

Greenwood & Earnshaw

2nd Edition

Chapter 14

Oxygen

Oxygen

$^{16}_8\text{O}$ 99.763 %

Oxygen makes up 45.5% of the earth's crust.

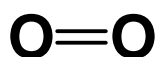
$^{17}_8\text{O}$ 0.037%

$I = 5/2$, poor sensitivity, 2.9% of ^1H , but oxygen very important nucleus so nmr is important.

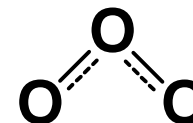
$^{18}_8\text{O}$ 0.20 %

Allotropes:

Dioxygen: O_2



Ozone: O_3



$d = 120.74 \text{ pm}$

$\Delta H_{\text{diss}} = 493.4 \text{ kJ/mol}$

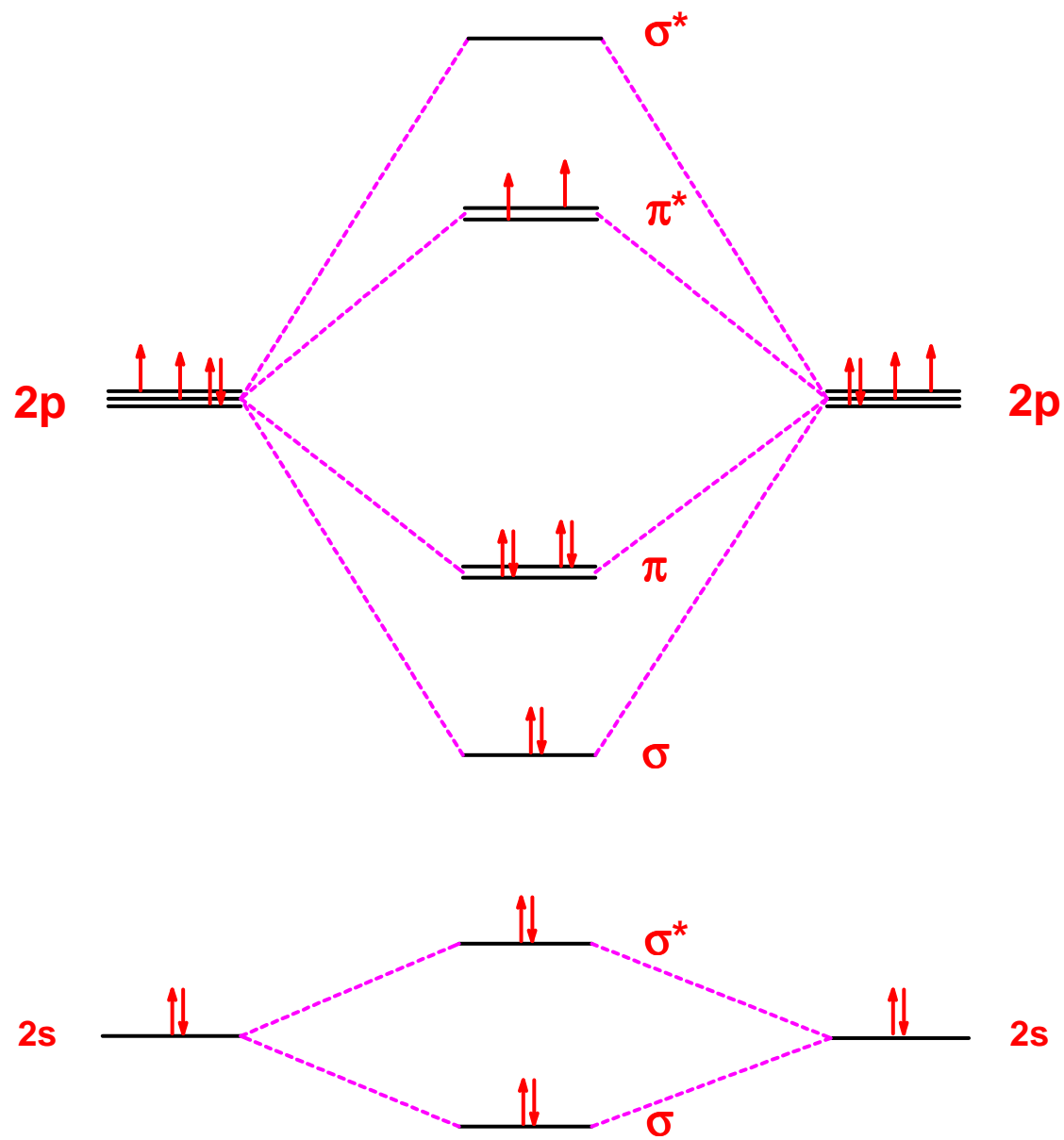
$d = 127.8 \text{ pm}$

$\angle = 117^\circ$

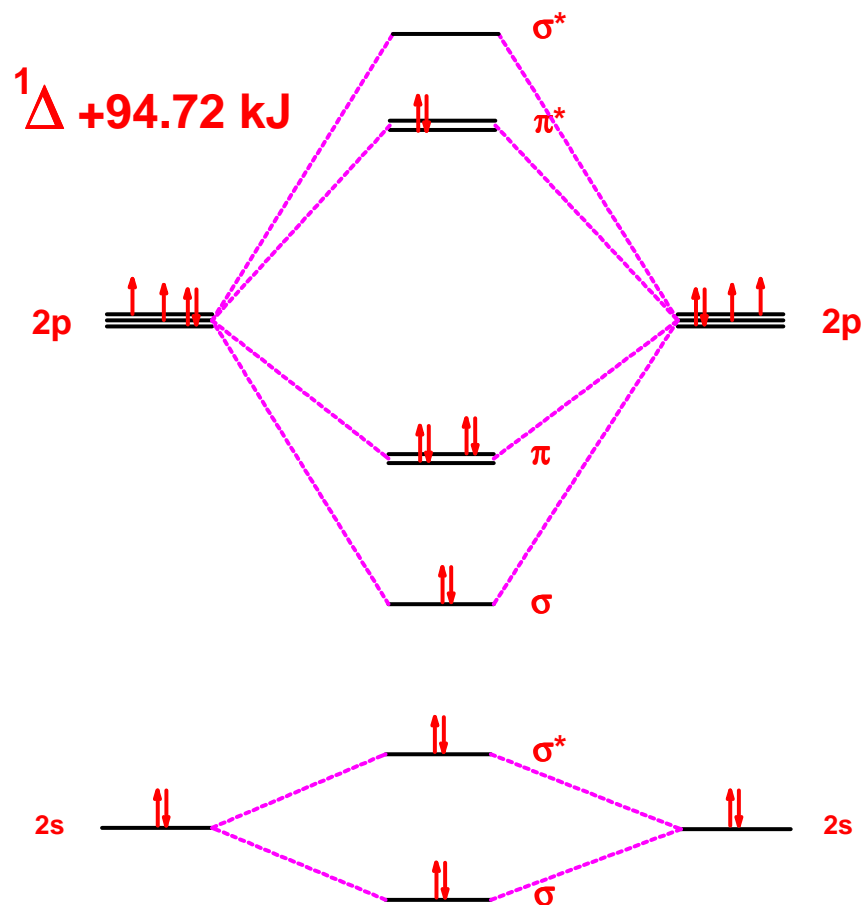
Oxygen comprises 23% of the atmosphere by weight, 46% of lithosphere, 85% of the hydrosphere. Dioxygen is paramagnetic, bp -183°C , slightly soluble in water, more soluble in organic solvents, very soluble in perfluorocarbon solvents (artificial blood). Highly