CSO 203: Inorganic Molecules, Materials & Medicine

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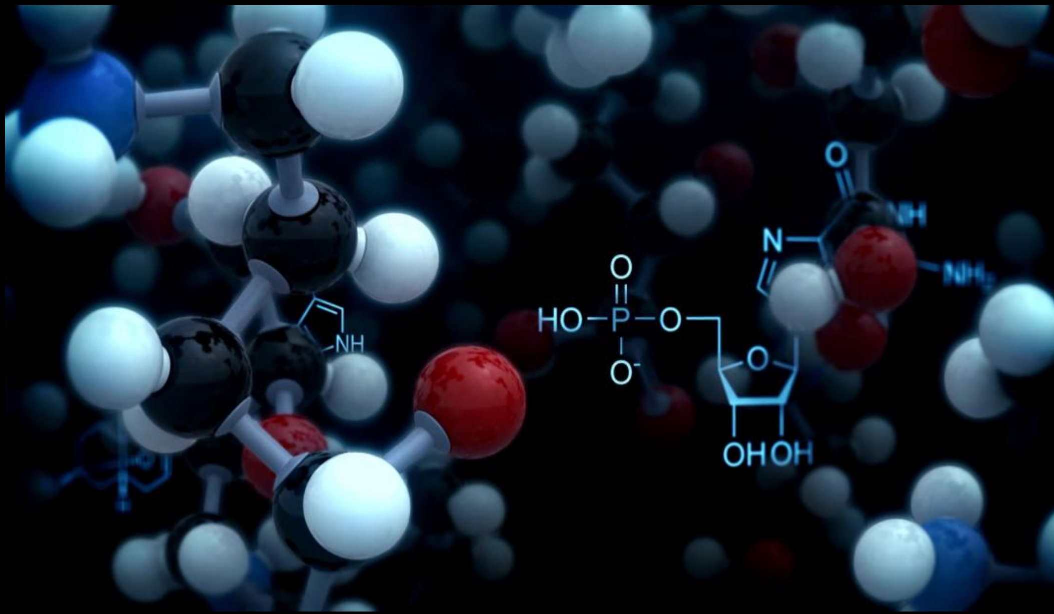

Appu

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First Course Handout (FCH)

Lecture notes, course materials, and related documents can be accessed from **Mookit (Resources)**.

Lectures: L3
Mon, Wed and Thu 9.00-09.50

Tutorials: L3
Fri 9.00 – 09.50 am

Course Guidelines

1. **Attendance Policy:**
   - Minimum **75% attendance** (lectures) required to sit for Mid- and End-semester exams.
2. **Examinations:**
   - The DOAA will announce Mid- and End-semester schedules.
   - **No makeup exams for quiz and Mid-Semester exams.**
   - End-semester makeup exam is **ONLY for valid medical cases approved** by SUGC/SPGC/DOAA.
3. **Classroom Rules:**
   - No electronic gadgets during lectures/tutorials.
   - If carrying a mobile, keep it switched off or on silent mode.
   - Laptops are not permitted during class time.

Examinations and Marks Distribution:

Exam schedule	Marks
Quiz 1 (1st week of September)	20
Mid-Sem (as per the DoAA schedule)	50
Quiz 2 (1st week of November)	20
End-Sem (as per the DoAA schedule)	50
Attendance	10

Course Contents

Module I: Life with Oxygen

Module II: Metals and Medicine

Module III: Electron Transfer Process

Module IV: Catalysis and Sustainability

Module V: Electrochemistry and its Applications

Module VI: Supramolecular Chemistry

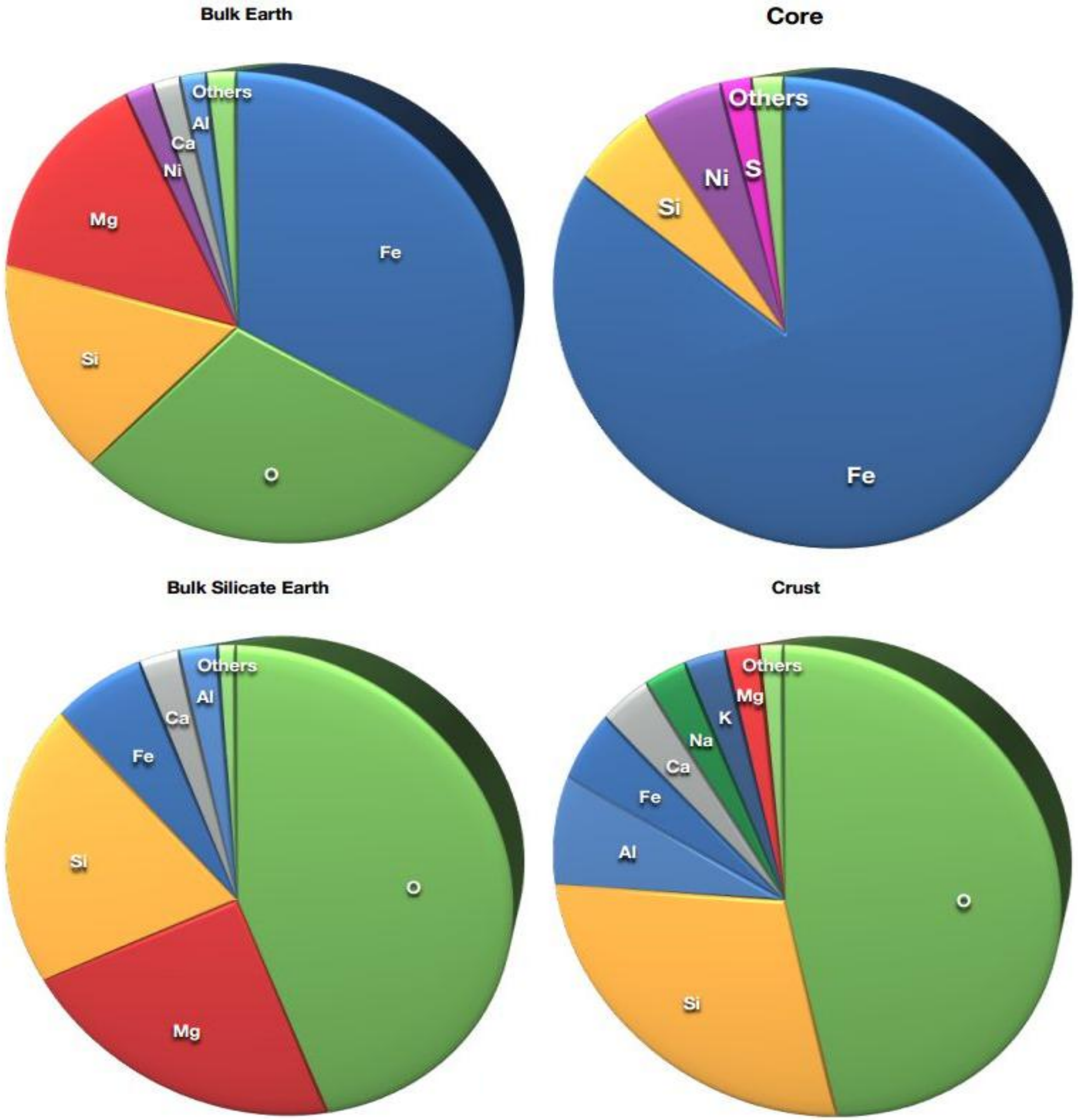
Module VII: Graphene and Carbon Nanotubes

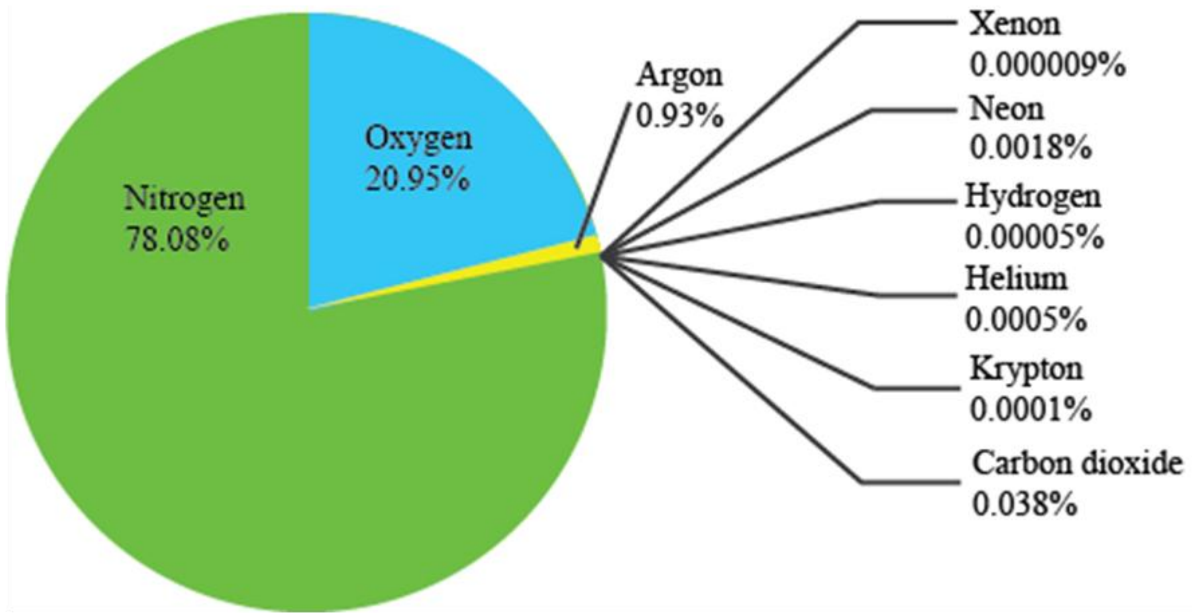
Life with Oxygen

$4Fe + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_3$ $\quad$ $\mathrm{Fe(OH)_3} \rightarrow Fe_2O_3 \cdot xH_2O$

$4Cu + O_2 \rightarrow 2Cu_2O$ $\quad$ $2Cu_2O + O_2 \rightarrow 4CuO$

Oxygen: Abundance!

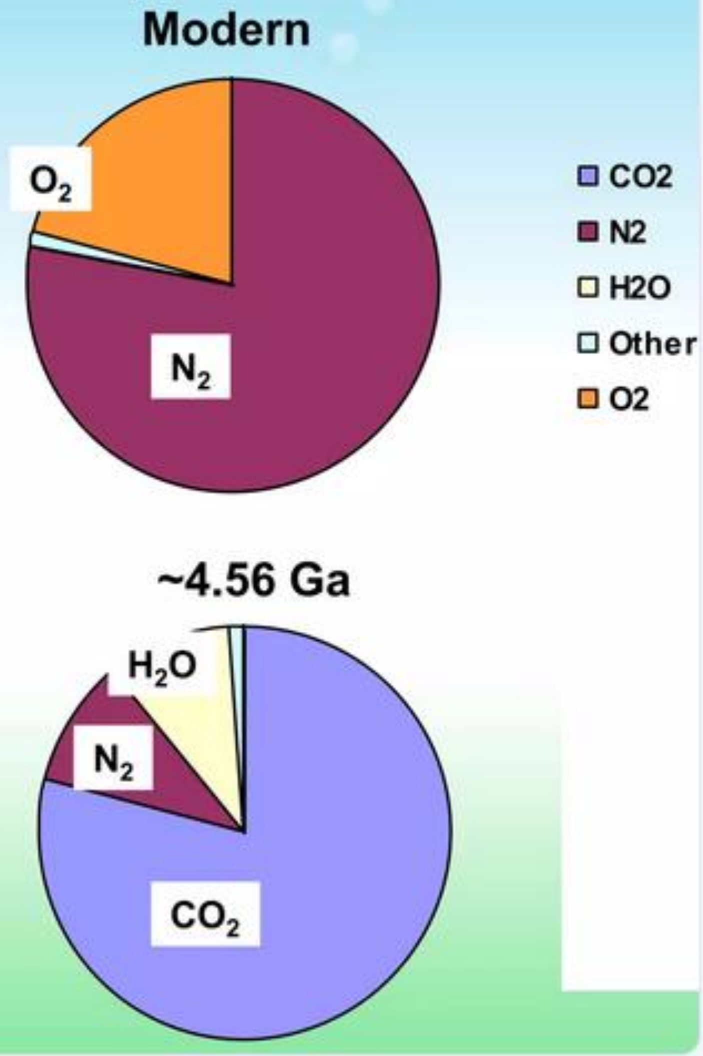




- Most abundant in earth (as whole)
- Third most abundant in the universe (preceded by H and He)

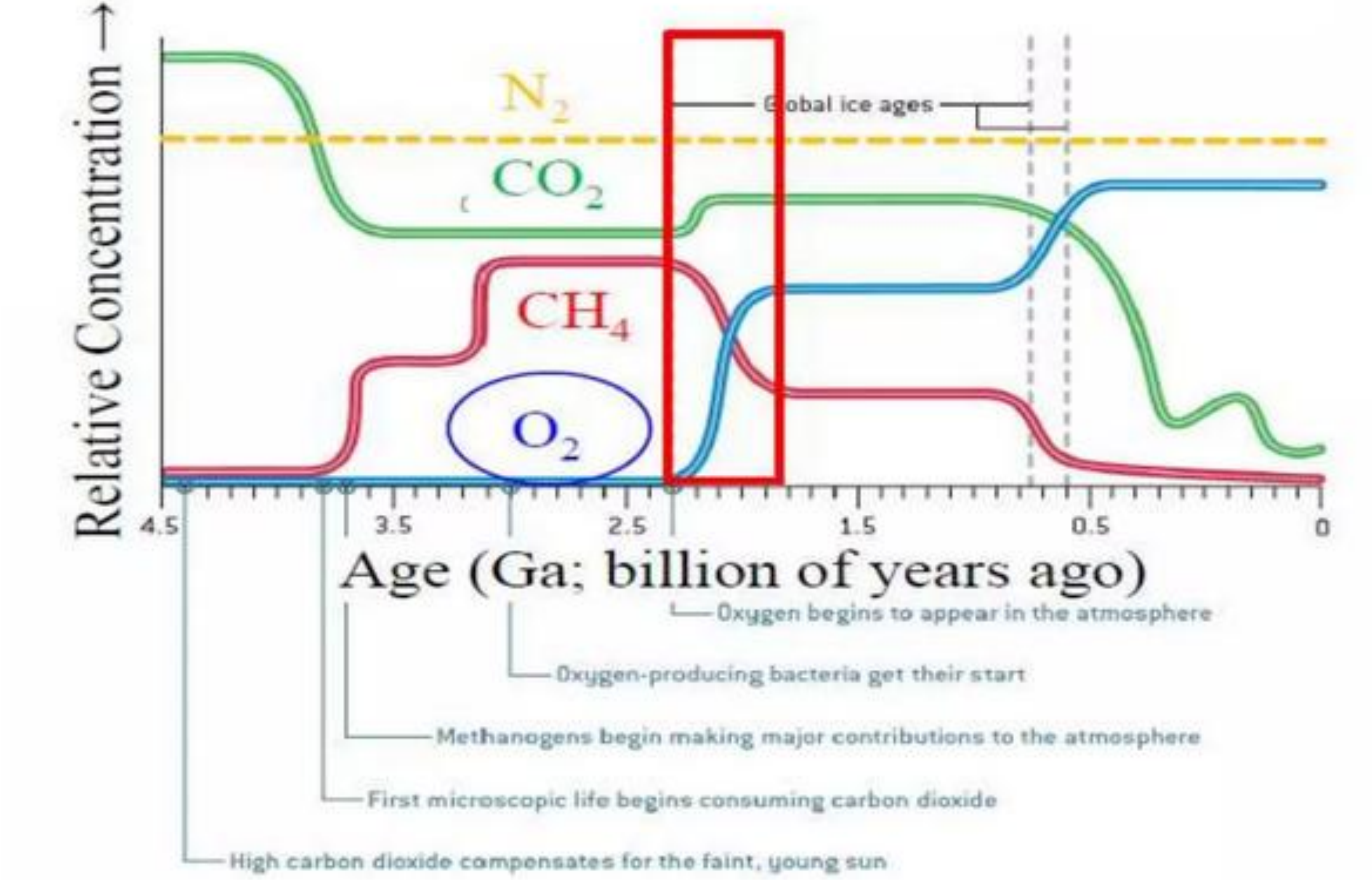
Composition of Early Atmosphere

- Secondary atmosphere composition
  - No O_2: No photosynthetic organisms to produce free O_2
  - Some N_2: Inert gas, so all N_2 from volcanic and impact degassing would have remained in atmosphere
  - Lots of CO_2: Chemical weathering rates would have been lower because continents would have been smaller– 30,000x present value!
  - Lots of H_2O: Due to vaporization of oceans
- Global warming!
  - Due to high CO_2, surface temperatures may have been 80-90° C



The Great Oxidation Event (GOE)

- The first significant buildup in atmospheric oxygen



Rise of Oxygen

Great Oxidation Event: rise in atmospheric oxygen levels between 2 and 2.4 Ga

- Cyanobacteria (prokaryotes) develop ability to photosynthesize
  - Appeared 1 billion years before rise of oxygen
  - Increase O_2 source
- Oxidation of mantle
  - Decrease O_2 sink
- Switch from mainly submarine to sub-aerial volcanoes
  - Due to development of thick continental crust
  - Decrease O_2 sink

