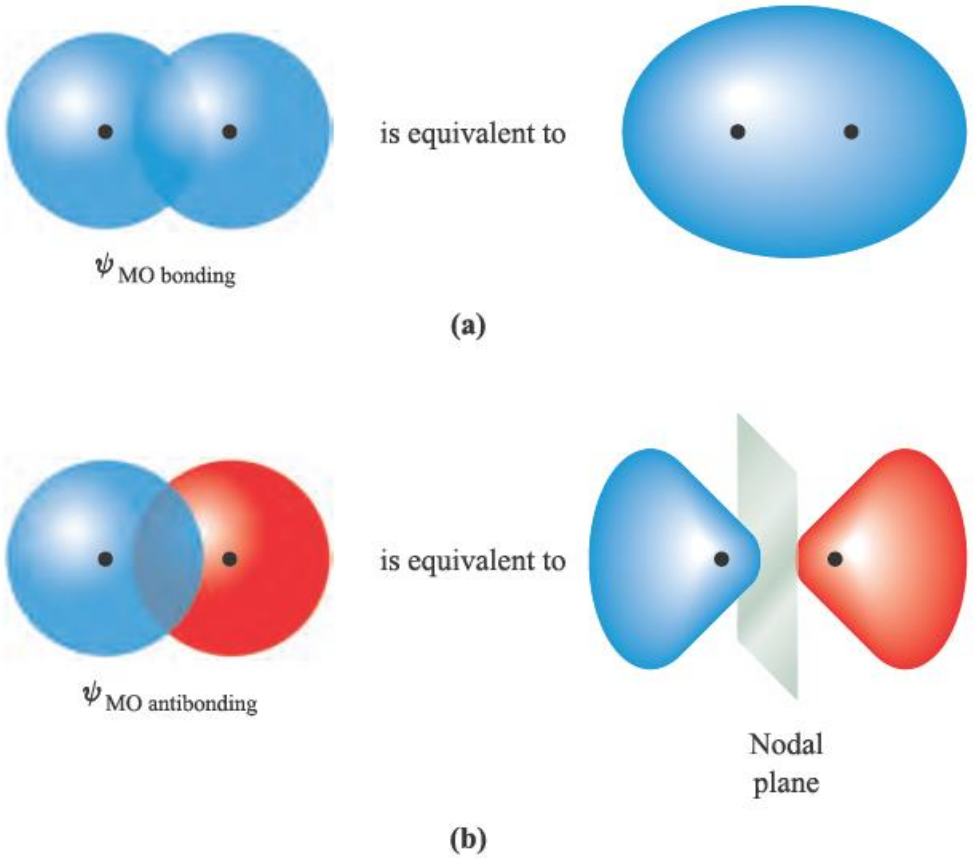
- **Effect of CO on Human Health**
  - Even the CO is most abundant air pollutant, it is not very toxic at the levels usually found in the atmosphere, however if allowed a build up in a confined space, it can cause serious health problem
  - CO interferes with the oxygen carrying capacity of blood; normally hemoglobin (Hb) in red blood cells combine with oxygen in the lungs to oxyhemoglobin (HbO_2). The HbO_2 is carried in the blood stream to various part of the body, where oxygen is released to the tissues
  - Carbon monoxide binds much more strongly to Hb than oxygen – Why?
  - If CO is present in the lungs, it displaces oxygen from Hb and thus reduces the amount of oxygen that can be delivered to the tissues

$$HbO_2 + CO \longrightarrow HbCO + O_2$$

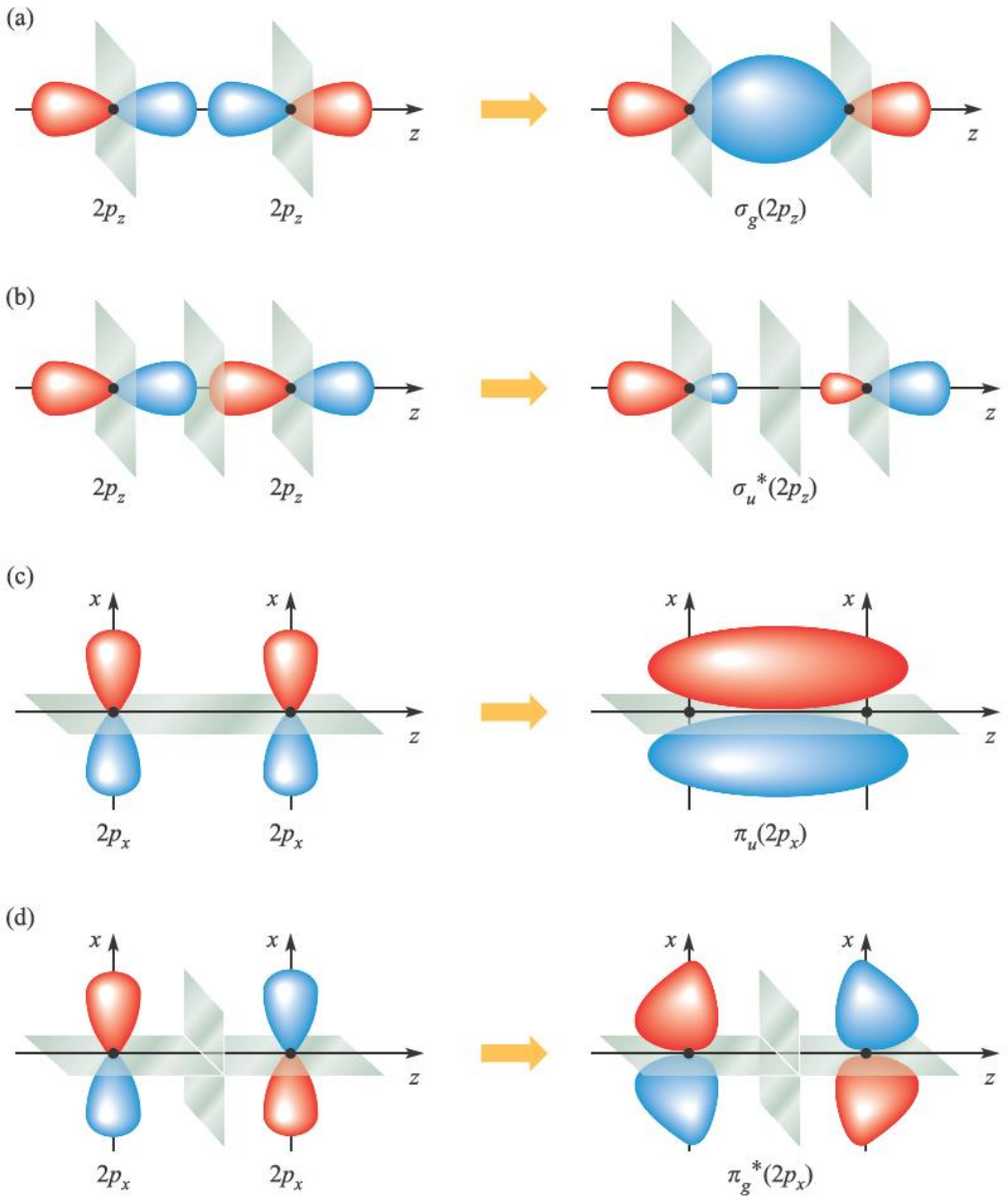
- **Treatment of CO poisoning:**
- **Symptoms of CO poisoning: headache, dizziness, impaired judgment, drowsiness, slowed reflexes, respiratory failure and death**