reactive when catalysed or with ignition. $^3\Sigma_g$ ground state is activated by conversion to $^1\Delta$ excited state, $+94.74 \text{ kJ/mol}$.

Ozone, bp -111.9°C , mp -192.5°C , blue liquid, blue-black solid, $\Delta H_f = -142.7 \text{ kJ/mol}$, $\Delta G_f = -142.7 \text{ kJ/mol}$, very slowly decomposes (unless catalysed) to dioxygen, a serious tropospheric pollutant, but essential component in stratosphere where it absorbs solar ultraviolet radiation (220-290 nm), very reactive gas, pungent irritating odor.

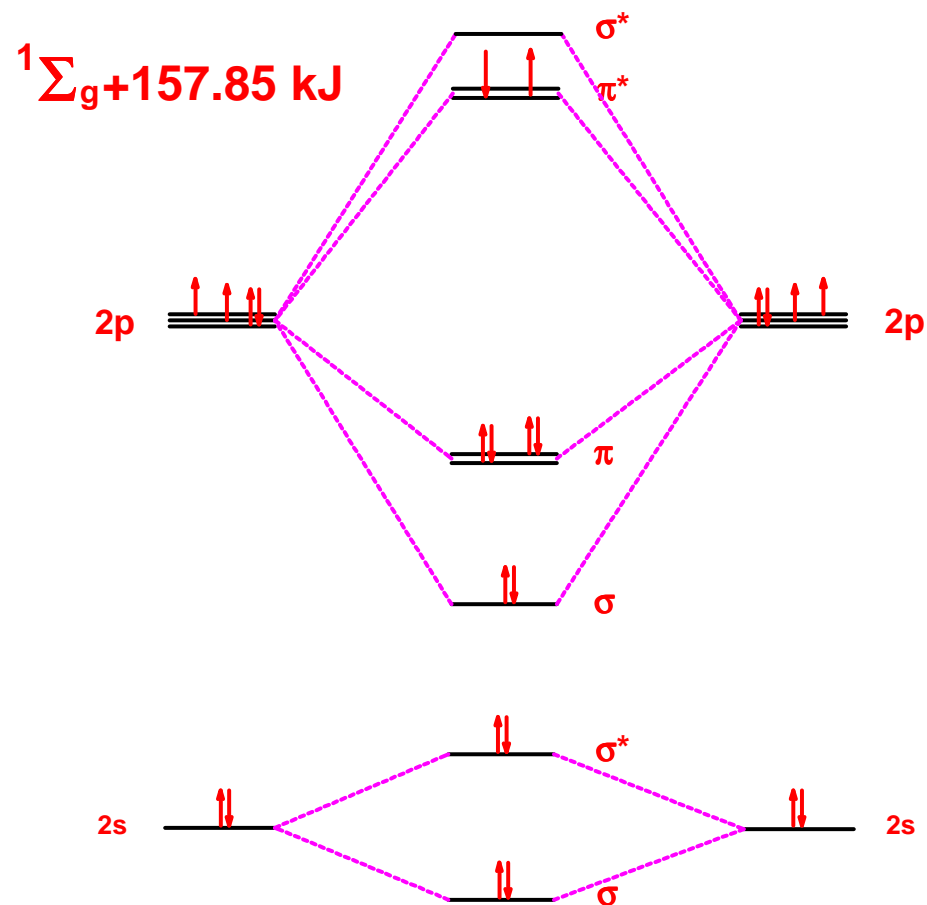
Molecular Orbital Diagram - Dioxygen



MO Diagrams - Singlet Dioxygen

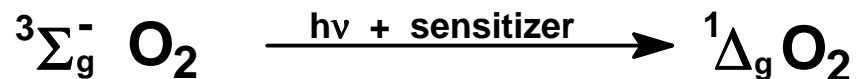


Pairs the anti-bonding electrons in one molecular orbital, leaving the other π^* available for π -back donation from a metal atom. Allows for symmetry allowed 2+2 addition to olefins and other π -bonds.