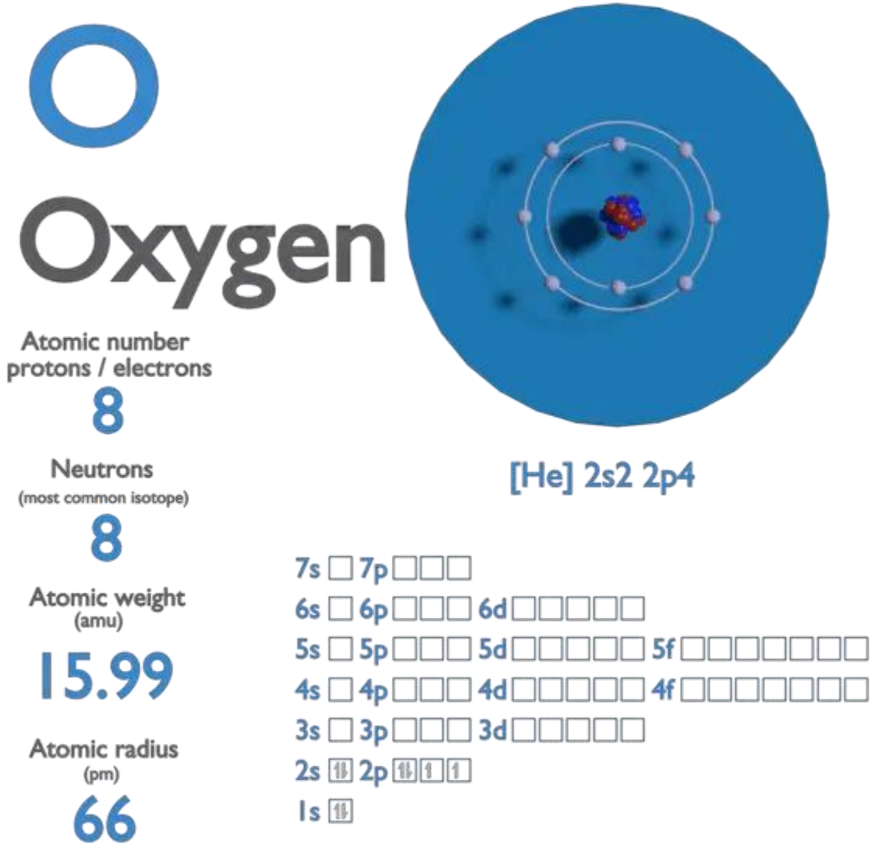
Cyanobacteria- first organisms to produce O_2 by photosynthesis

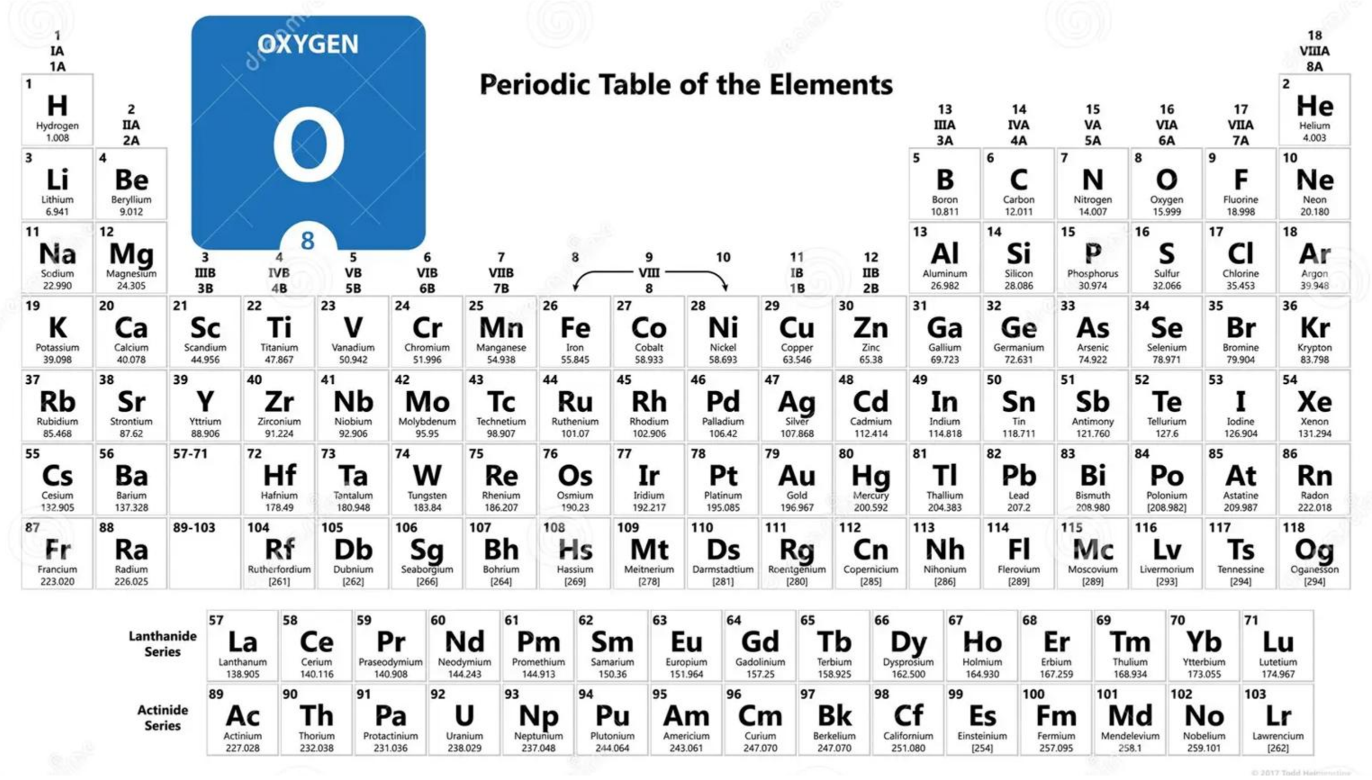
Photosynthesis:
$CO_2 + H_2O \dashrightarrow CH_2O + O_2$

Preferentially uses ^{12}C
$CO_2 + H_2O \dashrightarrow {}^{12}CH_2O + O_2$

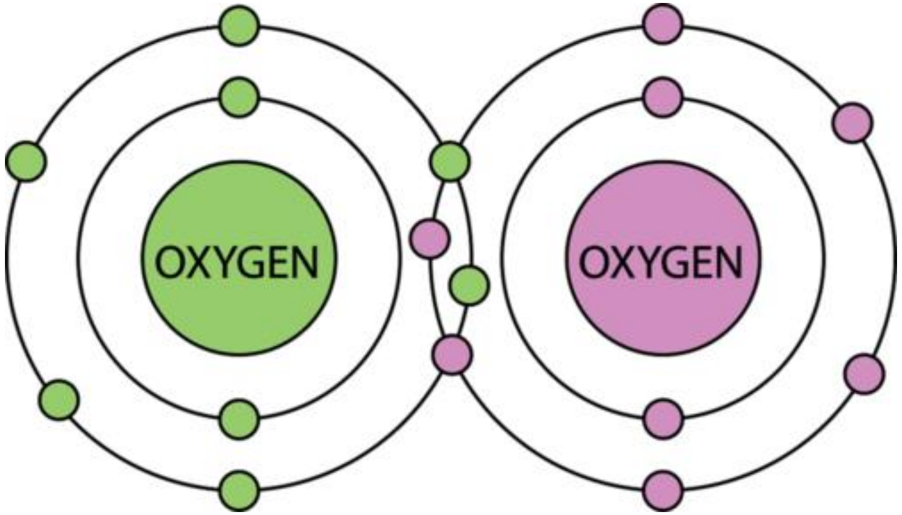
Results in an shift in $^{13}C/^{12}C$ preserved in limestones

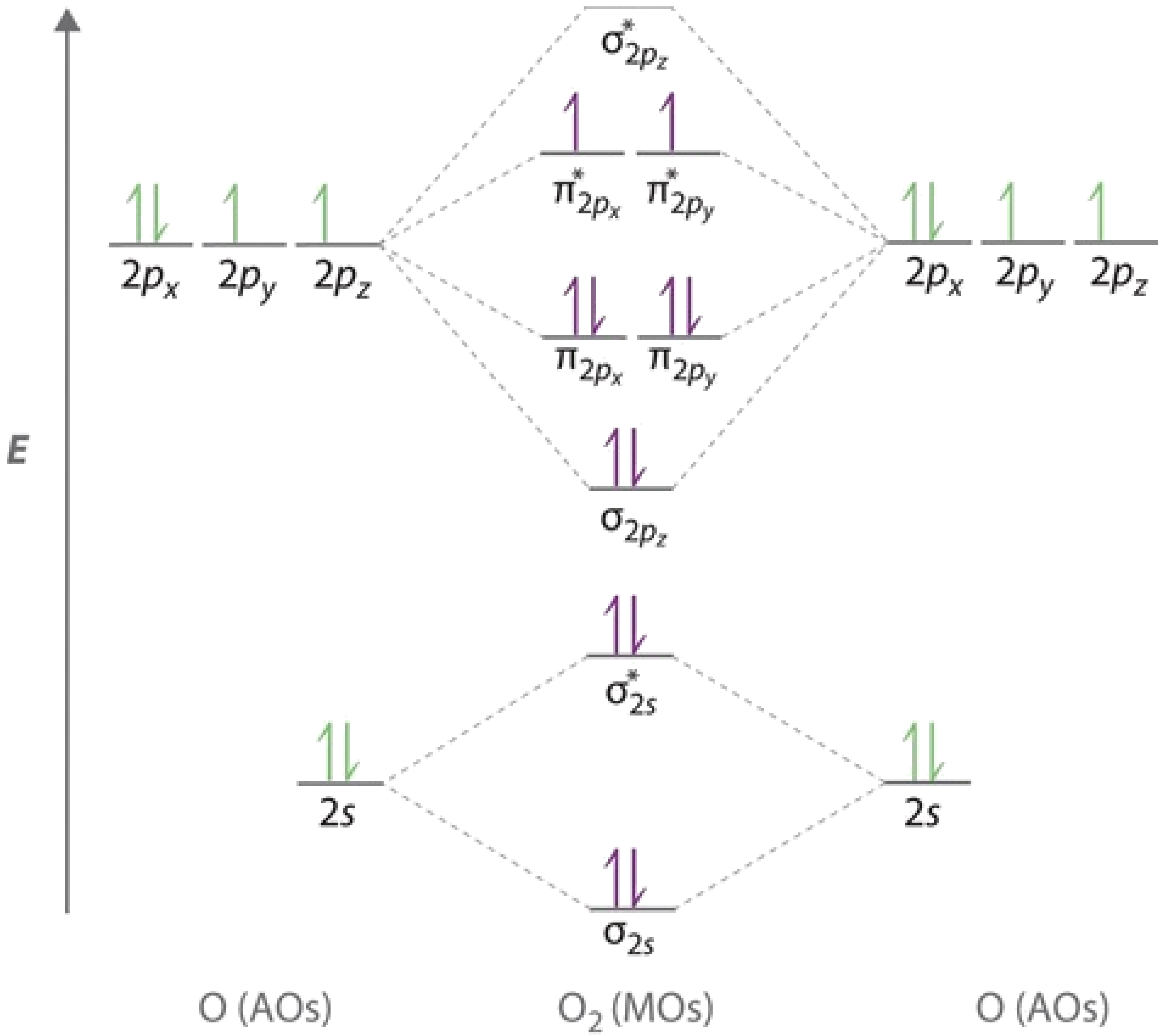
Oxygen: The Atom!





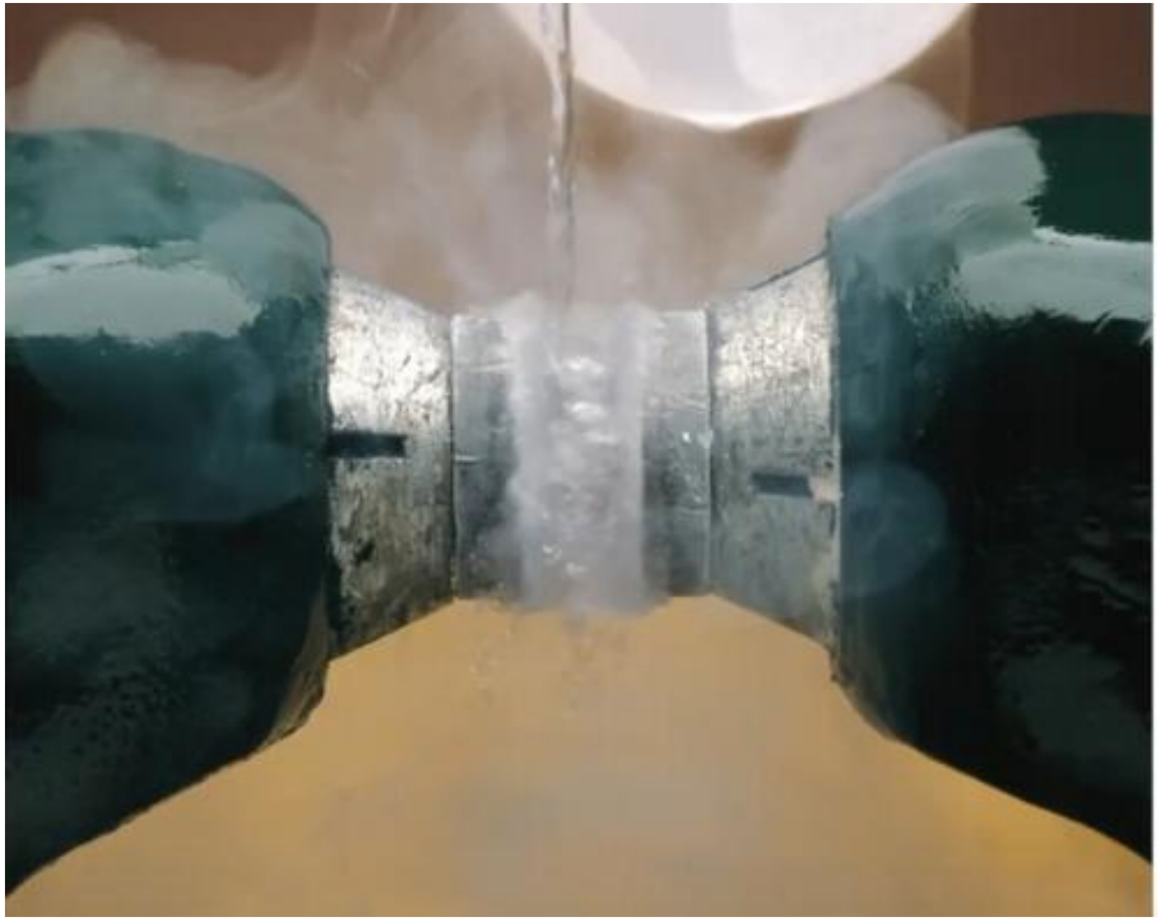
Oxygen: The Molecule (O_2)!





*Colors are for the ease of understanding
*Both O atoms forming O_2 are identical

Oxygen: Paramagnetic in nature!