Molecular Orbital Theory





Molecular Orbital Theory



$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^2, \pi 2p_z^2, \pi 2p_x^2$

$$\text{Bond order (CO)} = \frac{\text{Bonding - Antibonding}}{2}$$

$$= \frac{10-4}{2} = 3$$

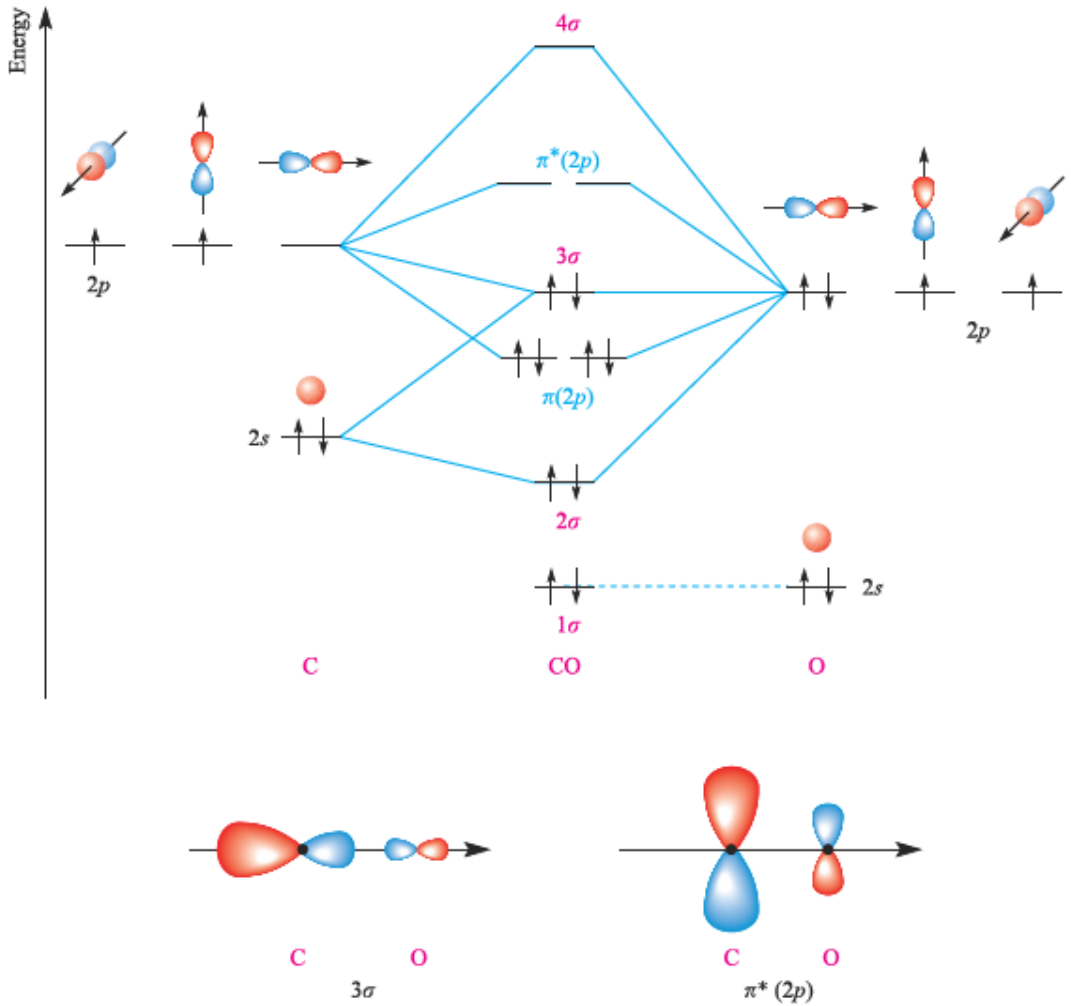
- **Carbon monoxide binds much more strongly to Hb than oxygen – Why?**