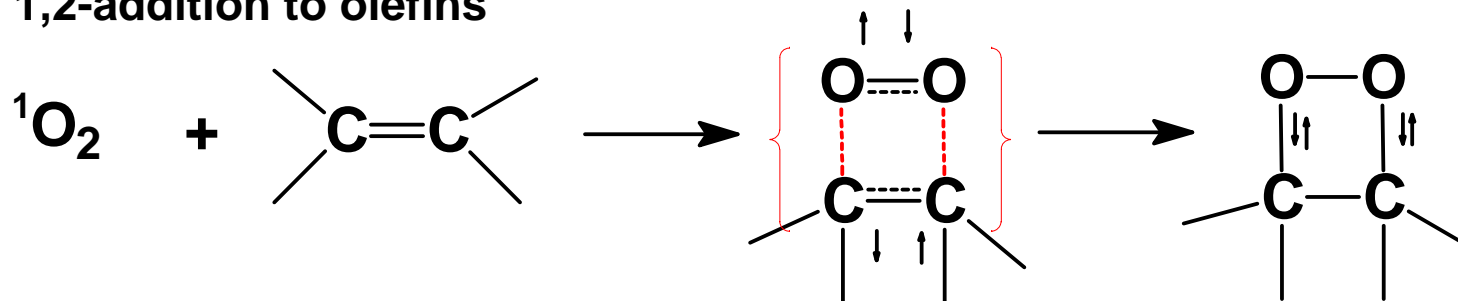
The two anti-bonding electrons are anti-parallel spins but are not paired in the normal sense.

Reactions of Singlet Oxygen

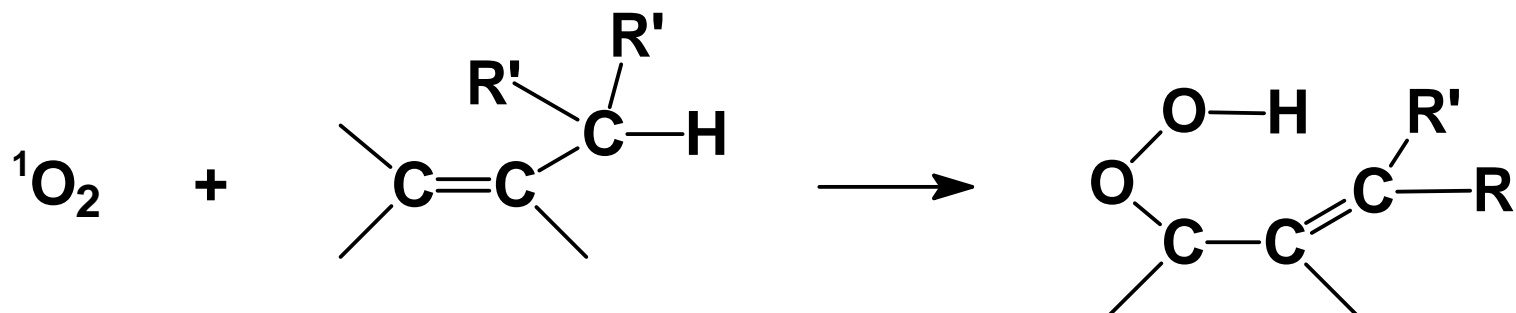


A sensitizer is a photoactive dye such as fluorescein or PAN

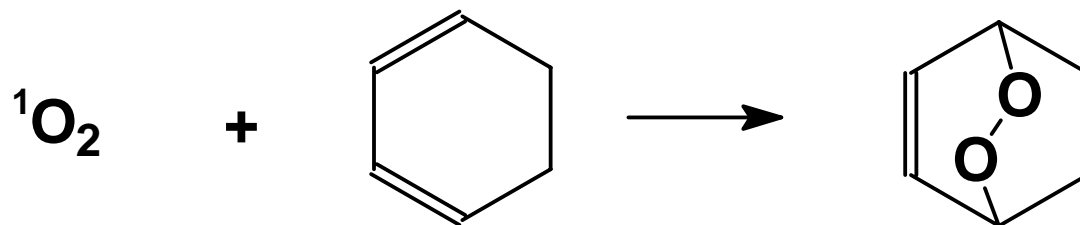
1,2-addition to olefins



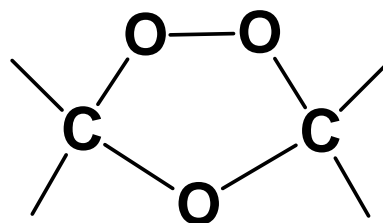
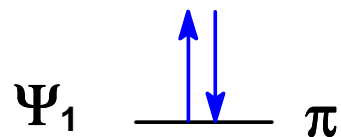
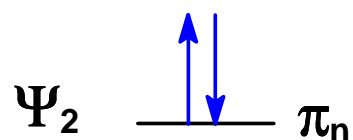
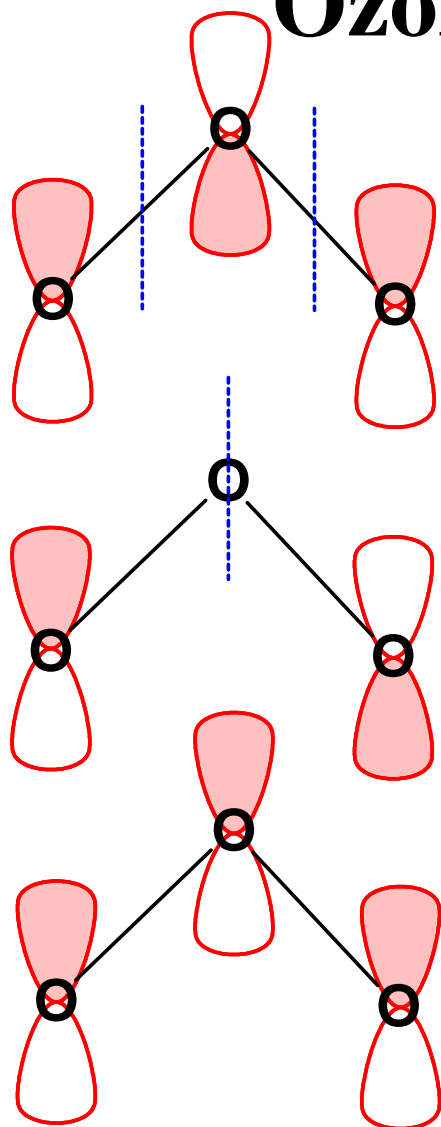
1,3-addition to olefins, the "ene" reaction.