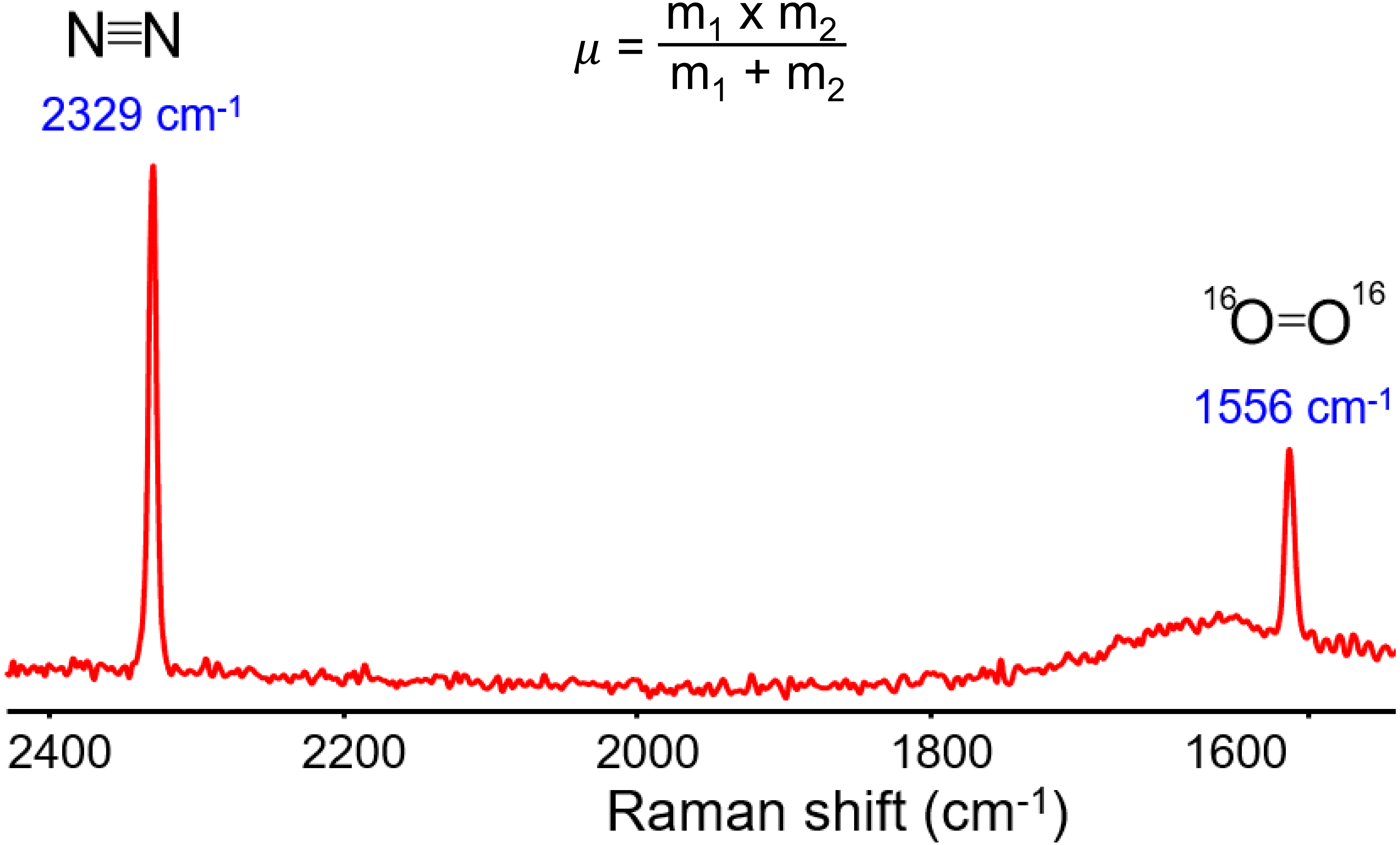


https://www.youtube.com/watch?v=WuG5WTId-IY&t=185s **2.30 to 4.10 min**

Raman spectrum of the atmosphere

$$\bar{\nu} = \frac{1}{2\pi c}\frac{\sqrt{k}}{\sqrt{\mu}} \longrightarrow \frac{\bar{\nu}_1}{\bar{\nu}_2} = \frac{\sqrt{\mu_2}}{\sqrt{\mu_1}}$$

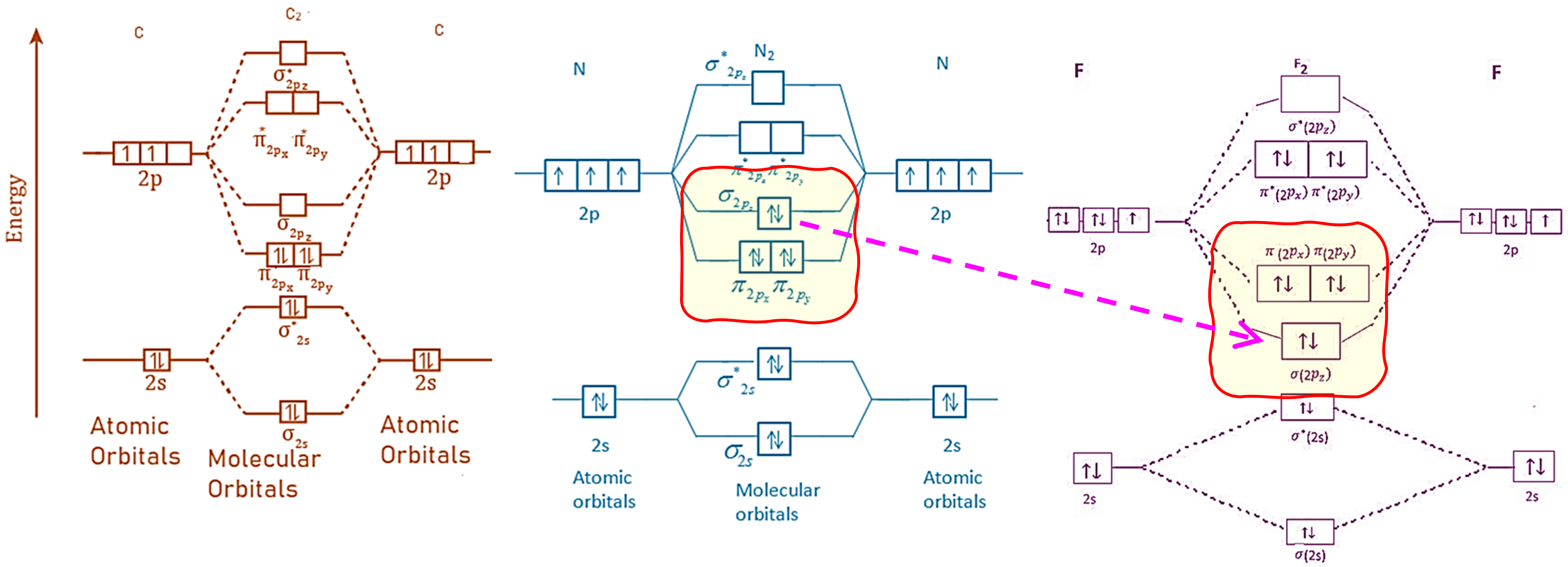
$$\mu = \frac{m_1 \times m_2}{m_1 + m_2}$$



@473 nm

MO Diagrams of Some Homonuclear Molecules!

C_2 **N_2** **F_2**



Constructing MO Diagrams!

1. Identify the Atomic Orbitals (AOs) Involved
2. Combine Atomic Orbitals to Form Molecular Orbitals
3. Consider the Energy Ordering of Mos
4. Fill Molecular Orbitals with Electrons
5. Determine the Bond Order
6. Analyse the Magnetic and Electronic Properties

Combining AOs to Form MOs!

- When two AOs combine, they form one bonding **MO** (lower energy) and one antibonding **MO*** (higher energy)

- $2s + 2s \rightarrow \sigma_{2s}$ (bonding) and σ^*_{2s} (antibonding).
- $2p_z + 2p_z \rightarrow \sigma_{2p_z}$ (bonding) and $\sigma^*_{2p_z}$ (antibonding).
- $2p_x + 2p_x \rightarrow \pi_{2p_x}$ (bonding) and $\pi^*_{2p_x}$ (antibonding).
- $2p_y + 2p_y \rightarrow \pi_{2p_y}$ (bonding) and $\pi^*_{2p_y}$ (antibonding).

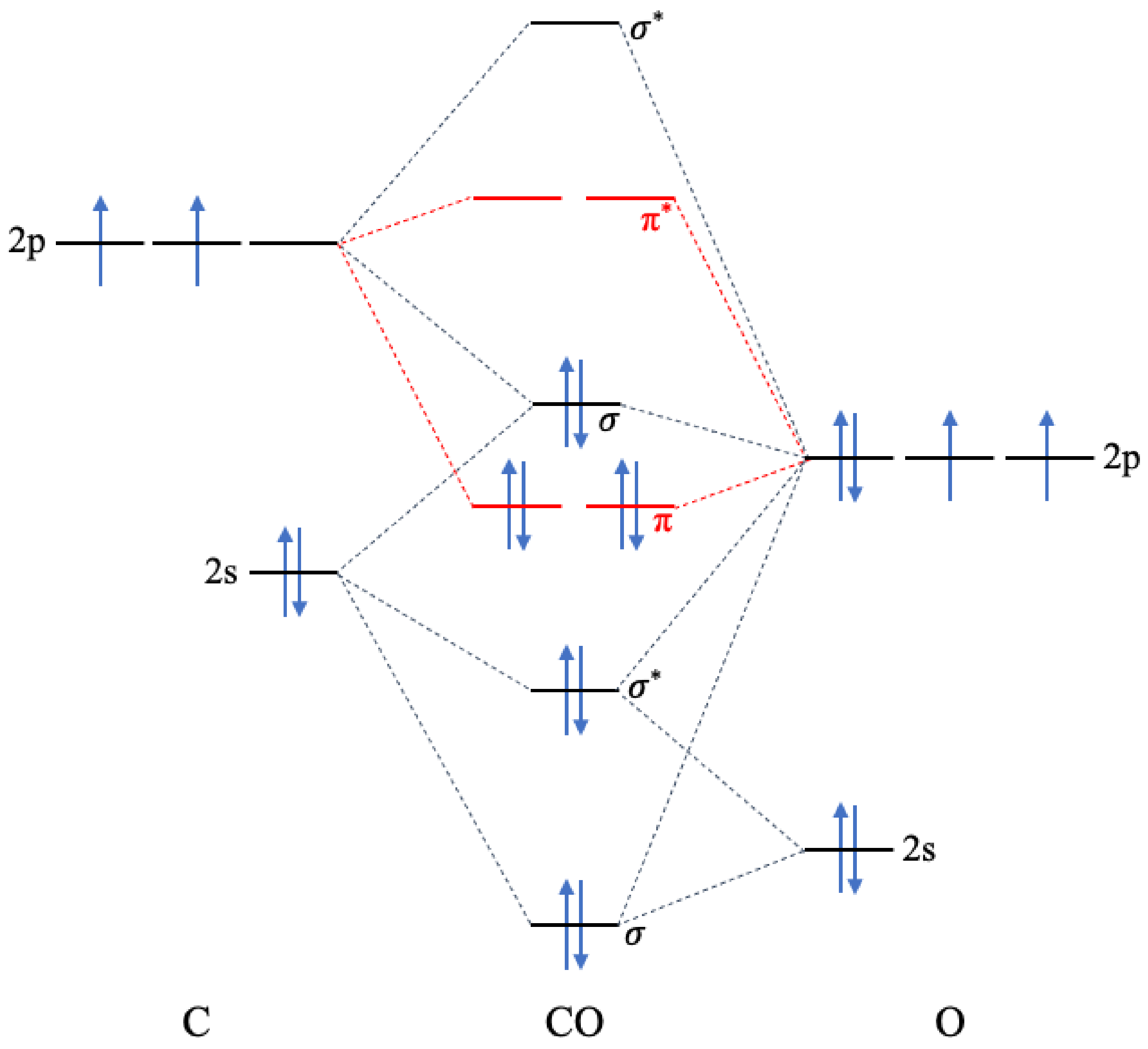
Energy Levels of MOs!

- The energy level of these MOs follow this order for Li_2-N_2.
- For O_2 and F_2, σ_{2pz} is lower in energy than the bonding π_{2px} and π_{2py} MOs.

$$\sigma_{2s} < \sigma^*_{2s} < \pi_{2p_x}, \pi_{2p_y} < \sigma_{2p_z} < \pi^*_{2p_x}, \pi^*_{2p_y} < \sigma^*_{2p_z}$$

MO of **CO**!

- Energies of AOs of oxygen is much lower than that of carbon
- Bonding orbitals resemble more like AOs of oxygen
- Antibonding orbitals must, in turn, resemble more like the AOs of carbon (Think why?)
- The most electronegative nuclei draw the shared pair towards them more

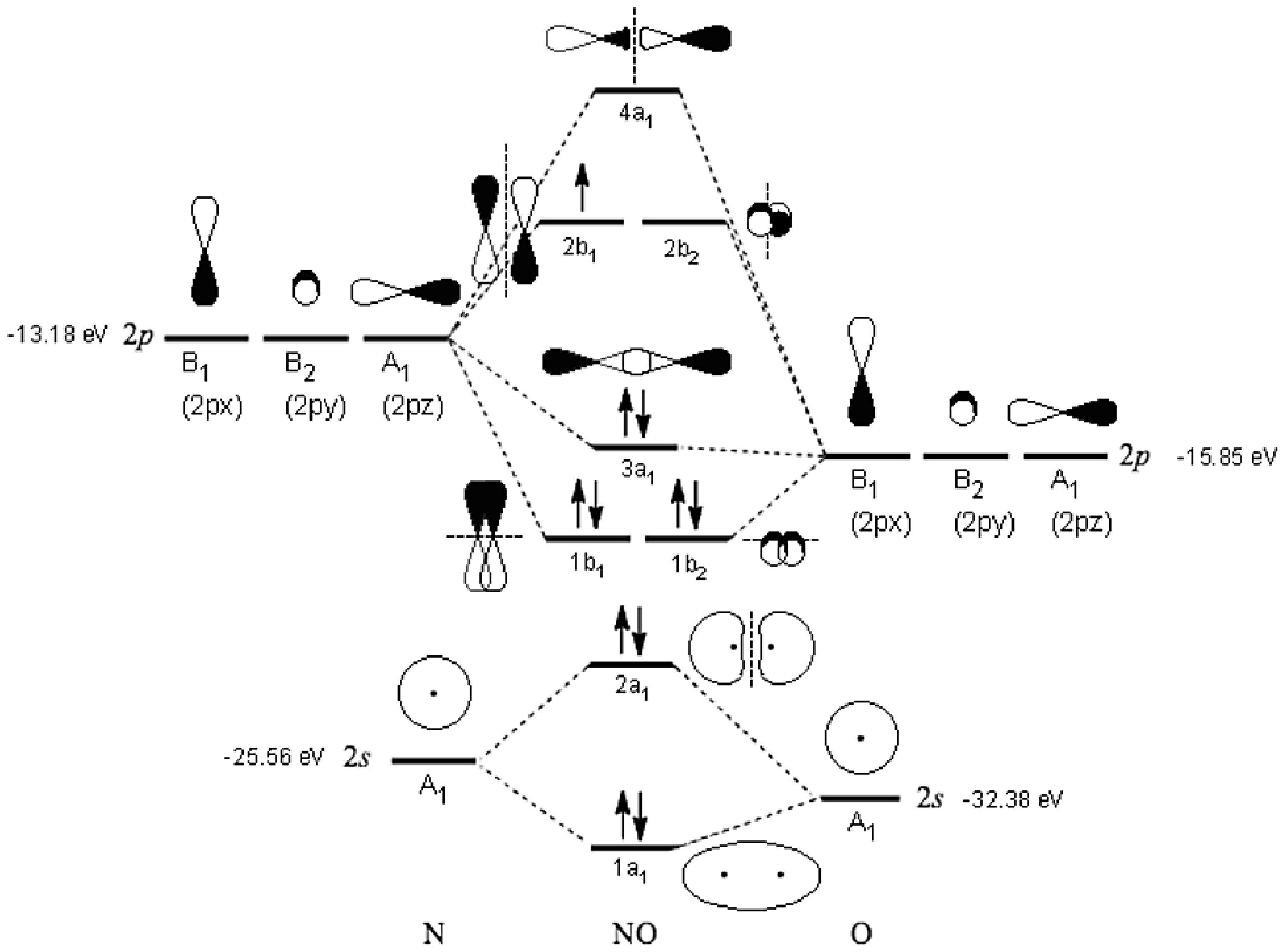


Bond Order!

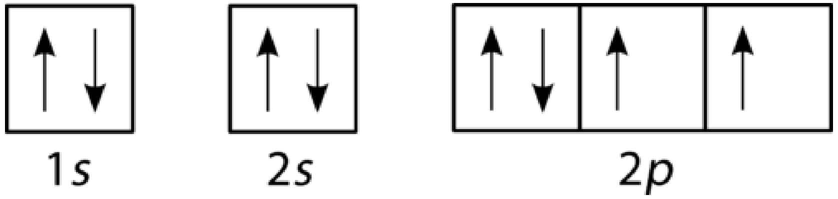
BO = $(n_B - nAB)/2$

= (8-3)/2

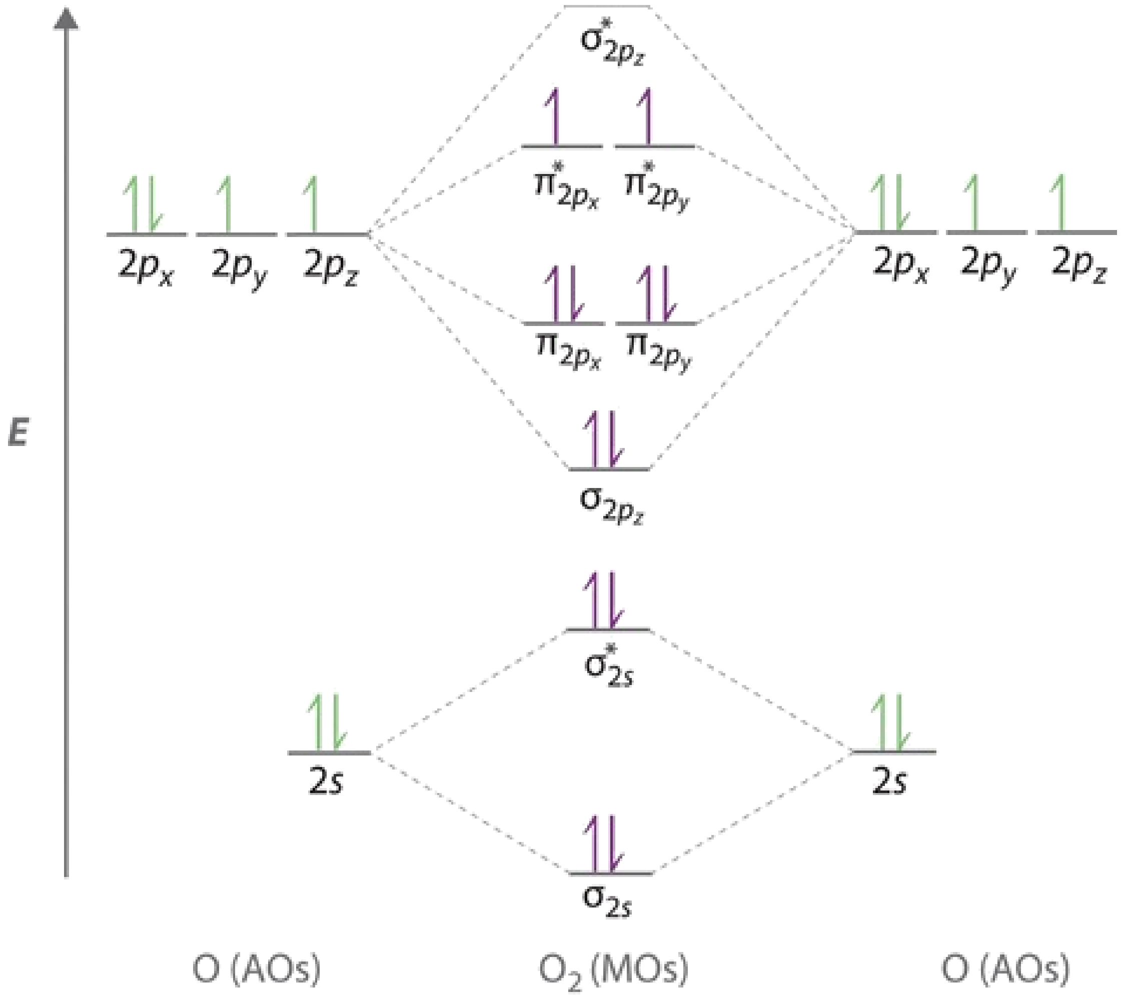
= 2.5



Oxygen: The Atom (O) vs The Molecule (O_2)!