Molecular Orbital Theory

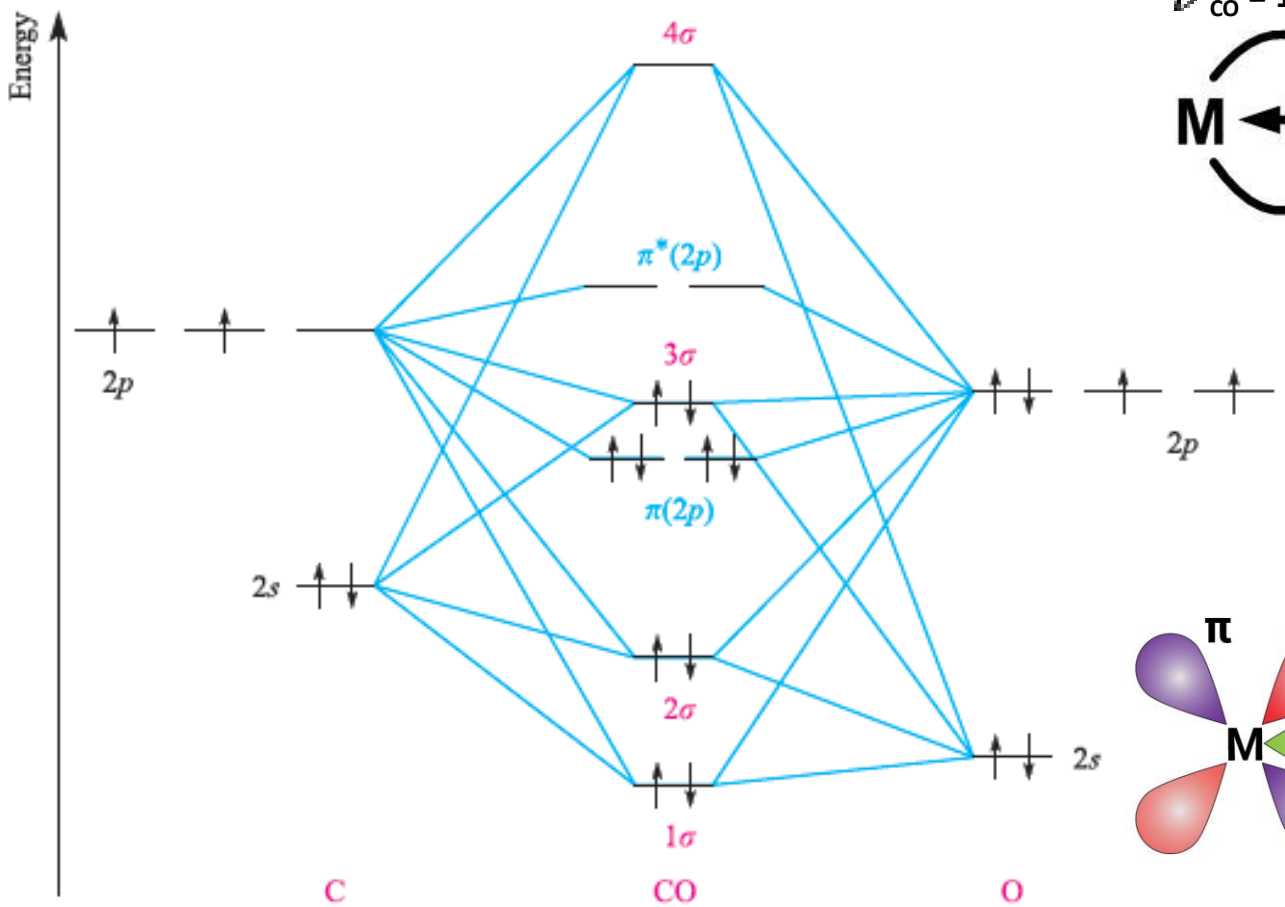
In order to investigate the way in which CO bonds to metals, we must appreciate the electronic structure of the CO molecule.

Before constructing an orbital interaction diagram for CO, we must take note of the following:

- **$Z_{eff}(O) > Z_{eff}(C)$;**
- **the energy of the O 2s atomic orbital is lower than that of the C 2s atomic orbital;**
- **the 2p level in O is at lower energy than that in C;**
- **the 2s–2p energy separation in O is greater than that in C**