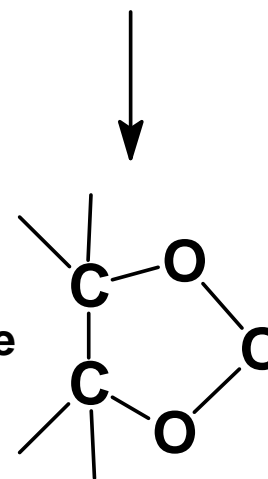
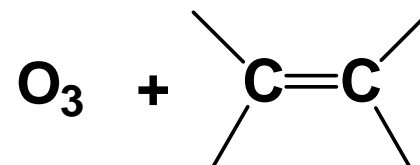
1,4-addition to olefins



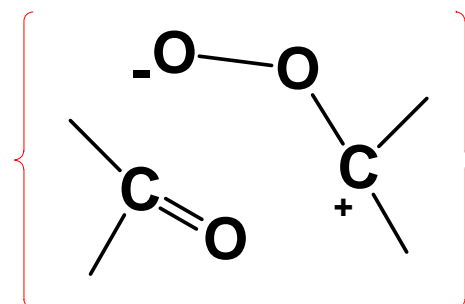
Ozone and its Reactions



Ozonide*

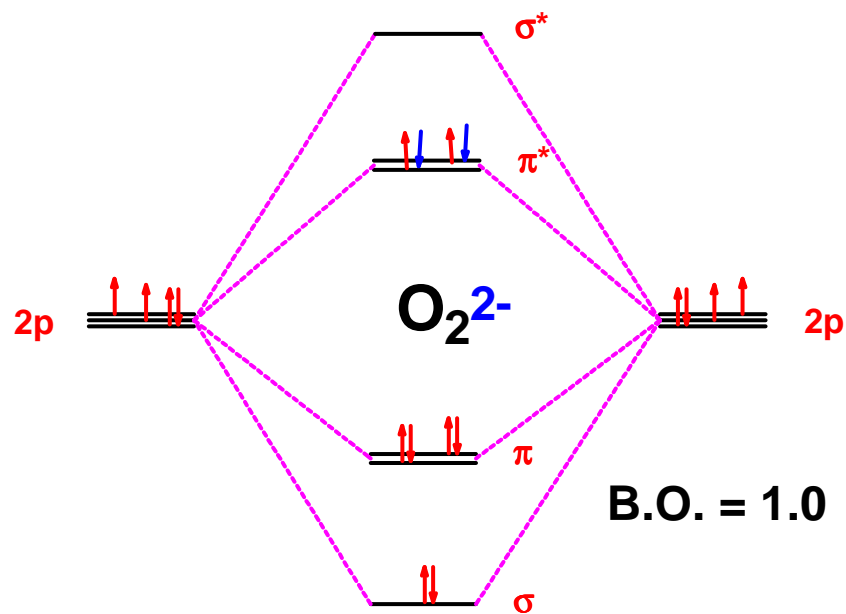
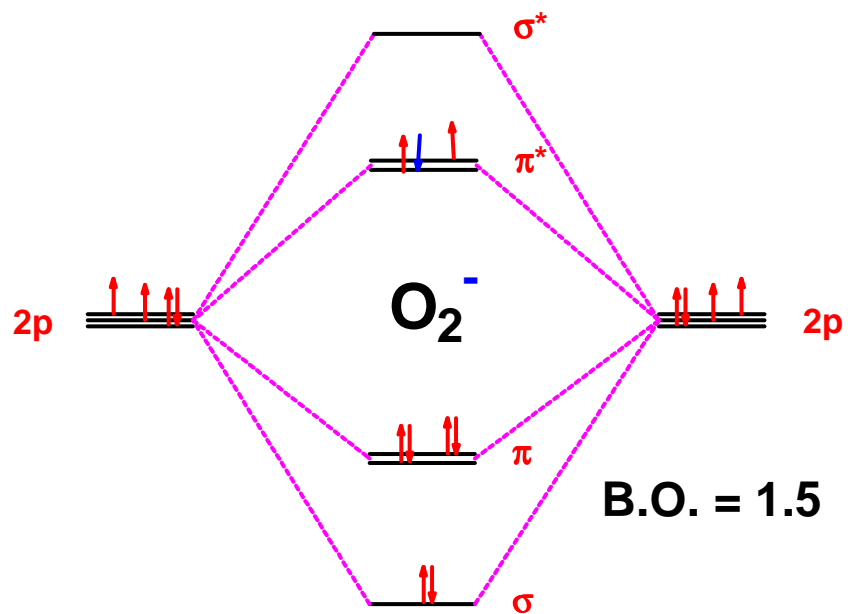
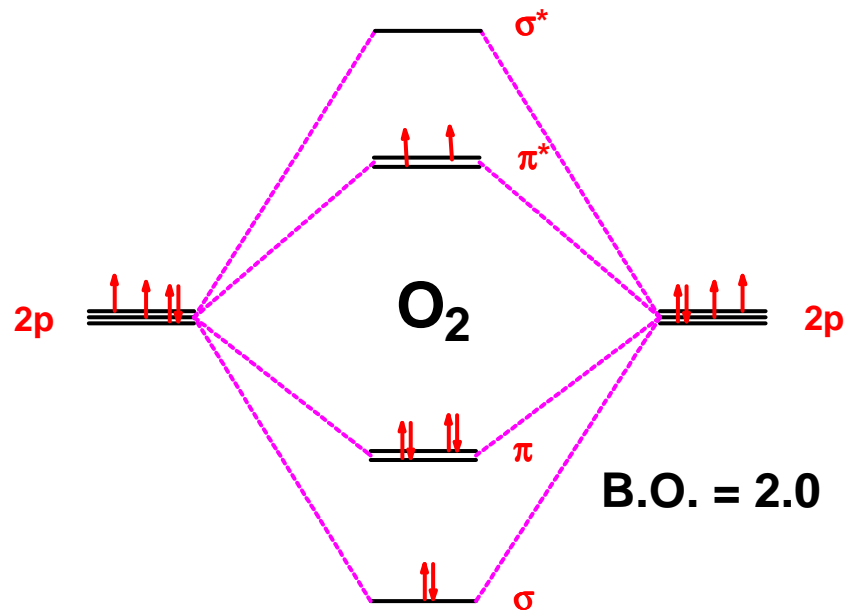
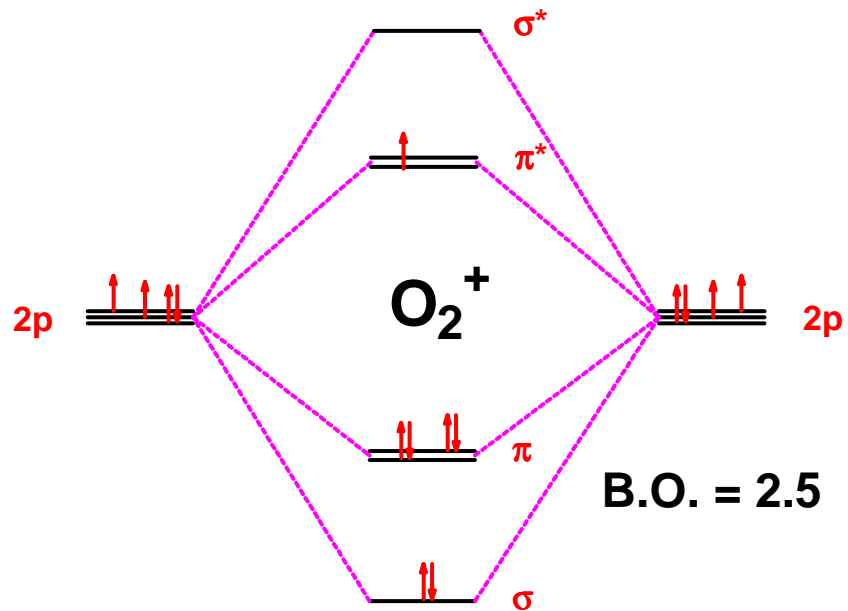