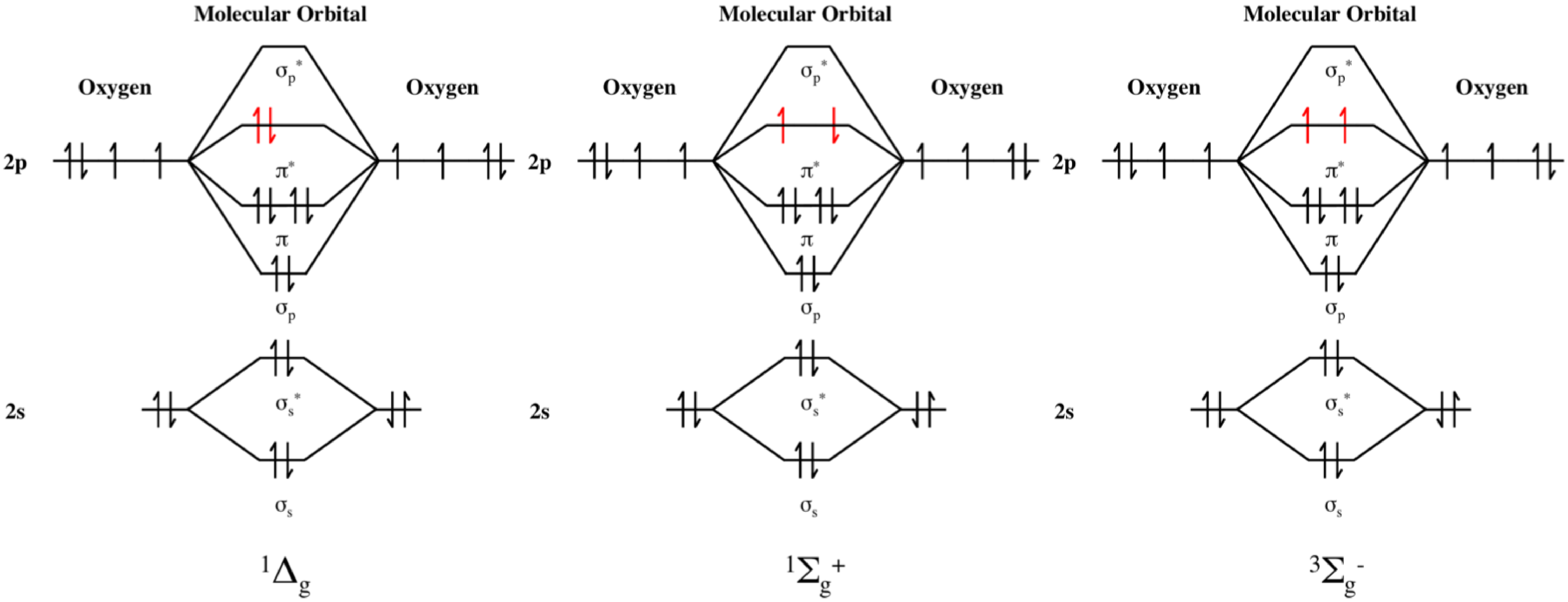


vs

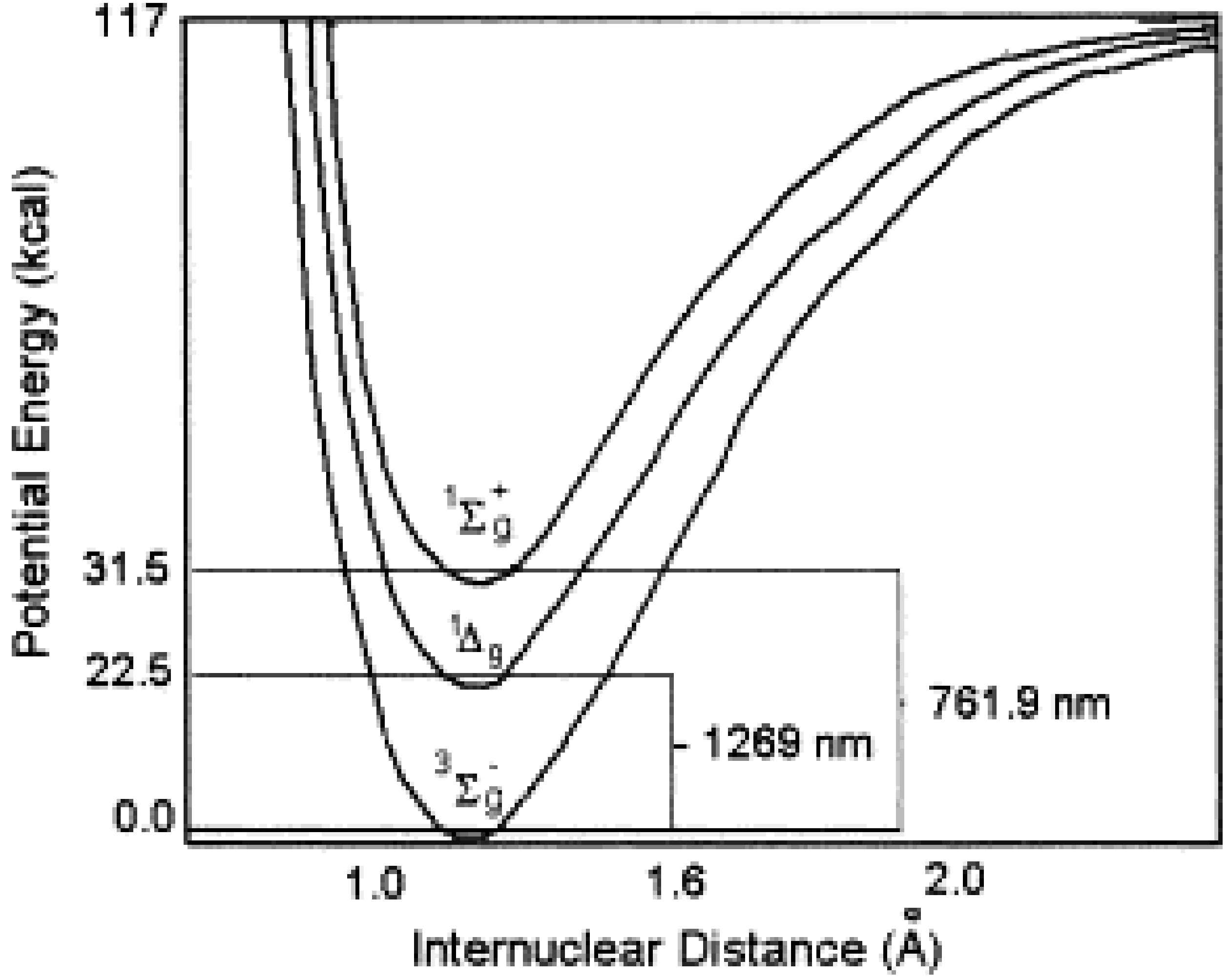


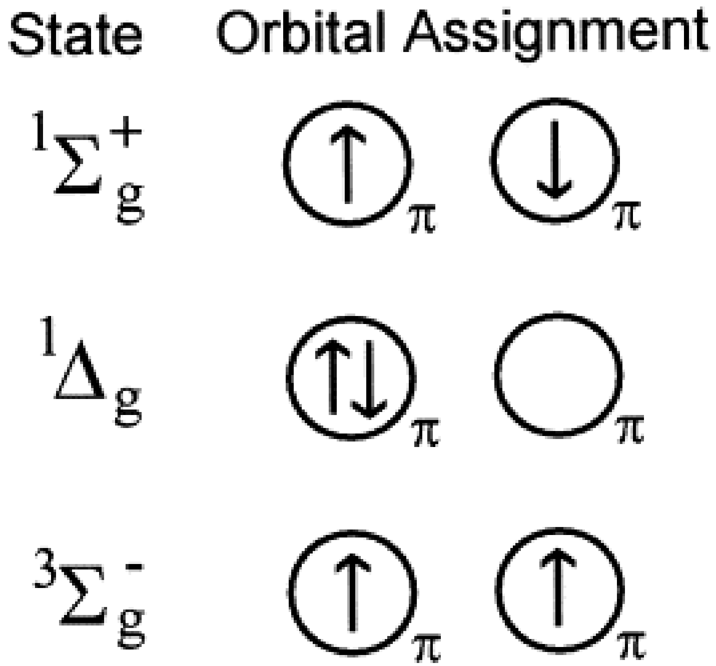
Both are Paramagnetic and Odorless!

Oxygen (O_2): Triplet vs Singlet States!

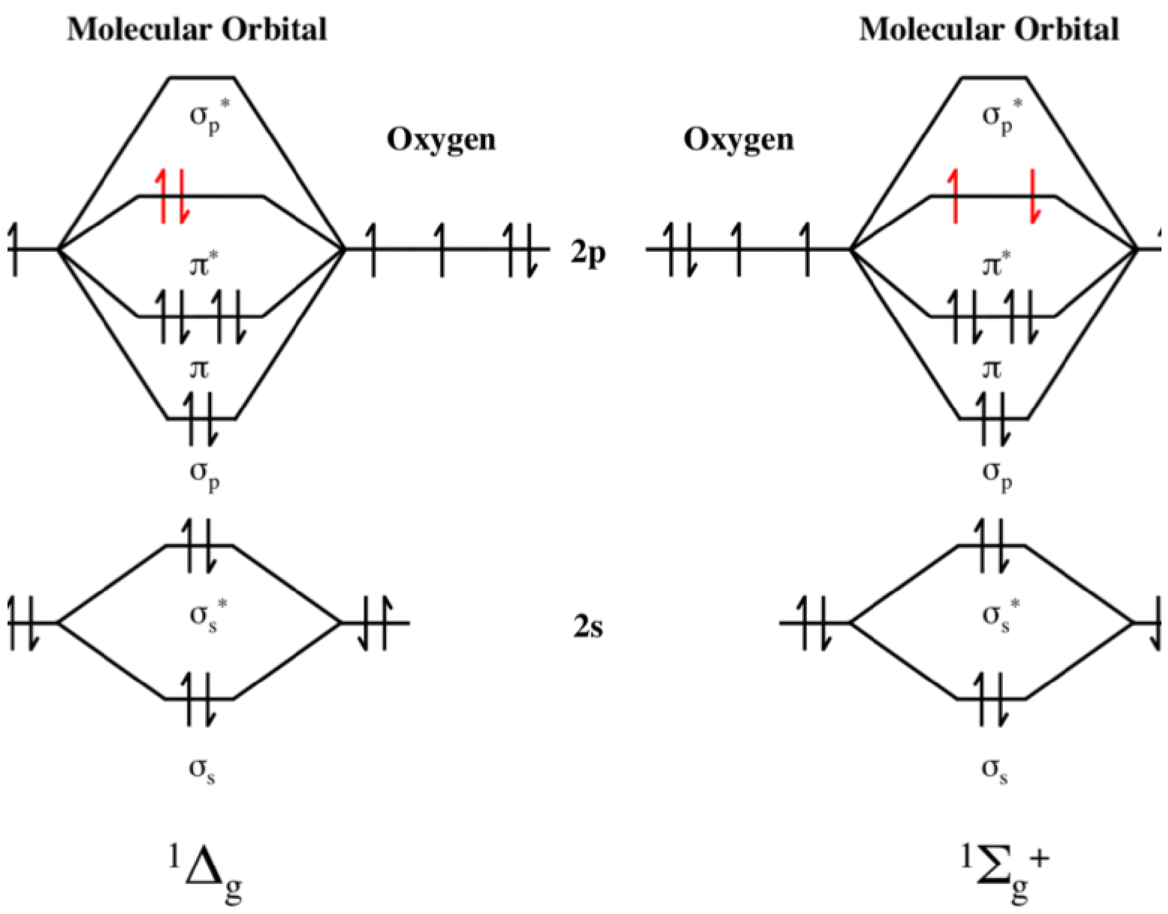


The Internuclear Distances in $^3O_2$ and $^1O_2$!





Oxygen (O_2): The Dioxidene (The Singlet State $^1O_2$)!

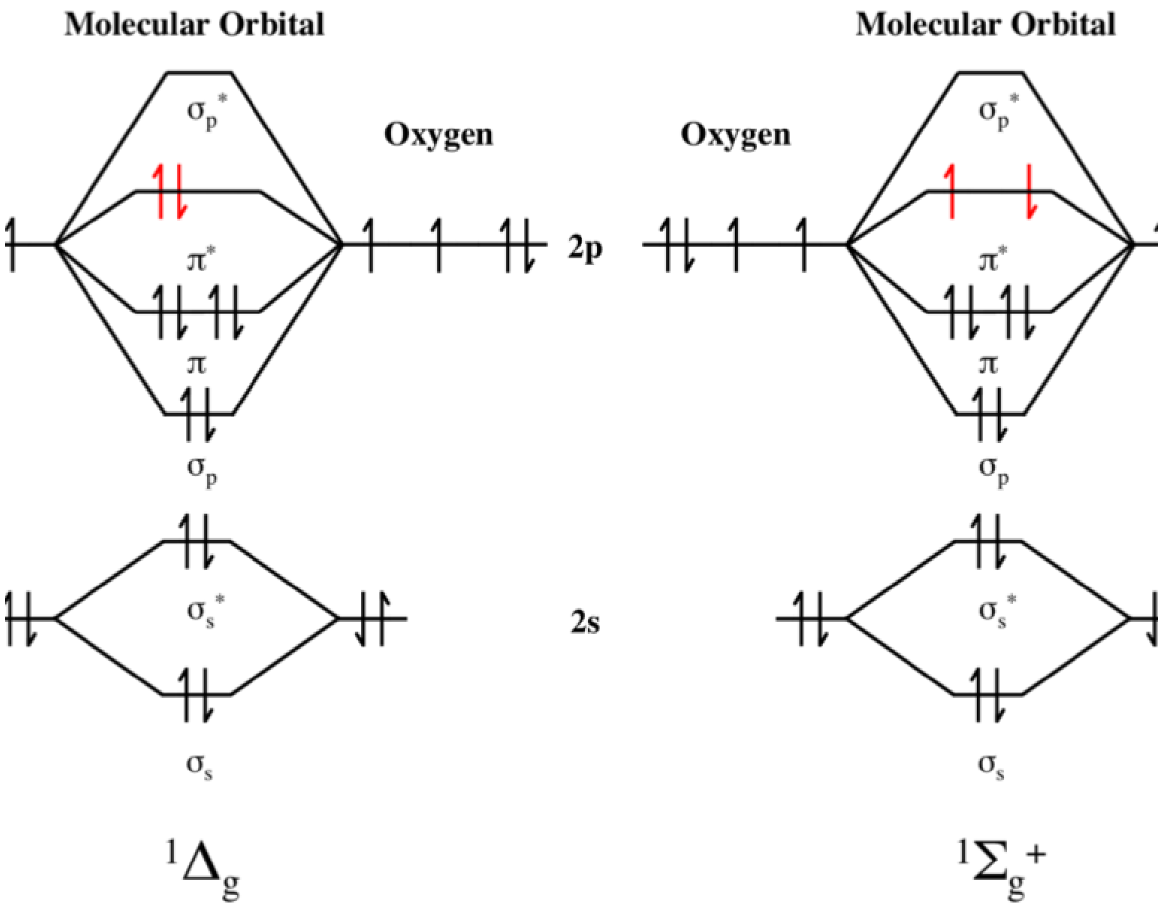


- A quantum state in which all electrons in O_2 are paired
- The lowest possible electronic excitation state of O_2
- Kinetically unstable but decays slowly
- Oxidizes almost everything
  - Forms NO in reaction with N_2
  - Responsible for the photodegradation of matters
  - Used in photodynamic therapy
  - Responsible for O_3 production
  - Used in industrial bleaching and advanced oxidation

Oxygen (O_2): The Dioxidene (The Singlet State $^1O_2$)!