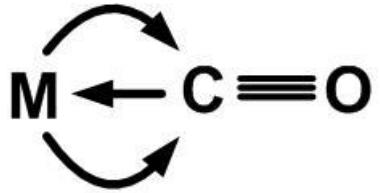


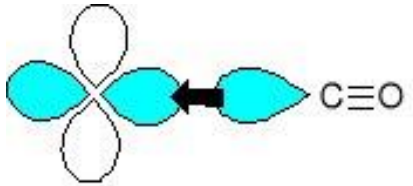
Molecular Orbital Theory



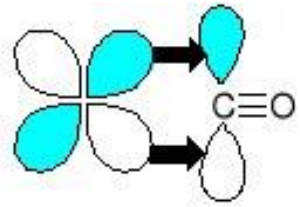
MO diagram

$\tilde{\nu}_{CO}$ = 1670-1820 cm^{-1}



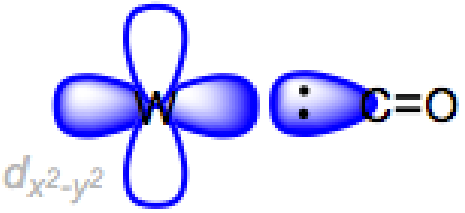


sigma bond

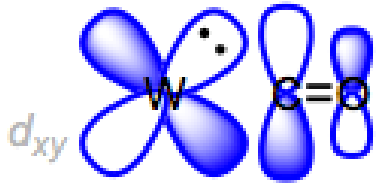


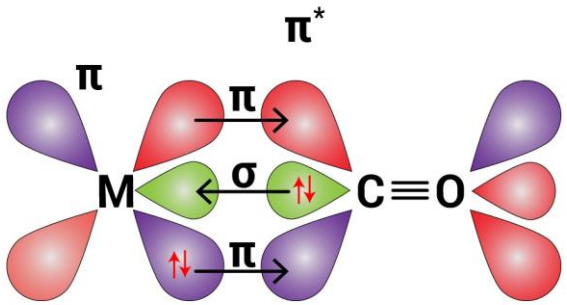
pi back-bond

σ-type orbital interaction



π-type orbital interaction



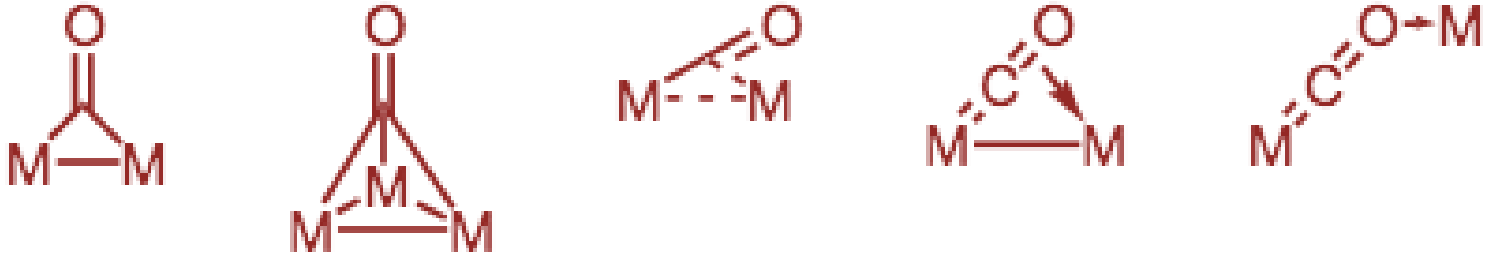


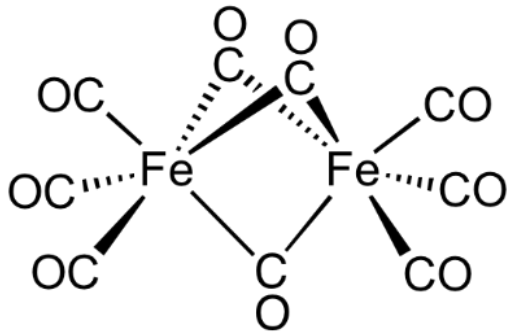
Electron donor!

Electron acceptor!

Carbon Monoxide

Bridging modes of CO



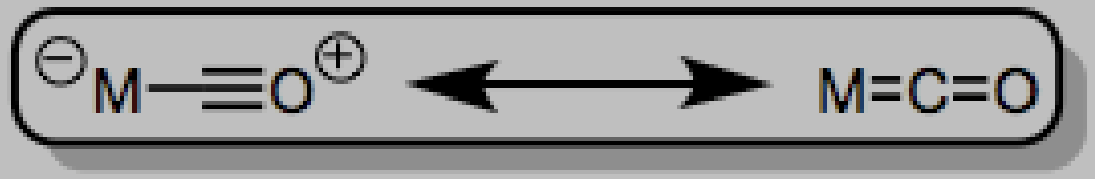


❖ **How the wave number of *CO* will change in metal carbonyl complexes**

Free CO
2143 cm^{-1}

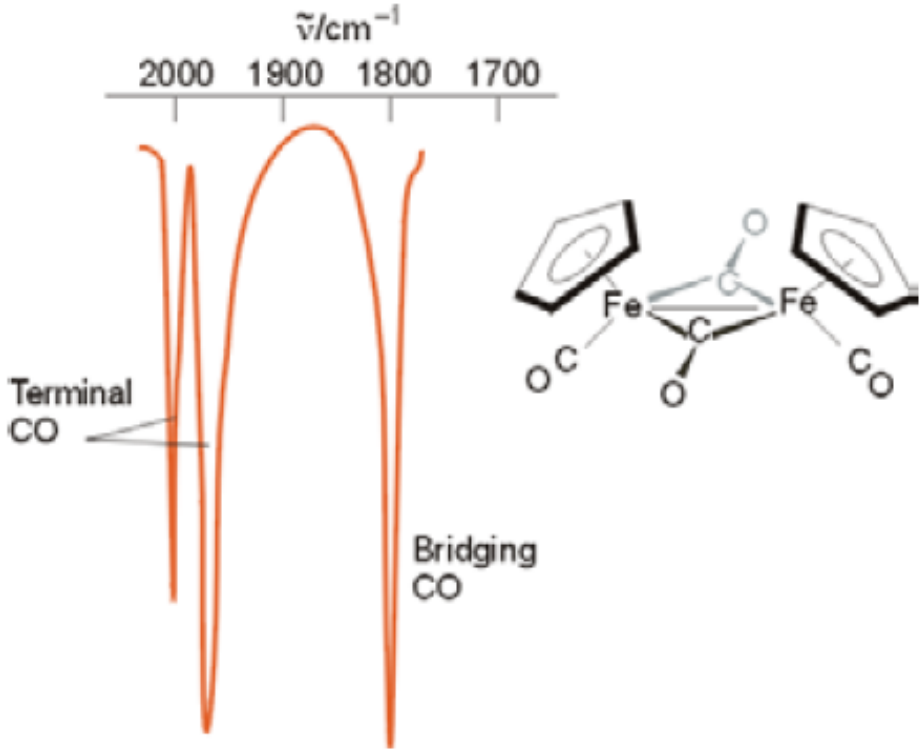
$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$
1976 cm^{-1}	2000 cm^{-1}	2013 cm^{-1}	2023 cm^{-1}	2044 cm^{-1}	2057 cm^{-1}