primary ozonide

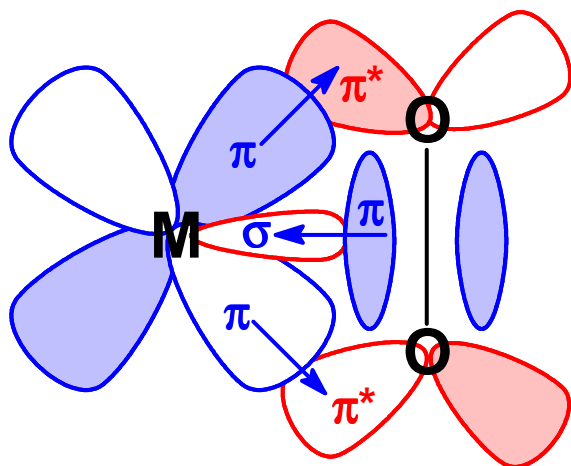


*Can be hydrolysed, oxidized or reduced to aldehydes, ketones or carboxylic acids.

Dioxygen and its Ions



Dioxygen as a Ligand

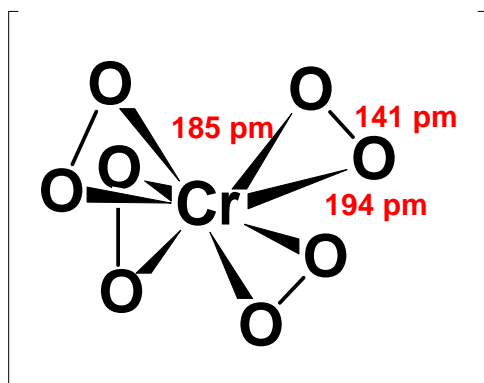
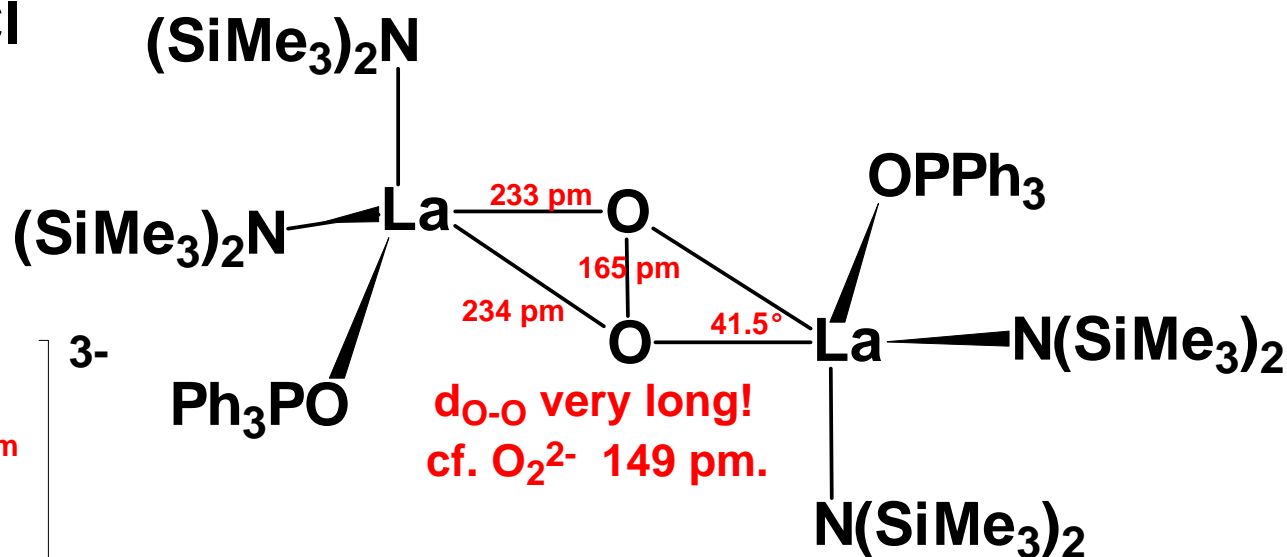
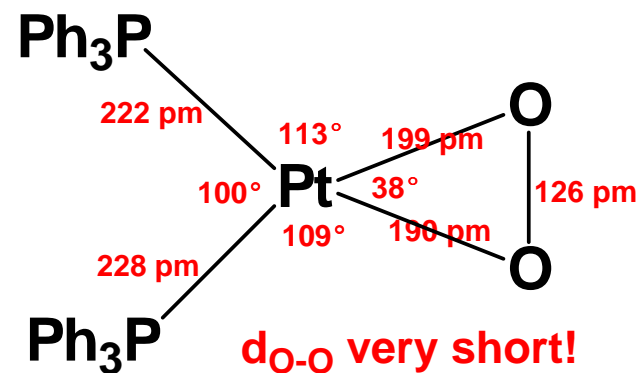
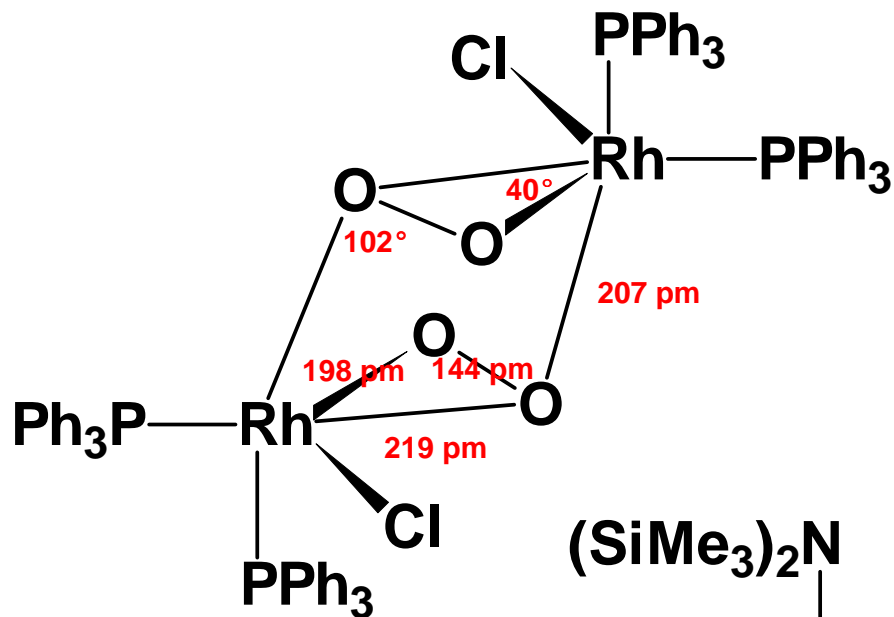


The bonding of dioxygen to a transition metal is in the η^2 -mode very similar to olefin dihapto bonding. The major difference is that dioxygen is such a powerful π -acceptor that most metals completely lose the electrons to the oxygen thus forming oxides. Transition metals that η^2 -bond to dioxygen cause dioxygen to assume the $^1\Delta$ configuration, and many are oxidation catalysts.