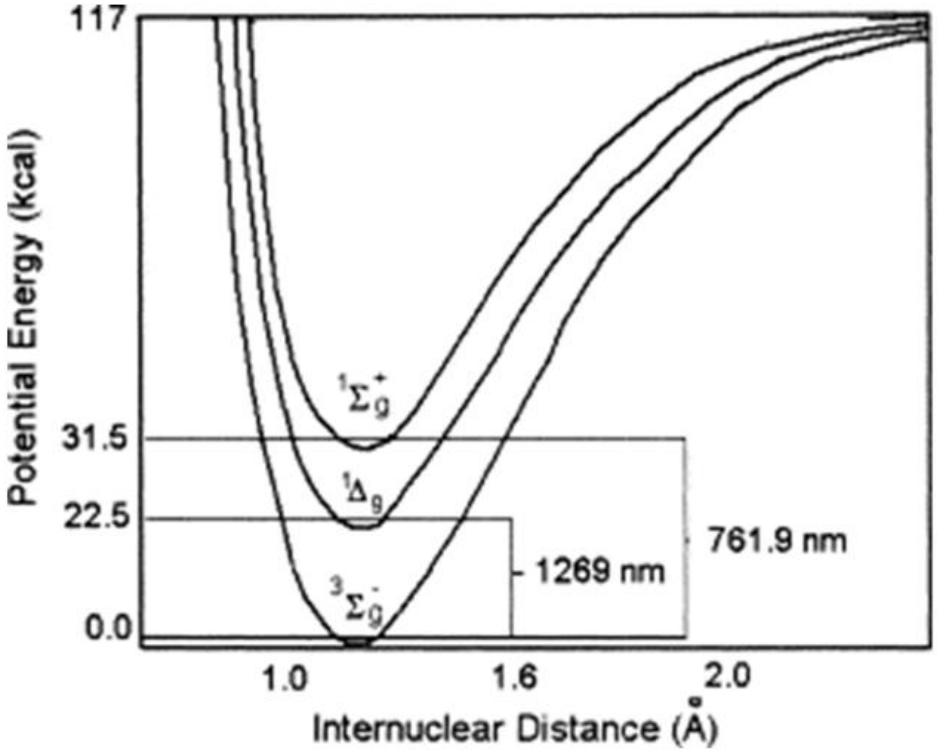
- $^1\Delta_g$ O_2 has its lifetime in milliseconds whereas for $^1\Sigma_g^+$ O_2, it is just in nanoseconds.

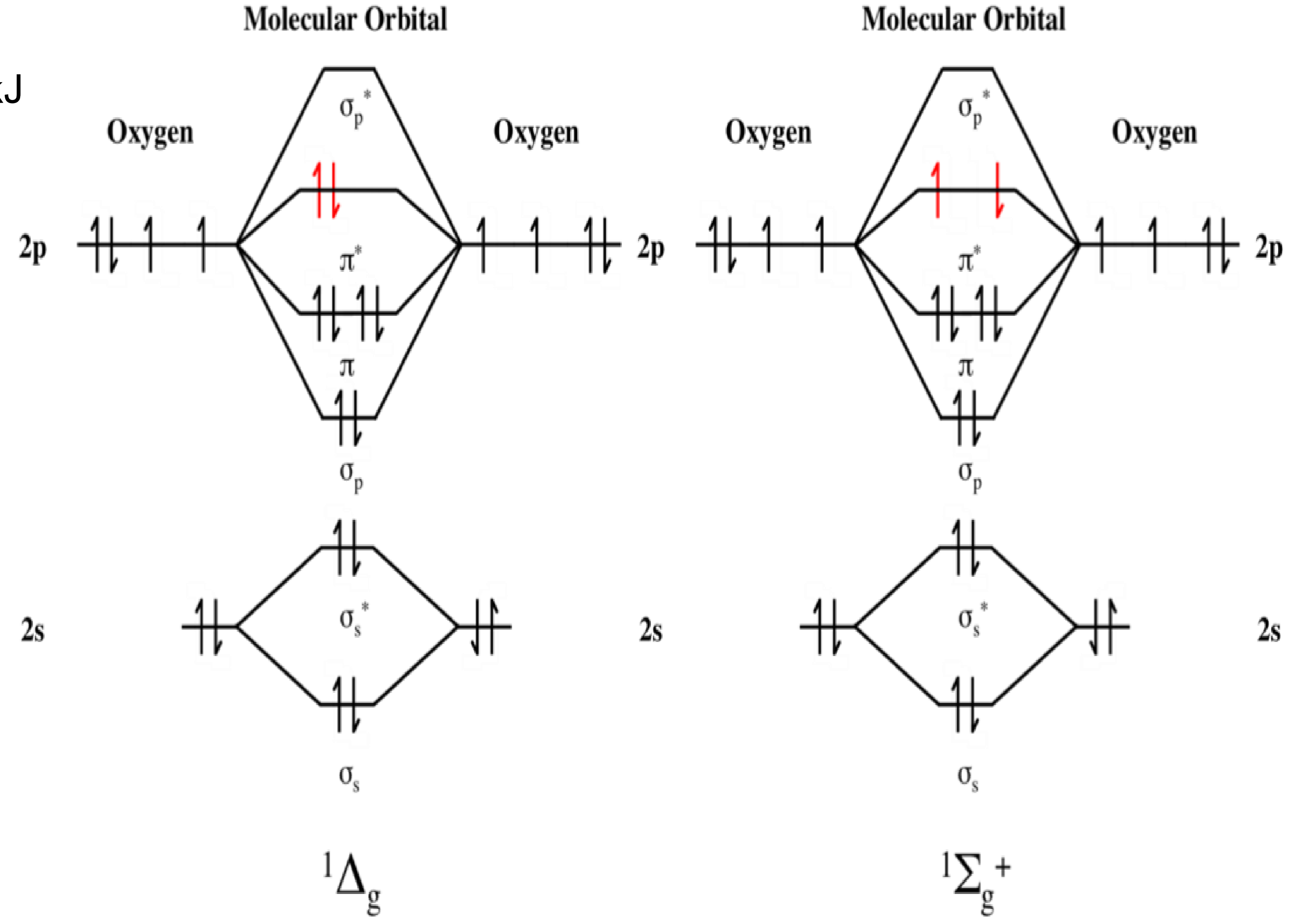
- In liquid phase or in contact with a solid surface, both of them are extremely short-lived (~just a few *picoseconds)*



$^1\Delta_g$ O_2 vs $^1\Sigma_g^+$ O_2

- ✓ Their energies of excitation are 94.3 and 157.0 kJ mol^{-1}, respectively





Singlet O_2 always goes back to triplet O_2, but $^1\Delta_g$ O_2 goes slowly compared to $^1\Sigma_g^+$ O_2. Why?

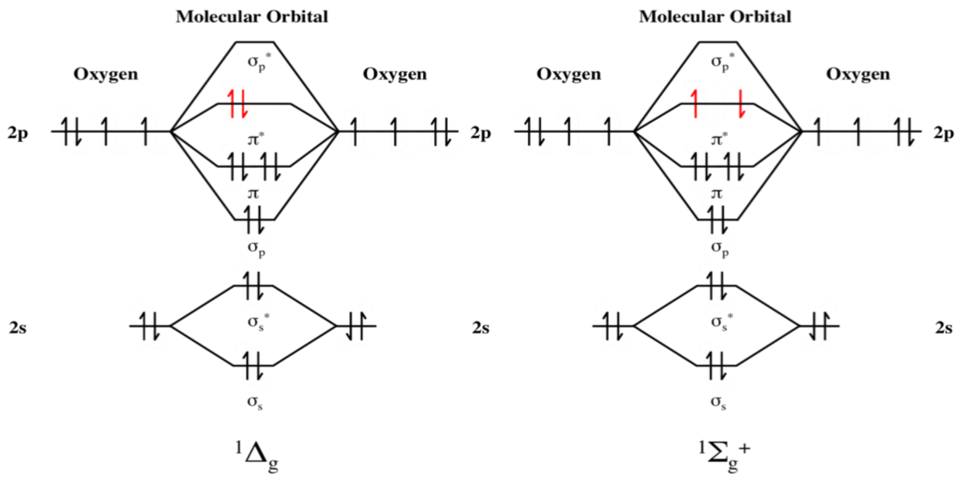
Comparison of Selection Rules

Selection Rule	Governs	Allowed Transitions	Forbidden Transitions
Spin Selection ($\Delta S = 0$**)**	Electronic transitions	Singlet ↔ Singlet, Triplet ↔ Triplet	Singlet ↔ Triplet (except via spin-orbit coupling)
Electric Dipole ($\Delta l = \pm 1$**)**	Orbital angular momentum	$s \rightarrow p$, $p \rightarrow d$	$s \rightarrow s$, $d \rightarrow d$
Parity Selection ($g \leftrightarrow u$**)**	Centrosymmetric molecules	$g \rightarrow u$, $u \rightarrow g$	$g \rightarrow g$, $u \rightarrow u$

Why $^1\Delta_g$ is more stable than $^1\Sigma_g^+$?

Despite the fact that $^1\Delta_g$ Confronts the Hund's rule,

- It gains stabilization from a **non-zero orbital angular momentum**
- Exchange energy is almost the same for both of them



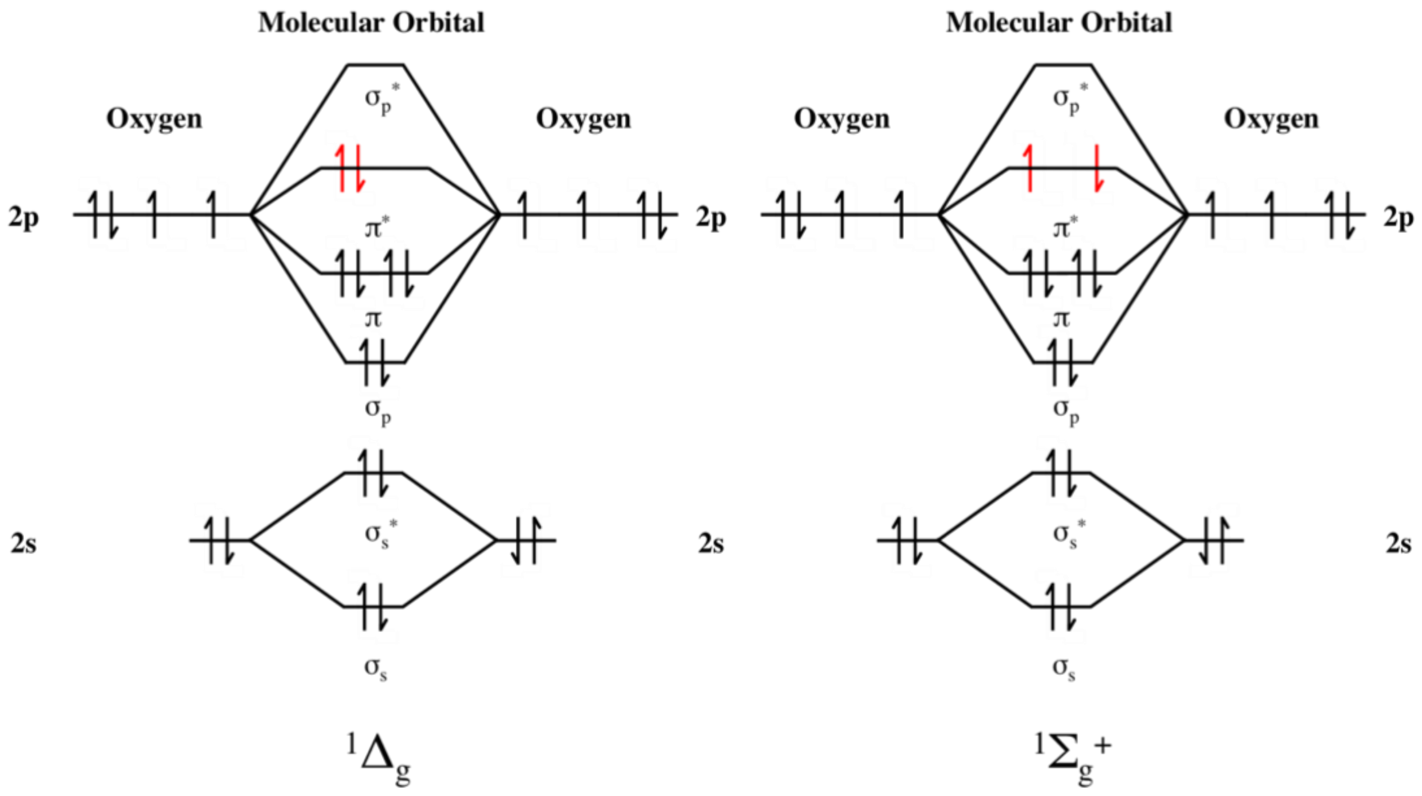
$^3\Sigma_g^-$ (Ground State, lowest energy) → Two parallel electrons in different π^* orbitals.

$^1\Delta_g$ (Metastable, lower energy than $^1\Sigma_g^+$) → Paired electrons in the same π^* orbital.

$^1\Sigma_g^+$ (Higher energy) → Electrons occupy different π^* orbitals with opposite spins.

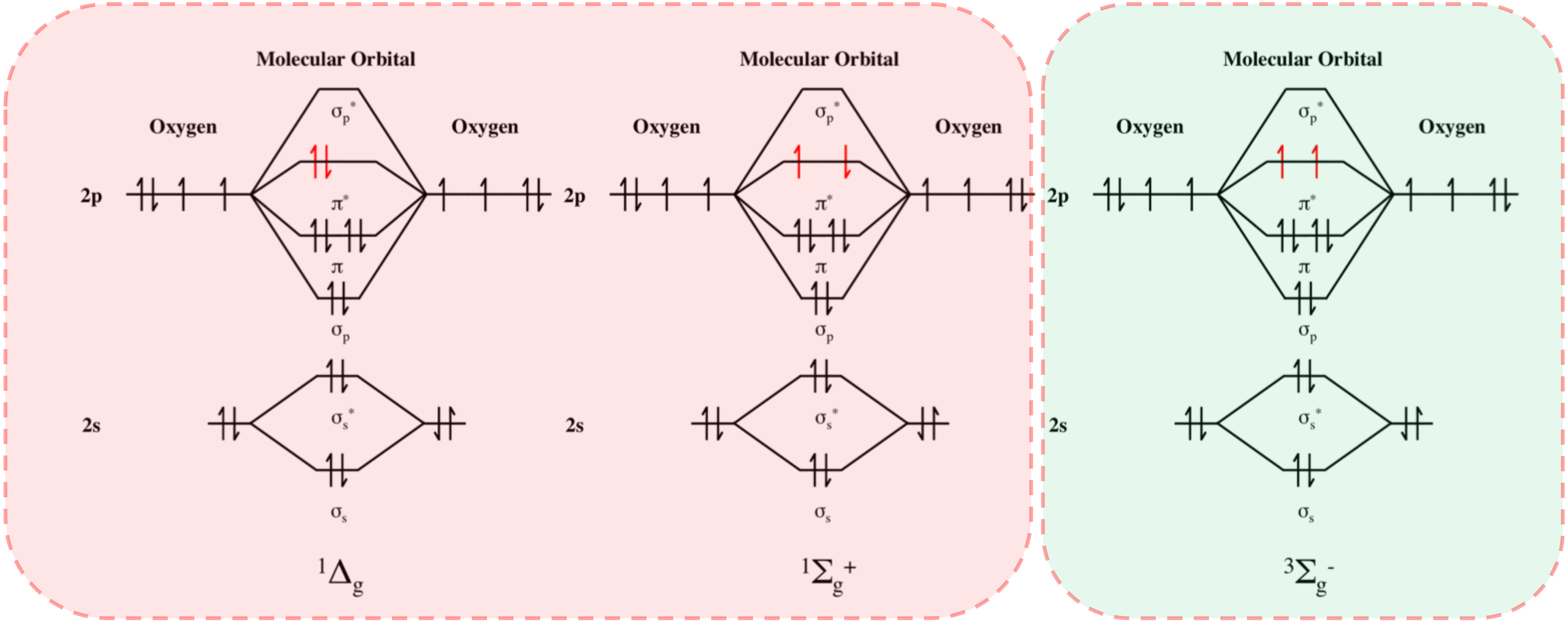
The Magnetic Property: $^1\Delta_g$ vs $^1\Sigma_g^+$

- $^1\Delta_g$ is slightly paramagnetic due to orbital contribution to the net magnetic moment
- $^1\Sigma_g^+$ is diamagnetic because there is a contribution neither from spin nor from orbital



Self-study: Spin and Orbital Contributions to Net Magnetic Moment!

Triplet vs Singlet States!