$[Ti(CO)_6]^{2-}$
1747 cm^{-1}



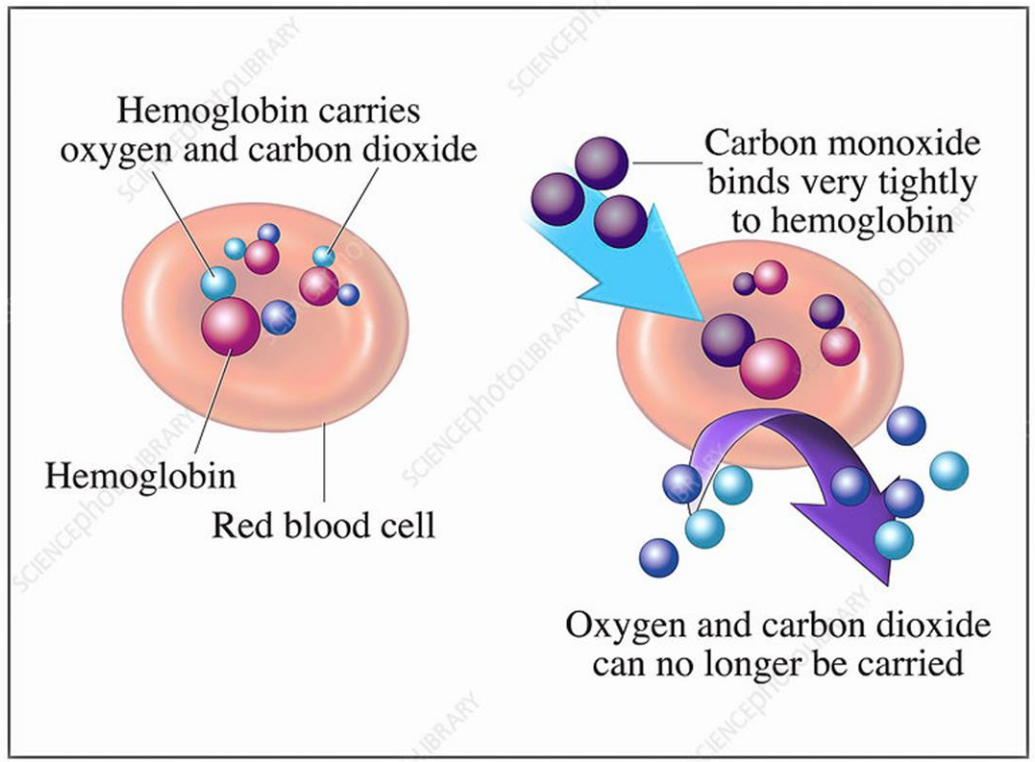
Example

- IR spectrum shows bands in the bridging and terminal regions
- Bridging IR band is single implying that the two COs are almost co-linear
- Two terminal IR stretch bands implying that the two COs are not co-linear

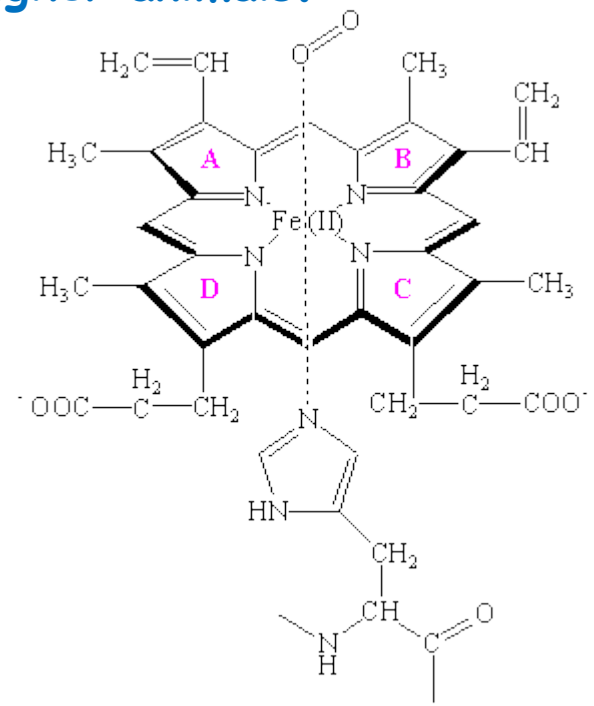


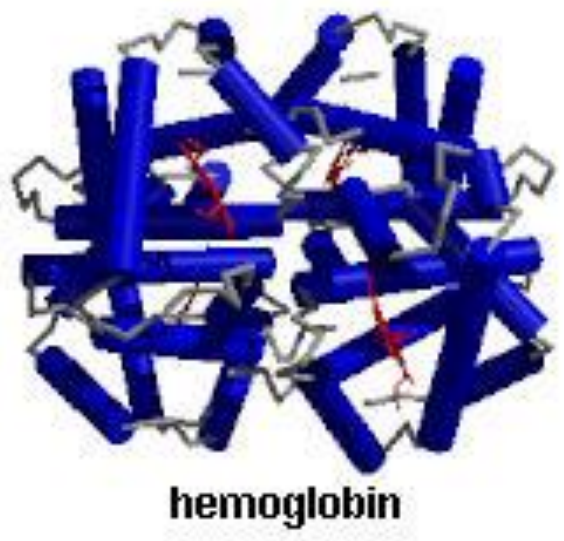
Carbon Monoxide

- **Carbon monoxide binds much more strongly to Hb than oxygen – Why?**



Myoglobin is a hemoprotein, isolated from the cells of vertebrate skeletal muscle that is both a structural and functional relative of **hemoglobin**, the oxygen-transport protein of the blood of higher animals.





Carbon Monoxide

- At the center of the heme is an Fe(II) atom. Four of the six coordination sites around this atom are occupied by nitrogen atoms from a planar porphyrin ring

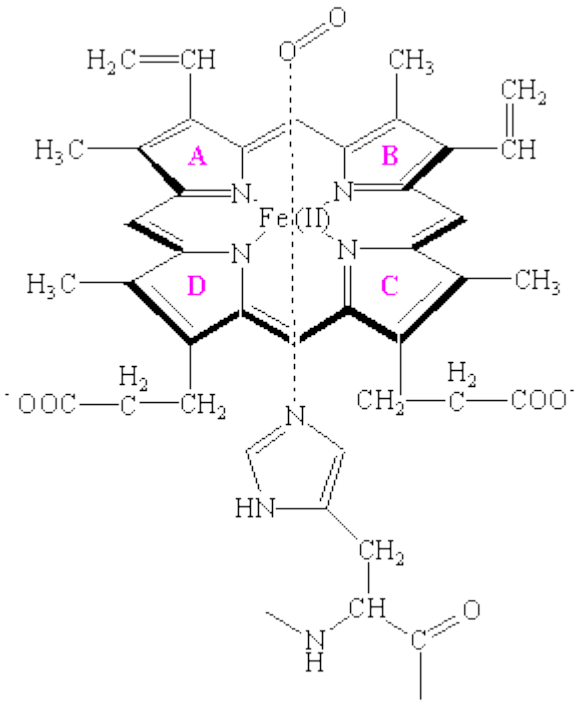
- The fifth coordination site is occupied by a nitrogen atom from a histidine side chain on one of the amino acids in the protein