Catalytic Oxidation

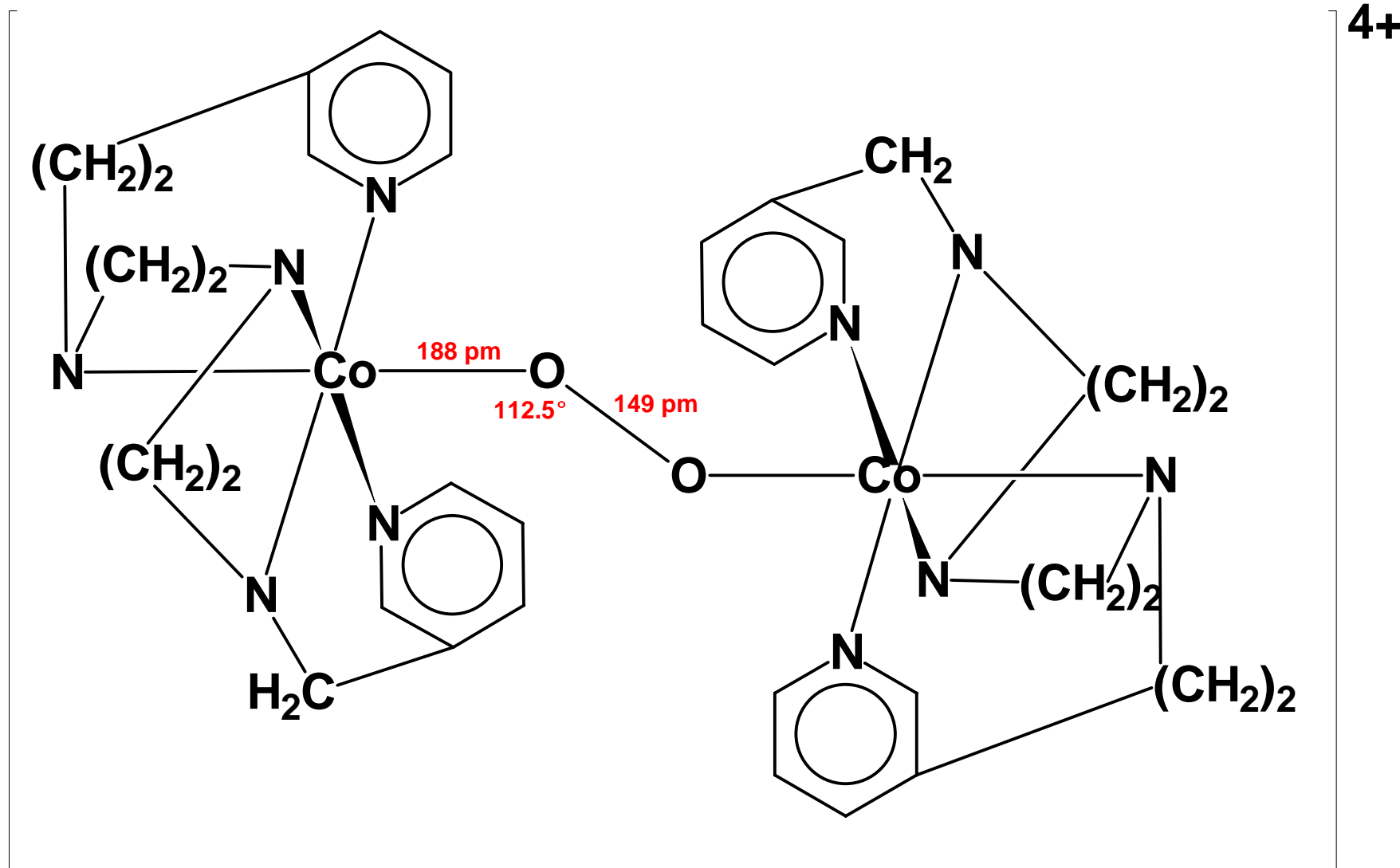
- Coordinated dioxygen is diamagnetic ($^1\Delta$ state) which allows spin conservation with singlet substrates.
- Coordinatively unsaturated complexes can hold O_2 and coordinated organic substrate in cis-proximity.