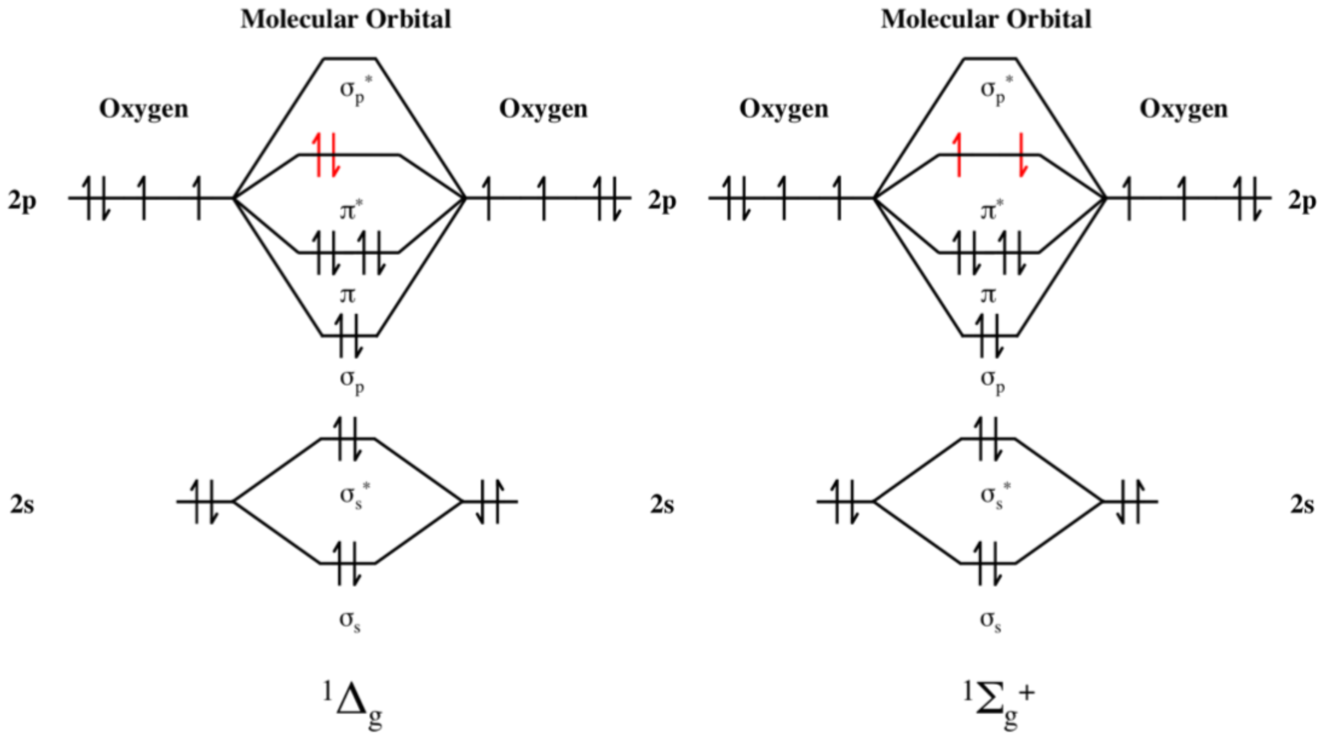
Dangerously Reactive

Triplet O_2

So, Why Aren’t We Burnt Alive?

Since the triplet to singlet transition requires just 94.3 kJ mol^{-1}

- Calculate the absorption of wavelength for this transition
- Where do they fall on the EMS?

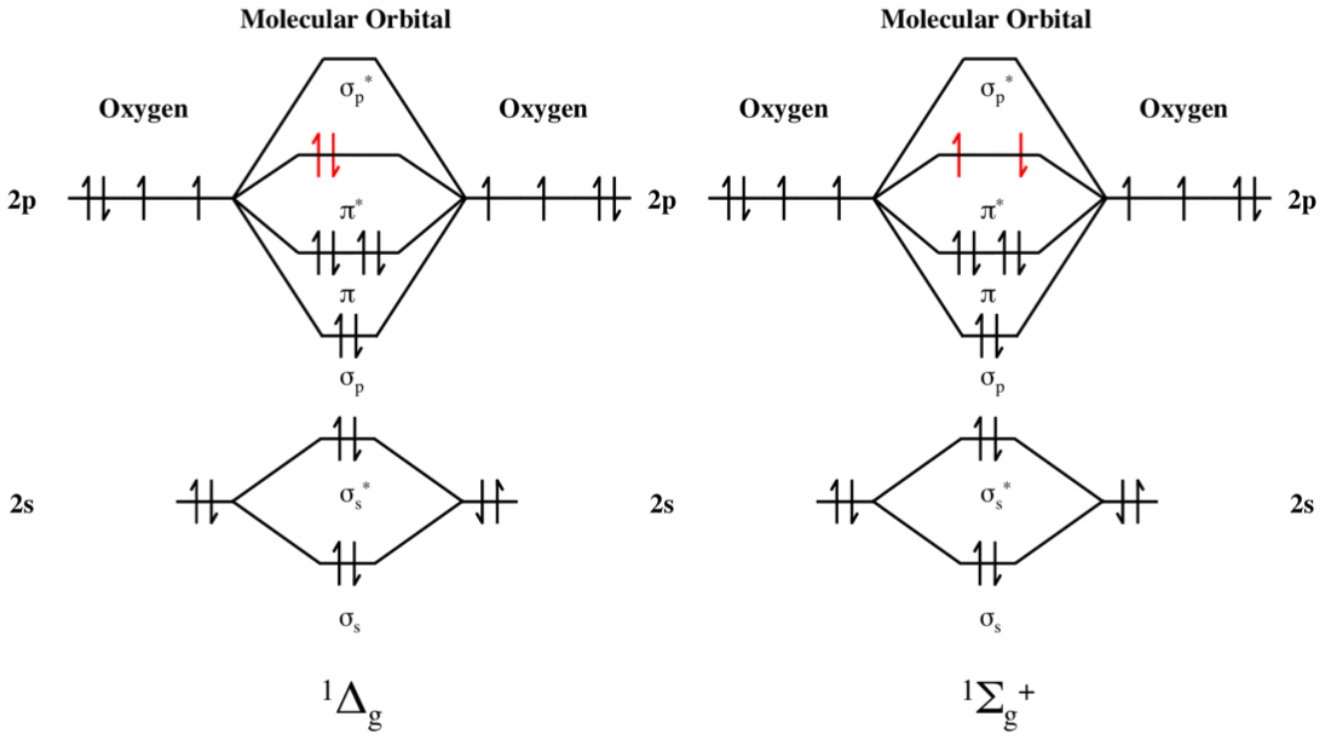


Planck’s constant: $6.62607015 \times 10^{-34}$ m^2 kg / s   C: 2.99792458×10^8 m / s

So, Why Aren't We Burnt Alive?

Because the fundamental principles of science protect us!

- This transition is forbidden by spin, parity, and electric dipole
- The excited states are too short-lived to cause any significant damage



A Brief History of The Discovery of O_2!

The Discovery of O_2: The ‘Phlogiston Theory’!

The alchemist and physician
J. J. Becher
(late 1600s)

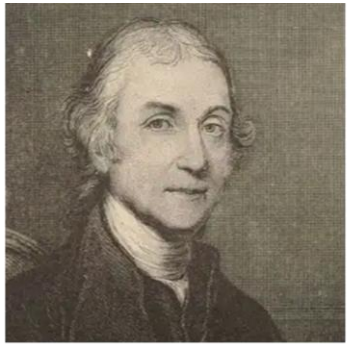
- Proposed in the **17th century** by **Johann Joachim Becher** and **Georg Ernst Stahl**.
- It claimed that **all combustible materials contained "phlogiston"**, a mysterious, massless substance that was released when something burned.
- Air was thought to **absorb phlogiston** from burning materials, allowing combustion to continue.

Issues with the Theory

- **Metals gained mass** when burned (forming oxides), but the theory claimed they should lose phlogiston and become lighter.
- **Air was necessary** for combustion, but phlogiston theory could not explain why.

The Discovery of O_2: The ‘Dephlogisticated Air’!

- **Joseph Priestley (1774)** isolated a gas that made flames burn intensely and allowed animals to live longer.
- He called it **"dephlogisticated air"** because it absorbed phlogiston efficiently, making combustion easier.



Chemist and Philosopher
Joseph Priestley
(1774)

1774:

$$HgO \xrightarrow[\text{Sun-light}]{} \underbrace{\{\text{Dephlogisticated Air}\}}_{}^{O_2} \rightarrow \text{Oxygen}$$

"I have discovered an air five or six times as good as common air"

Key Idea: Scientists at the time believed this gas helped remove phlogiston from burning substances, allowing combustion to continue.

The Discovery of O_2: The ‘Dephlogisticated Air’!

Whatever the gas was called, its effects were remarkable. "The feeling of it in my lungs," Priestley wrote, "was not sensibly different from that of common air, but I fancied that my breast felt peculiarly light and easy for some time afterwards. Who can tell but that in time, this pure air may become a fashionable article in luxury. Hitherto, only two mice and myself have had the privilege of breathing it."

Later, his close friend, Antoine Lavoisier, named it

Oxygen

Chemist and Philosopher
Joseph Priestley
(1774)

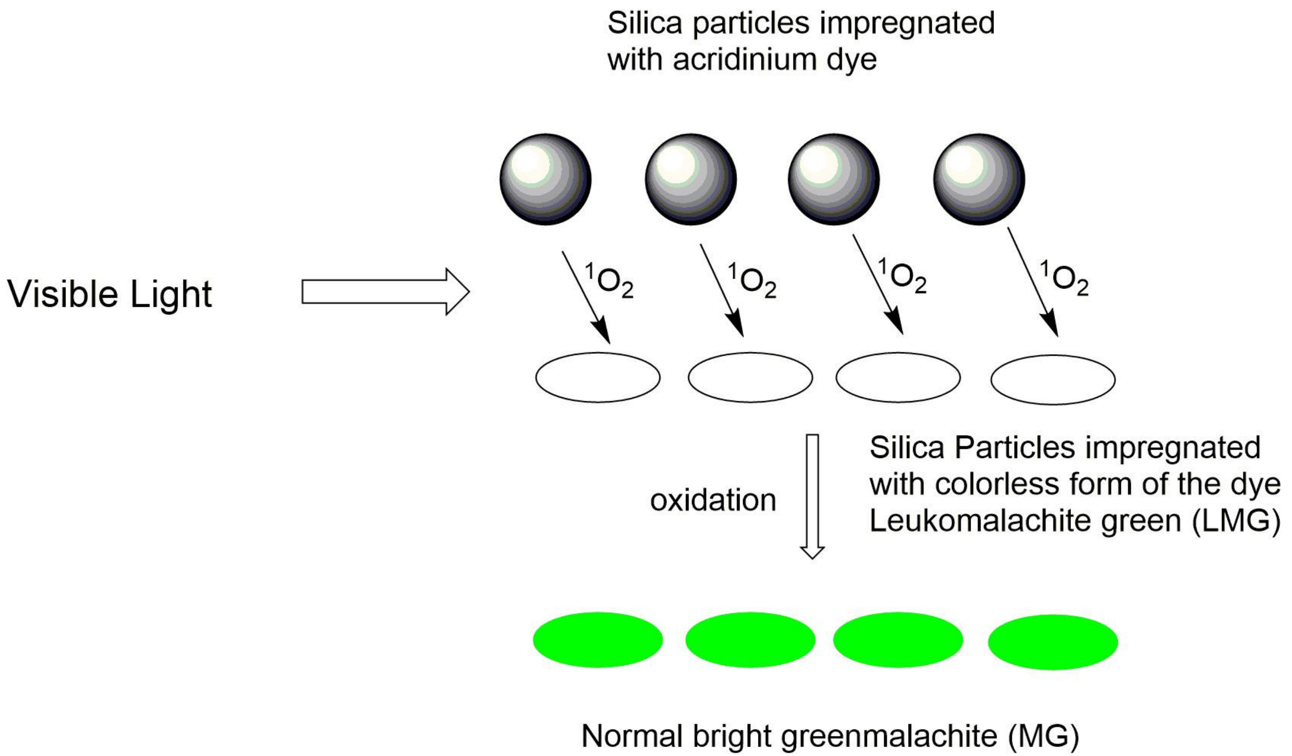
The Discovery of O_2: The 'Naming of O_2'!

- Lavoisier named the gas "oxygène" (from Greek: ὀξύς (oxys, meaning "acid") + γενής (genes, meaning "producer or generator")).
- He mistakenly believed that all acids contained oxygen.
- However, oxygen was correctly recognized as a key element in combustion and respiration.

Chemist and Philosopher
Antoine Lavoisier
(1777)

The Synthesis of Singlet O_2: The Kautsky Experiment (in the early 1930s)!

- Two different types of silica beads were taken (one with acridinium dye and the other with colorless Leukomalachite green (LMG)
- When irradiated, the 'active' oxygen that formed in the silica bead impregnated with acridinium dye diffused out and into other beads with LMG
- Leading to the oxidation of LMG to brightly colored MG
- 'Normal' oxygen couldn't do this.



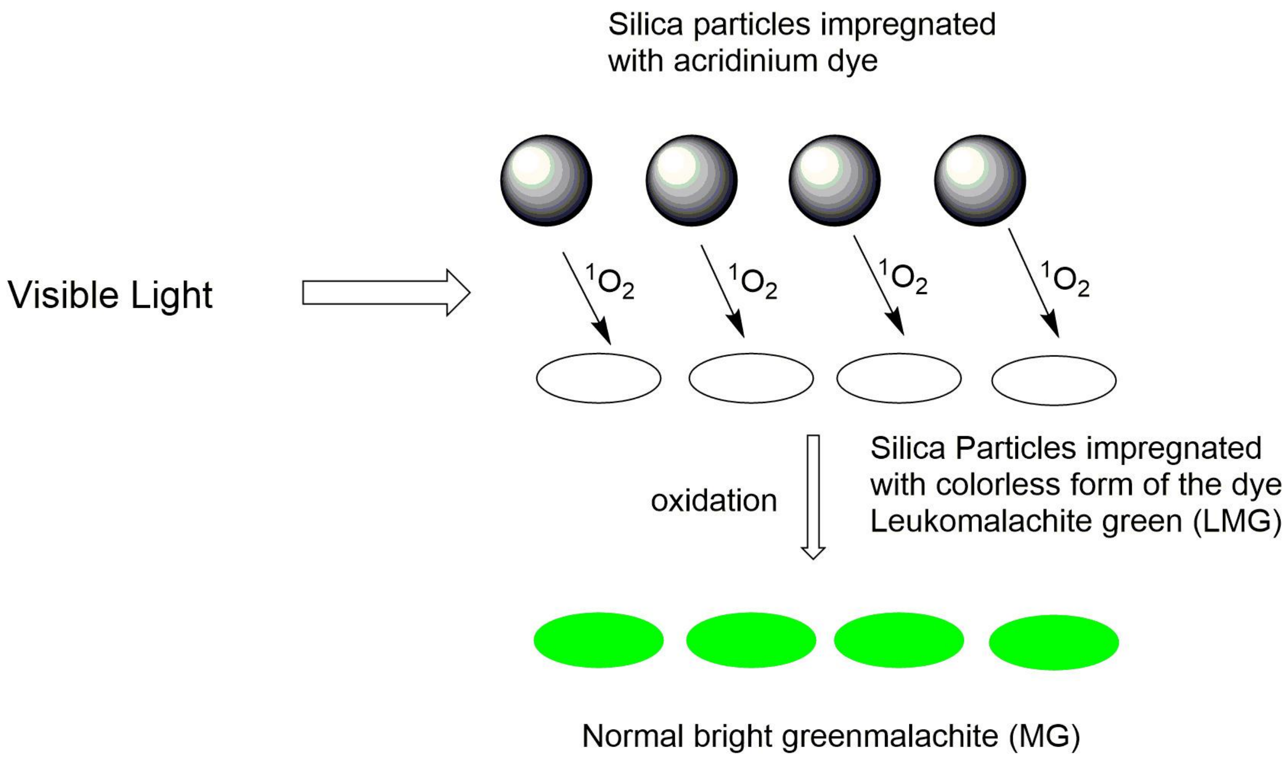
Thus, the Photosensitization assisted excitation of $^3O_2$ to $^1O_2$ was born and its diffusivity was proven.
Unfortunately, nobody understood it then.

The Synthesis of Singlet O_2: The Kautsky Experiment (in the early 1930s)!

This elegant work and logical thinking were largely ignored until 1964.

As Michael Kasha stated,

"it was just too early for people to follow."



The Synthesis of Singlet O_2: The Red Fluorescence of $^1O_2$!

M. Kasha and colleagues observed a red fluorescence characteristic for $^1O_2$ when they mixed H_2O_2 and NaOCl in solution and its lifetime was close to 1 s.

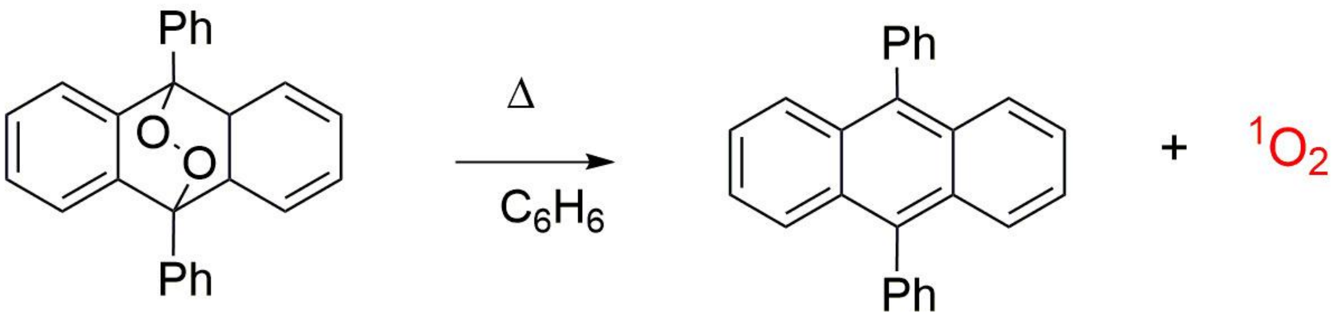
Type 1 Synthesis of Singlet O_2!