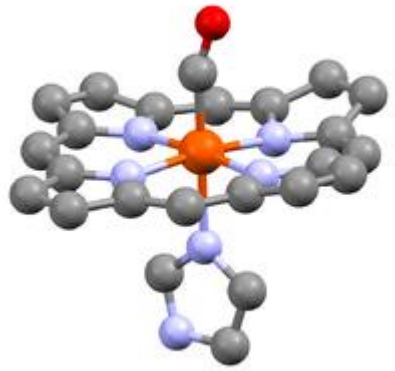
- The last coordination site is available to bind an O_2 molecule

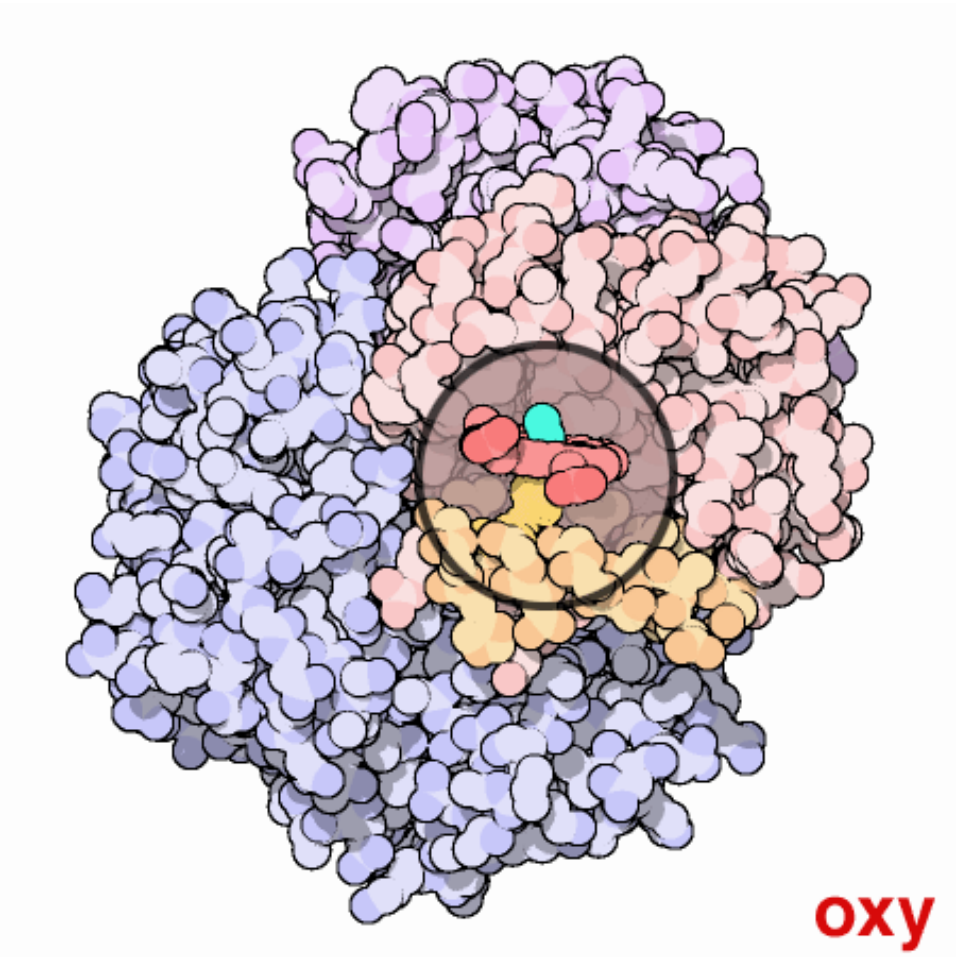
- The heme is therefore the oxygen-carrying portion of the hemoglobin and myoglobin molecules

- The structure of myoglobin suggests that the oxygen-carrying heme group is buried inside the protein portion of this molecule, which keeps pairs of hemes group from coming too close together

- This is important, because these proteins need to bind O_2 reversibly and the Fe(II) heme, by itself, cannot do this. When there is no globin to protect the heme, it reacts with oxygen to form an oxidized Fe(III) atom instead of an Fe(II)-O_2 complex






oxy

Carbon Monoxide

Fate of Atmospheric CO

It is generally believed that CO is removed from atmosphere by reaction with hydroxyl radical.

Oxidized by reaction with hydroxyl radical

- $CO + HO\bullet \rightarrow CO_2 + H$

Production of hydroperoxyl radical

- $O_2 + H + M \rightarrow HOO\bullet + M$

Additional reactions

- $HOO\bullet + NO \rightarrow HO\bullet + NO_2$
- $HOO\bullet + HOO\bullet \rightarrow H_2O_2 + O_2$
- $H_2O_2 + h\nu \rightarrow HO\bullet$

Soil microorganisms metabolize CO

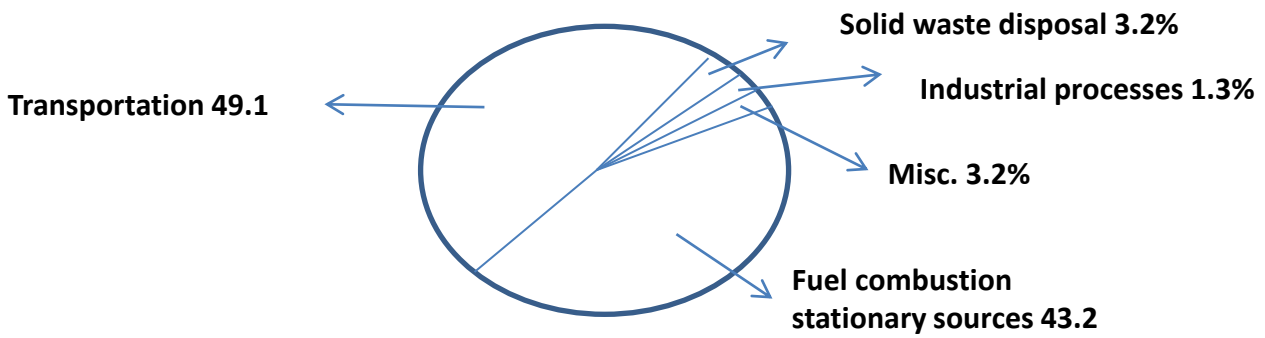
- **Soil is a sink for CO**

Nitrogen Oxides (No_x)

- **Nitrogen dioxide (NO_2) is the major pollutant in the atmosphere and is formed from nitric oxide (NO). Collectively nitrogen oxides are designated as NO_x**

- **Source of Nox**
- ***Anthropogenic NO_x enter the atmosphere from the combustion of fossil fuels by automobiles, aircraft and power plants***
- **At normal atmospheric temp. N_2 and O_2 does not react. However, at very high temp. atmospheric N_2 reacts with oxygen to give a series of complex reactions. Two gases combine to give NO**

$$N_2 + O_2 \longrightarrow 2\,NO \qquad 2NO + O_2 \longrightarrow 2NO_2$$



Nitrogen Oxides (No_x)

- When NO is released, it combines rapidly with atmospheric oxygen to form NO_2.