- Coordination of O_2 partially reduces it (O_2^- & O_2^{2-}) which activates O_2 in many reactions.

Dioxygen as a Ligand

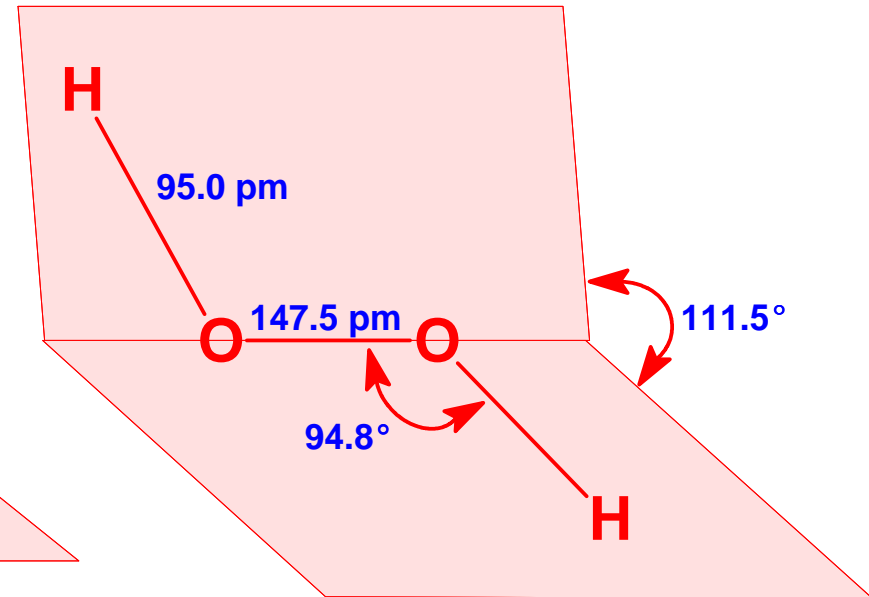
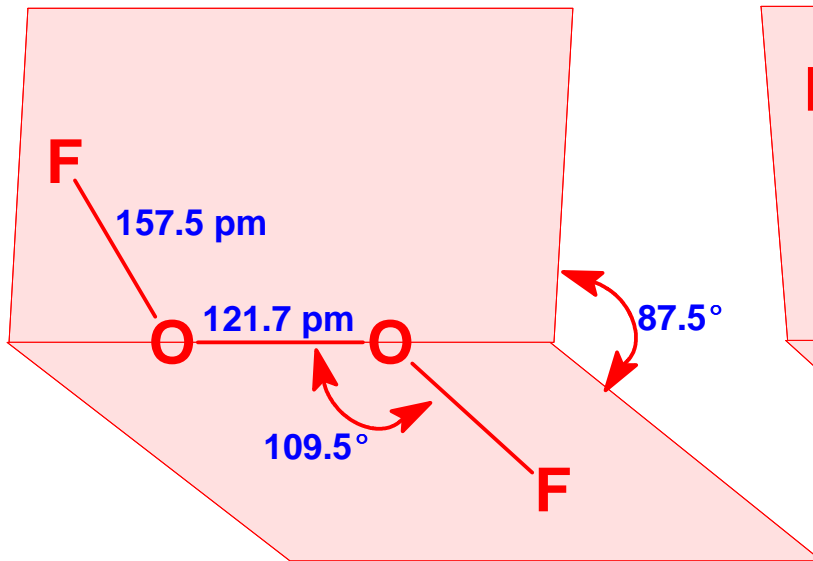
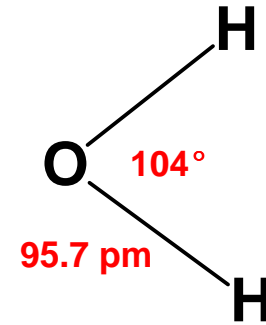
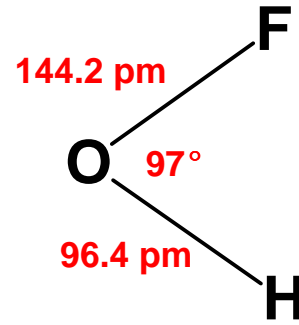
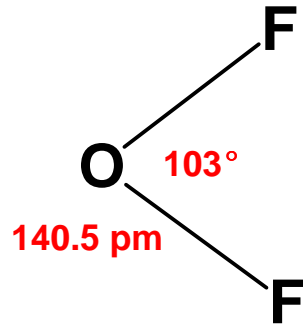