Oxygenated species reacting together or disintegrating through radicals and radical ions to give $^1O_2$.

Examples:

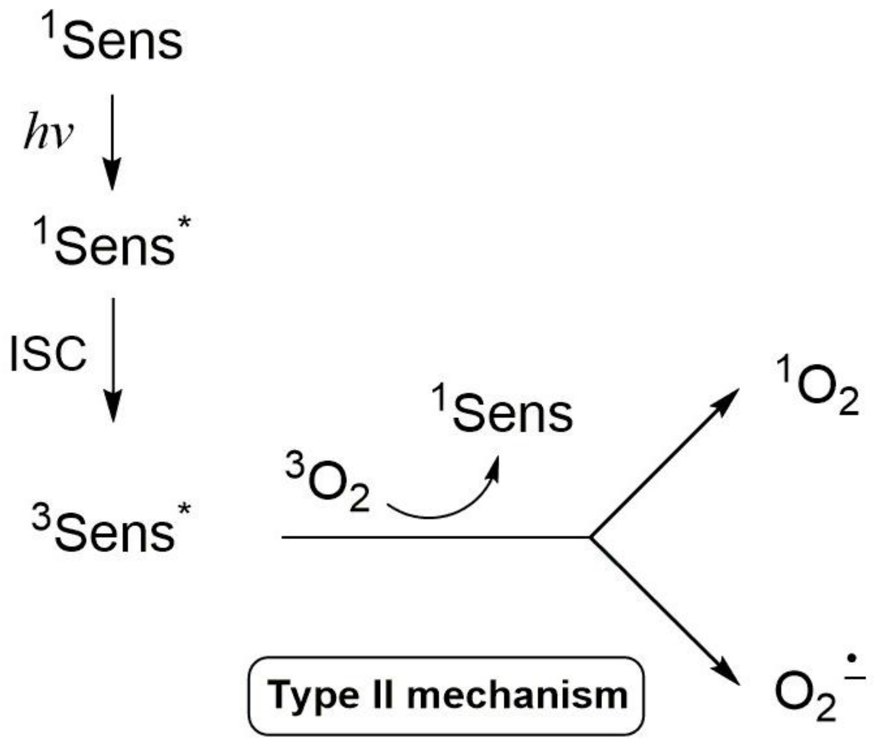
$$NaOCl + H_2O_2 \longrightarrow H_2O + NaCl + {}^1O_2$$

$$Cl_2 + H_2O_2 \longrightarrow H_2O + 2HCl + {}^1O_2$$

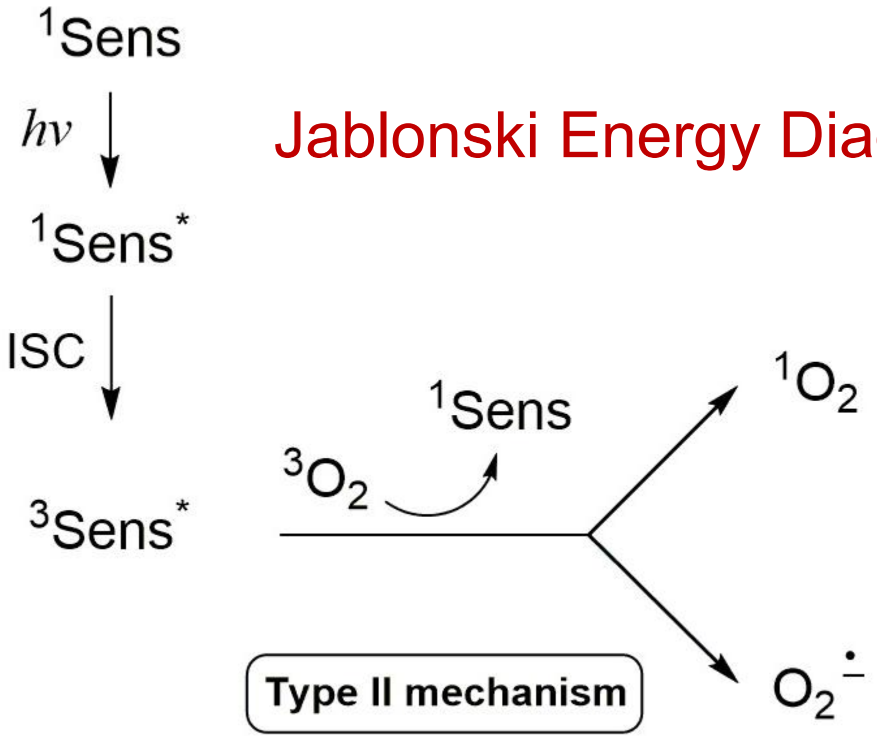


Type 2 Synthesis of Singlet O_2!

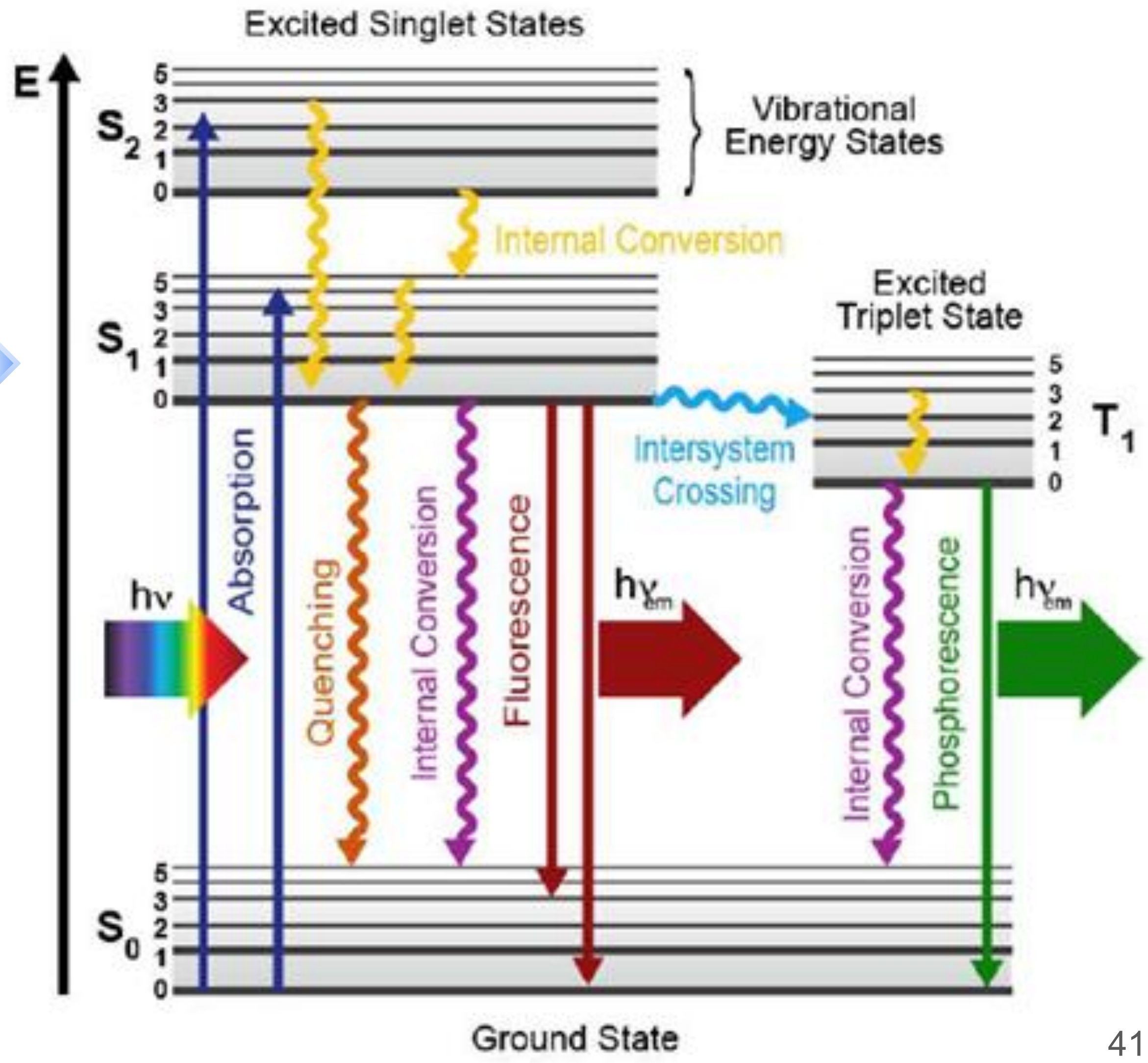
A photosensitizer excited to a singlet state after ISC to its triplet state can transfer its energy to $^3O_2$ to excite to $^1O_2$



Understanding Type 2 Mechanism!

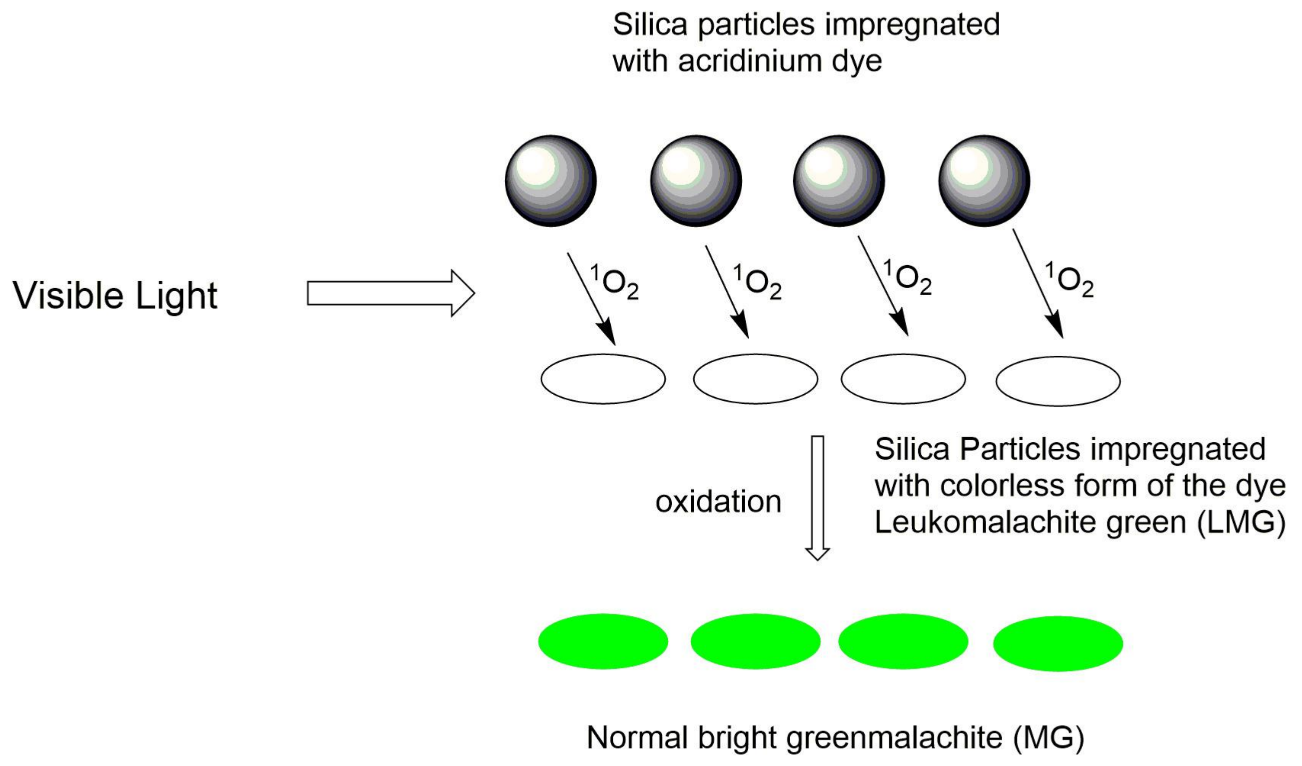


Jablonski Energy Diagram



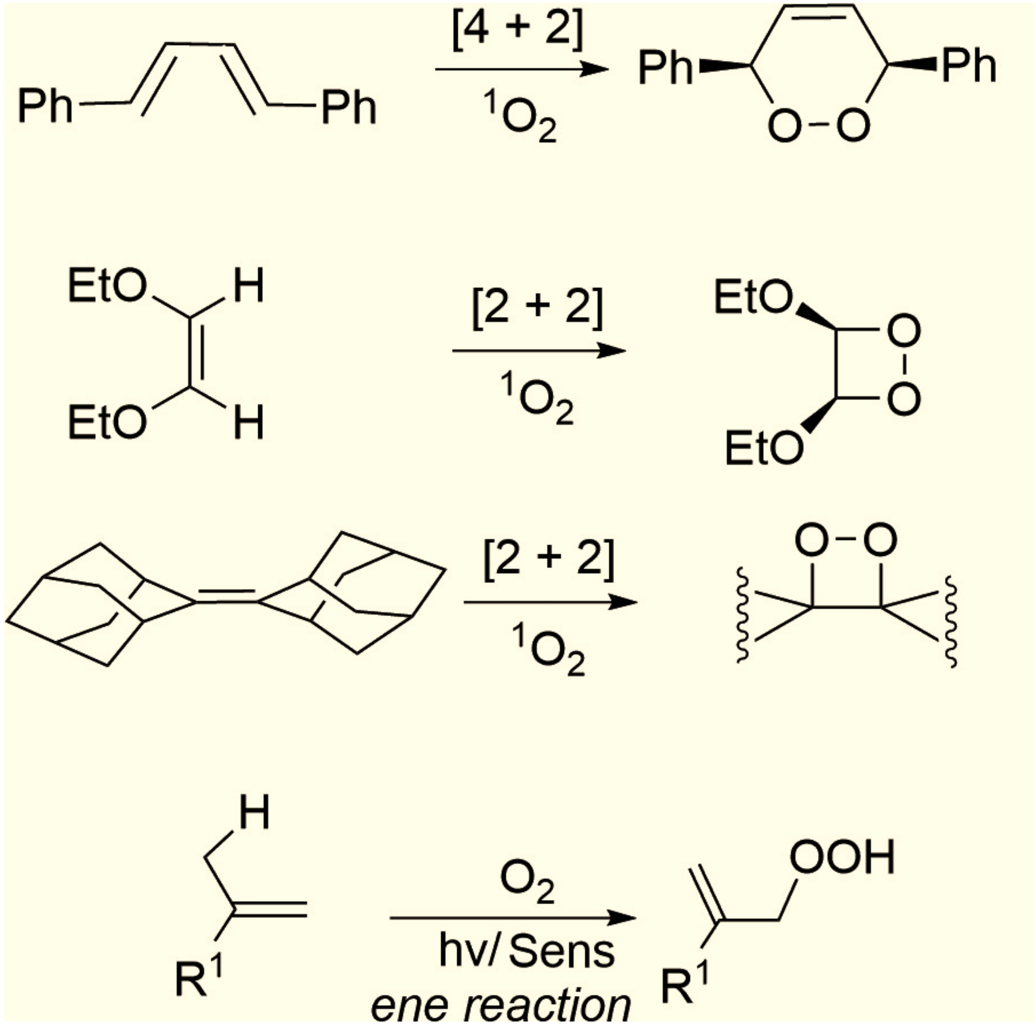
The Synthesis of Singlet O_2: The Kautsky Experiment (in the early 1930s)!

This is Type II



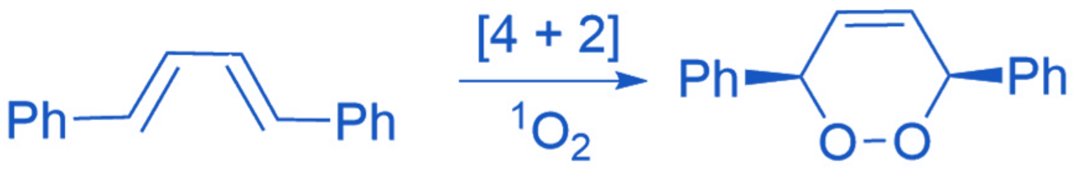
Ene Reactions: Accessing Organoperoxides which were once a dream for chemists!

- $^1O_2$ acts as electrophile
- It adds to the e⁻ rich C
- Occurs at low T and P (0–5 °C & 10–50 mmHg)
- $^3O_2$ does not react with C=C at these conditions



Ene Reactions: Types!

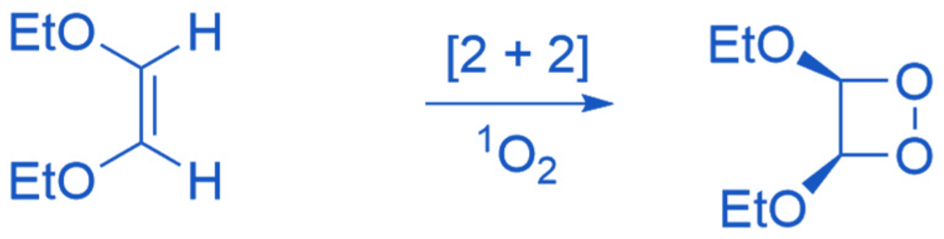
1. [4+2] Diels-Alder reactions producing endoperoxides.*



*An unusual peroxide functionality found in natural products and have always puzzled chemists how they form till this discovery.

Ene Reactions: Types!