  NO has an unpaired electron and can be written as $NO^{\bullet}$.

Bacterial decomposition of nitrogen containing organic matter in soil is another natural source of NO_x

❖ Fate of Atmospheric NOx

1. Regardless of its source, NO_2 ultimately removed from the atmosphere as nitric acid and nitrates in dust and rain fall. In a series of complex reactions involving hydroxyl radicals, NO_2 combines with water vapor to form nitric acid. The simplified overall reaction is

$$4\,NO_2 + 2\,H_2O + O_2 \longrightarrow 4\,HNO_3$$

2. Much of the nitric acid in the atmosphere is formed within aqueous aerosols. If the weather conditions are right, the aerosols coalesce into larger droplets in clouds and the result is **acid rain.**

❖ Fate of Atmospheric NO_x

- ❖ Some of the nitric acid formed reacts with ammonia and metallic particles in the atmosphere to form nitrates

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3$$

- ✓ Nitrates dissolve in rain and snow or settle as particle. The combine fallout contribute to acid deposition

Effect of NO_x on Human Health and Environment

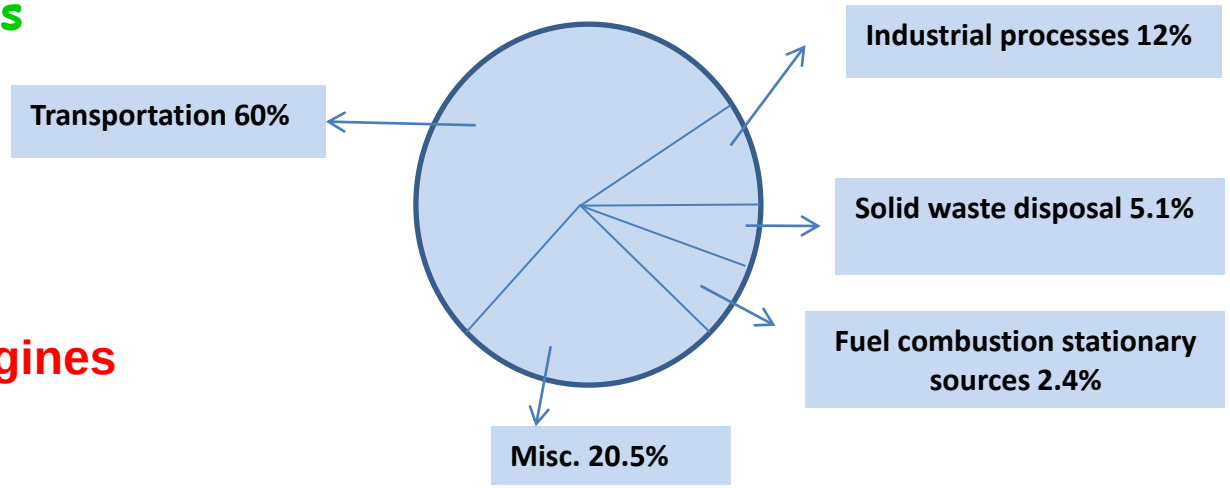
- ➢ NO_2 is red brown toxic gas and has unpleasant acrid odor. It can cause irritation of the eyes, inflammation of lung tissue, and emphysema.
- ➢ NO_x is a serious health problem because of its role in the formation of secondary pollutants associated with photochemical smog.
- ❖ Most of the research has concentrated on reducing automobile emission by means of the catalytic converter

Volatile Organic Compounds (VOCs)

- A great variety of VOCs, including many HCs enter the atmosphere from both natural and anthropogenic sources
- The petroleum industry is the main anthropogenic source of HCs in the atmosphere
- Gasoline is a complex mixture of many volatile HCs and in urban areas, gasoline vapors can escape into the atmosphere in several ways