A great number of dioxygen "peroxo" complexes can be made from hydrogen peroxide.

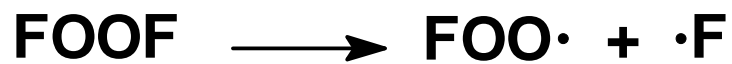
Dioxygen as a Ligand



Oxygen Fluorides

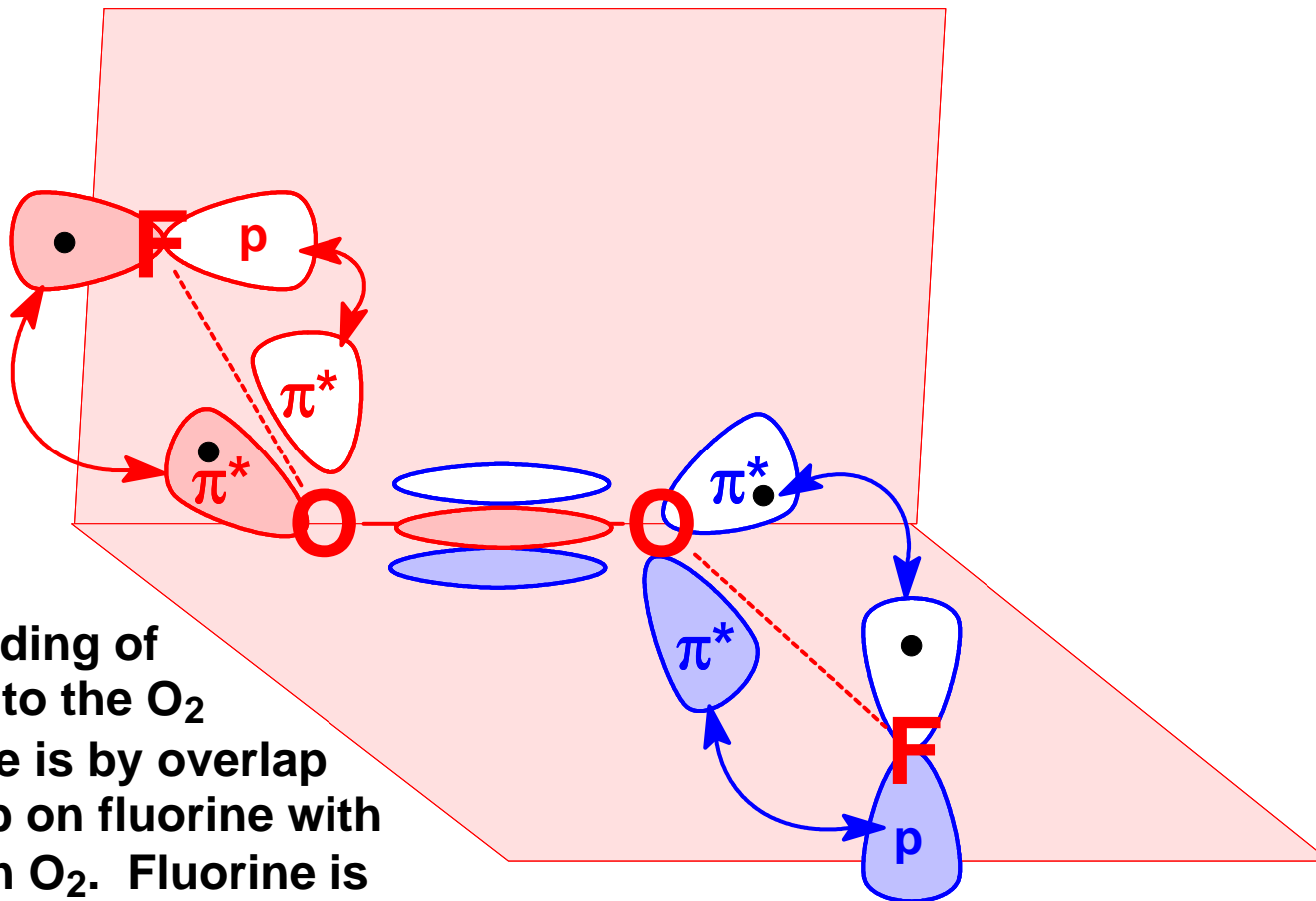


cf O=O 120.74 pm



O-F very long, weak, O-O very short, strong.

Bonding in Dioxygen Difluoride



The bonding of fluorine to the O_2 molecule is by overlap of the $2p$ on fluorine with the π^* on O_2 . Fluorine is unique in being more electronegative than oxygen, so there is little increase in π^* electron density thus preserving the double bond of O_2 .