1. When gas is pumped at gas stations
2. During filling of storage tanks
3. Unburned gasoline in exhaust

from automobiles and small combustion engines

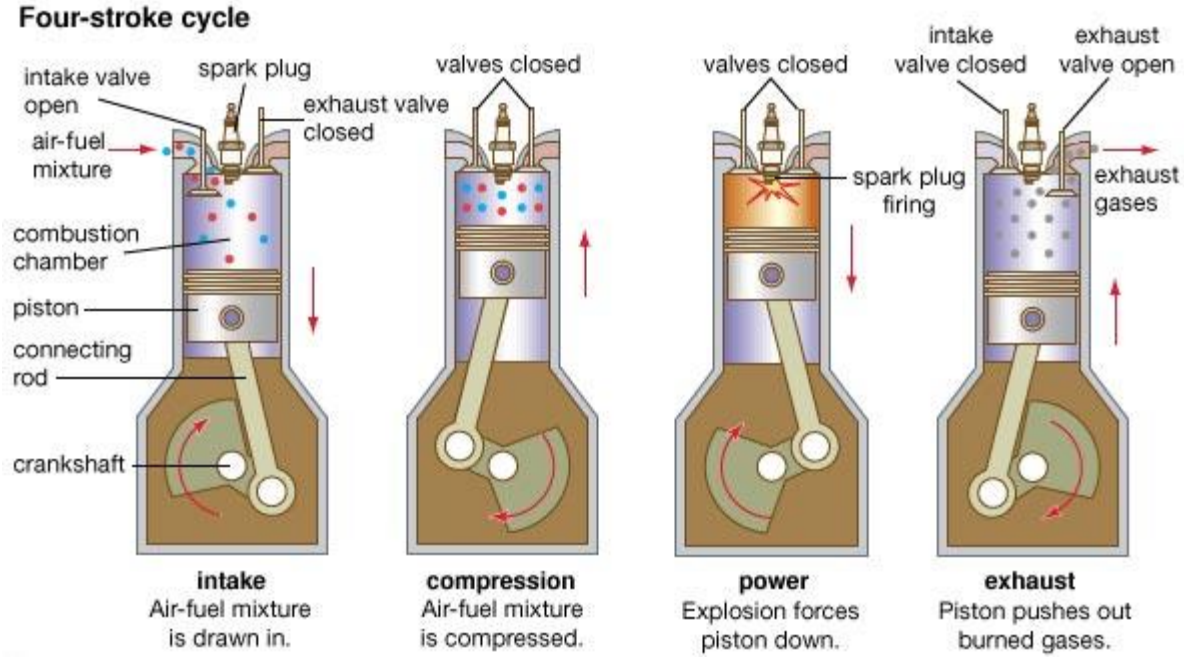


- In the natural world, the pleasant aroma of pine, eucalyptus and sandal wood trees are caused by the evaporation of VOCs called terpenes from their leaves
- Natural sources account for 85% of total emission; anthropogenic source contributes 15%

Volatile Organic Compounds (VOCs)

❖ Automobile Four-Cycle Internal Combustion Engine

- ➢ Gasoline powered four cycle internal combustion engine is predominant in more developed countries
- ➢ To know how NOx, CO and HCs are produced through this we have to know how this engine works
- ➢ There are four steps in one complete cycle of the gasoline engine
- ➢ In the confined space of the internal combustion engine, oxygen is in limited supply and CO is formed and released to the atmosphere



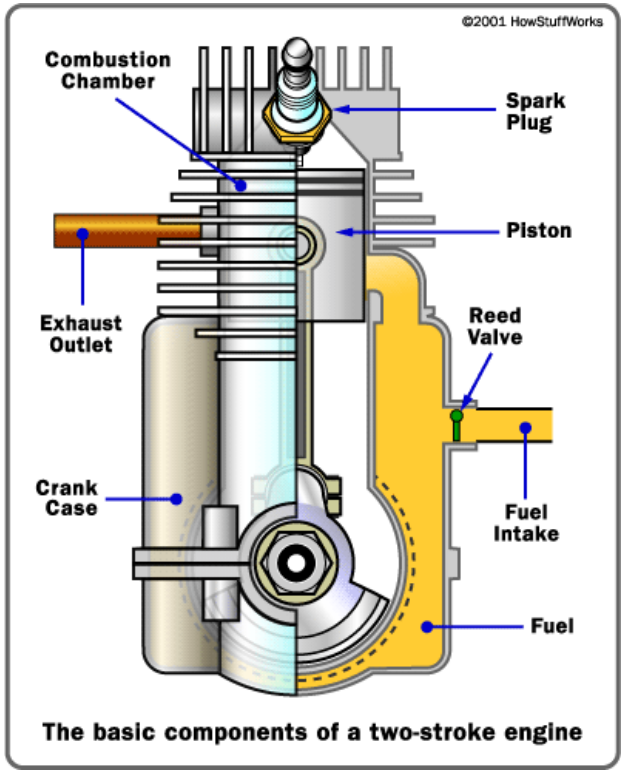
Volatile Organic Compounds (VOCs)

- **Automobile Four Cycle Internal Combustion Engine**
- In the internal combustion engine, temp and pressure is very high and NO is formed from N_2 and O_2. The unburned HCs are emitted with the burned gas as pollutant VOCs
- The air/fuel ratio has a dramatic effect on the emission of pollutants from the four cycle engine
- During the engine tune up, adjustment of the carburetor or the fuel injection system can greatly reduce emission of pollutant
- The ideal stoichiometric air/fuel ratio is 14.5
- Adjustment to a more fuel rich (lower air/fuel) ratio makes the car easier to start and decrease the emission of Nox and HCs; unfortunately it also decreases the fuel efficiency and the car will get fewer Km per liter. The emission of CO is also increased as air is less available
- Adjustment to a more air rich (higher air/fuel) ratio will make the car harder to start, although it increases fuel efficiency, the emission of Nox is increased
- The ideal ratio is a compromise between fuel efficiency and the emission of the lowest collective amount of pollutant

Volatile Organic Compounds (VOCs)

- **Gasoline Powered Two Cycle Engine**
- **Two cycle engine is used to power motor scooter, mopeds, snowmobiles. It is less complicated than the four cycle engine and also less expensive**
- **It takes fuel, releases exhaust in the same stroke and emits from 25% to 30% of the fuel consumed as unburned HCs**
- **The two cycle engine has no valves and that power is produced in one of two steps rather than one in four steps; this means the two cycle engine runs faster and hotter than the four cycle engine**

1. **In two cycle engine motor oil ; gasoline 1: 40 ratio**
2. **Motor oil has C_{18} to C_{25} HCs i.e. higher molecular weight**
3. **In two cycle engine, combustion takes place at a lower temperature that the four cycle engine**
4. **Due to higher molecular weight motor oil is not vaporized and burned efficiently like gasoline**
5. **Two step cycle requires that the exhaust gases from combustion are leaving the cylinder through the exhaust port while the fresh air/fuel mixture for the next power stroke is simultaneously entering the cylinder from the side arm**



The basic components of a two-stroke engine

Volatile Organic Compounds (VOCs)

- **Comparison**

1. A comparison of the emission from marine outboard two and four cycle engines of the same horse power was made. The result of those tests show that the exhaust of a two cycle engine contained more then 12 times the amount of HCs than a four cycle engine of the same power

Type of Marine outboard Engine	CO(g)	NOx(g)	HC(g)
Two cycle Engine	165	0.3	89
Four Cycle engine	127	0.7	7
Source: Juttner F. D. et al., Water Research **1995**, *29*, 1976-1982