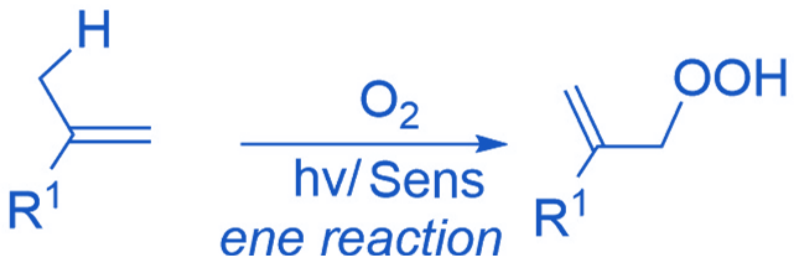
2. [2+2] cycloadditions where no allylic hydrogen is present producing endoperoxides.*



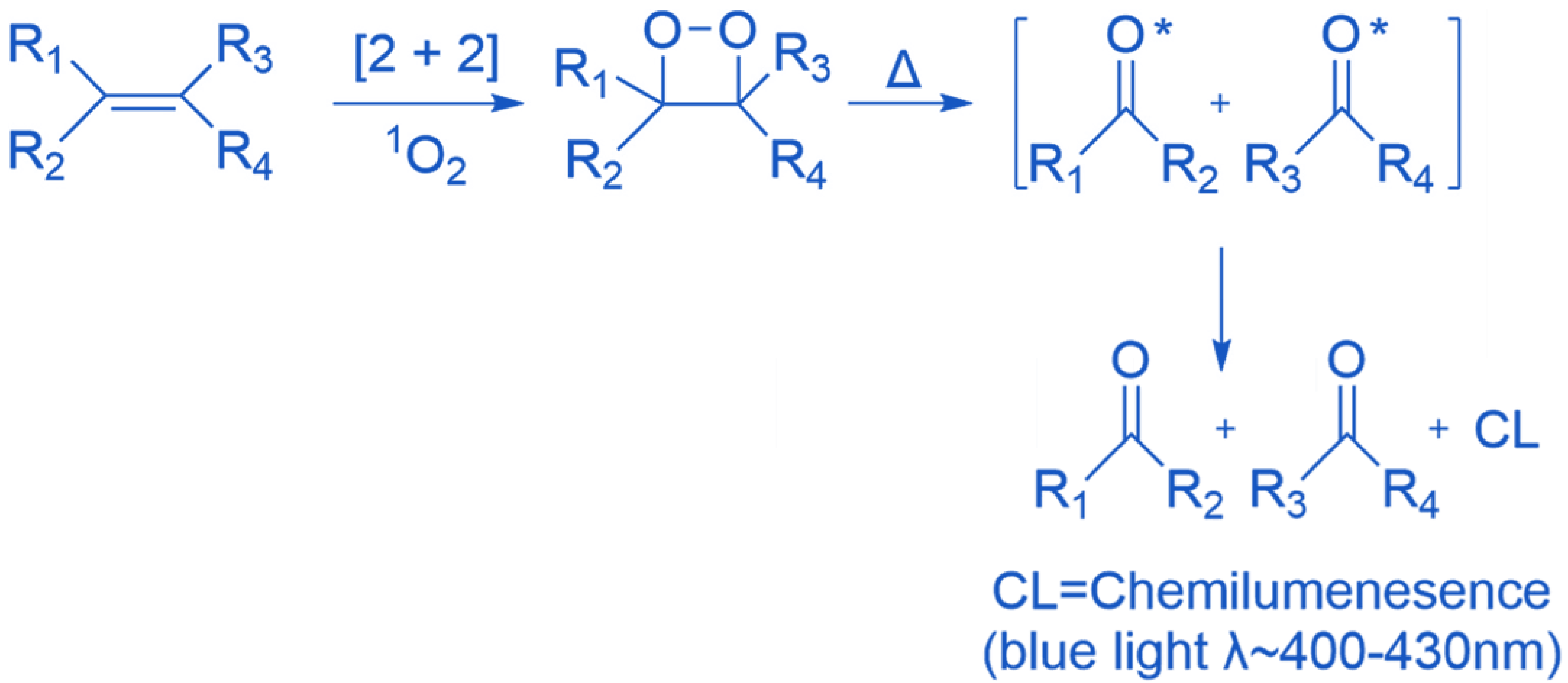
*An unusual peroxide functionality found in natural products and have always puzzled chemists how they form till this discovery.

Ene Reactions: Types!

3. Electrophilic addition to enes with allylic hydrogen producing allyl hydroperoxides.*

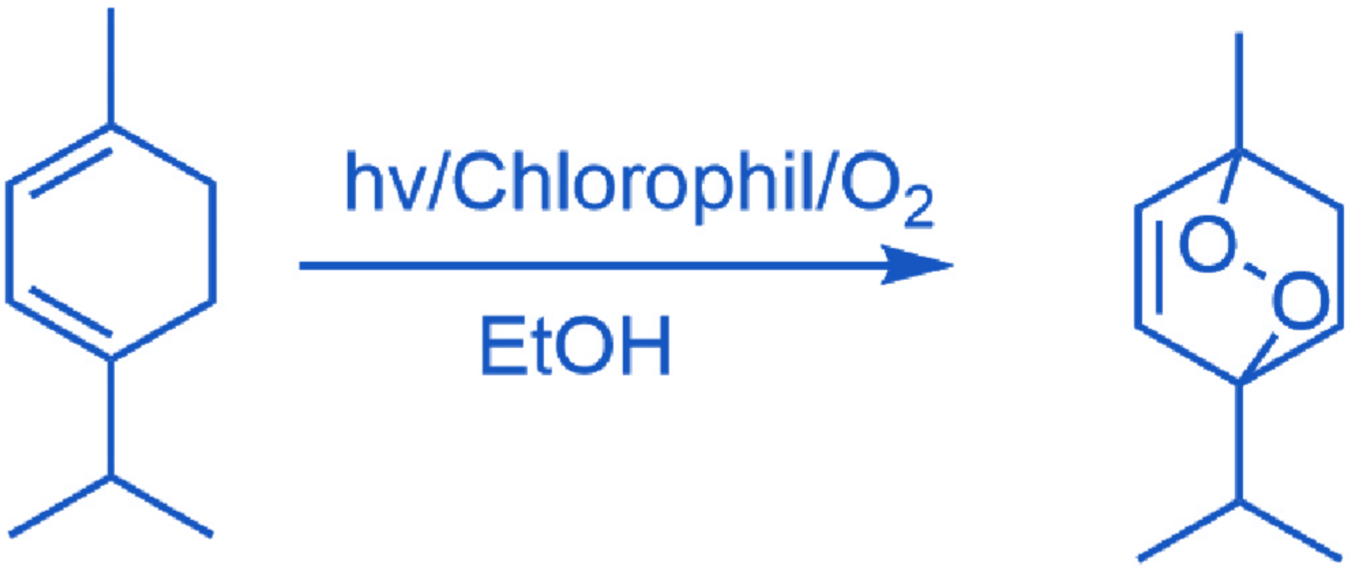


Breaking heavily substituted C=C with [2+2] additions



Ene Reactions: Synthesizing Natural Products with $^1O_2$

Synthesis of ascaridole an anthelmintic drug using [4+2] addition!



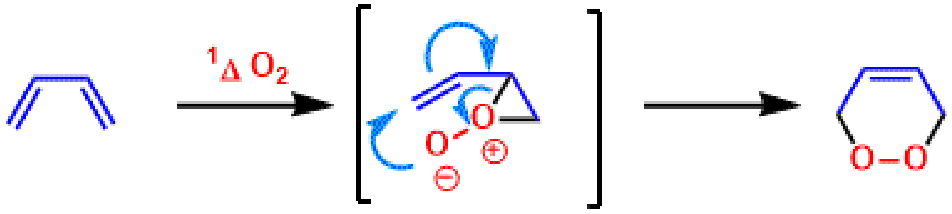
Identify the photosensitizer here!

α - Terpene

Ascaridole

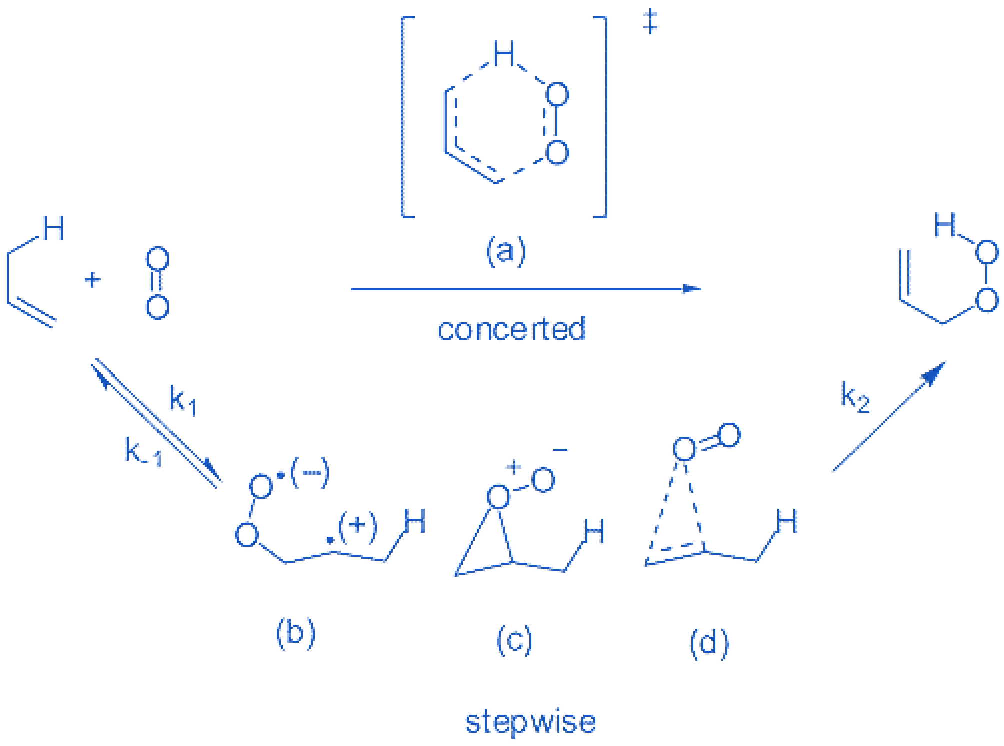
Proposed Mechanisms!

[4+2] Addition



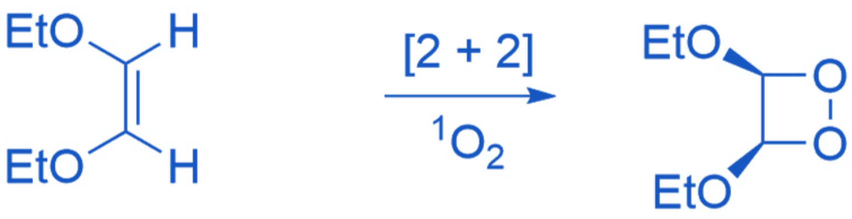
This can also follow a similar concerted mechanism

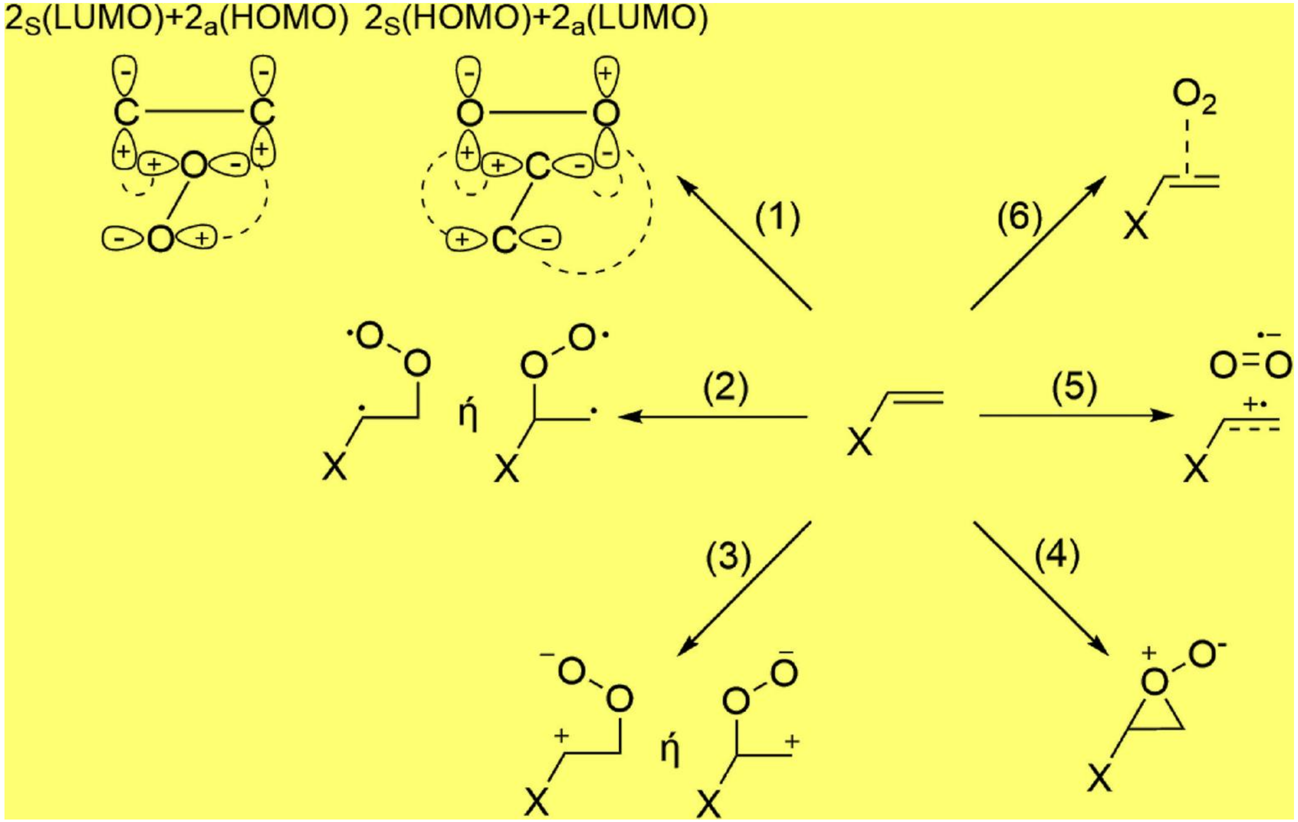
[4+2] Allylic Hydrogen Abstraction



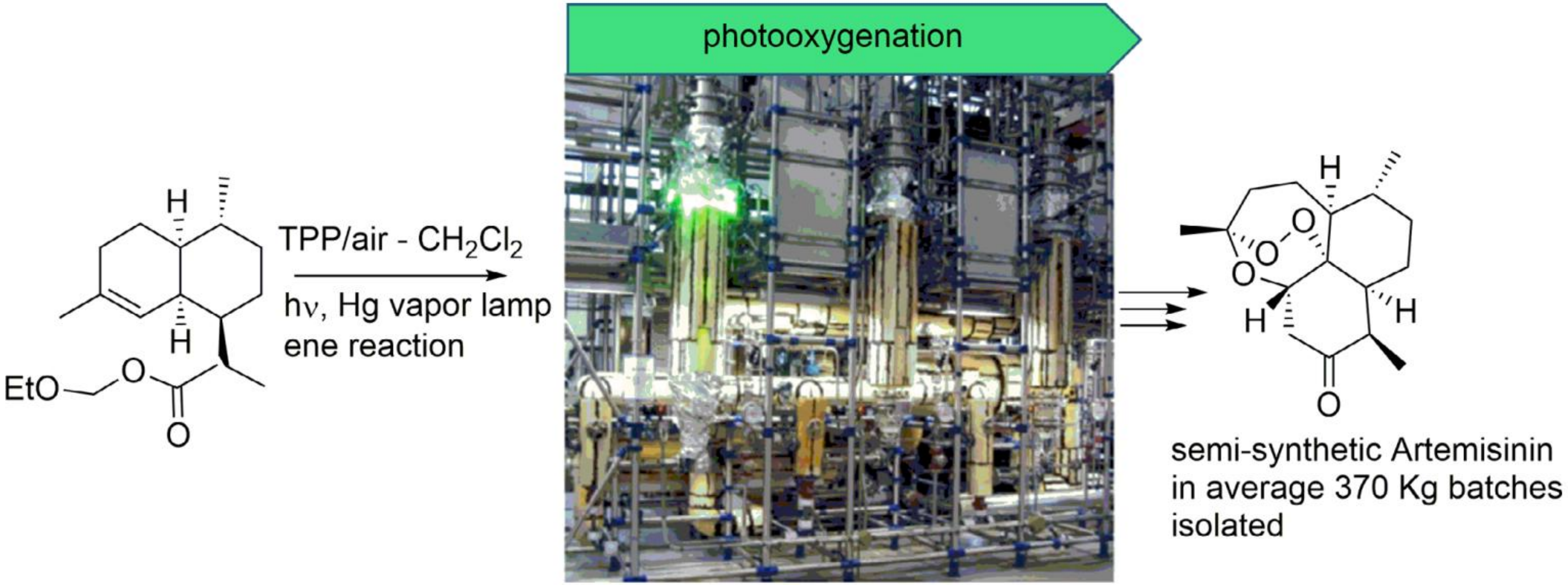
Proposed Mechanisms!

[2+2] Addition





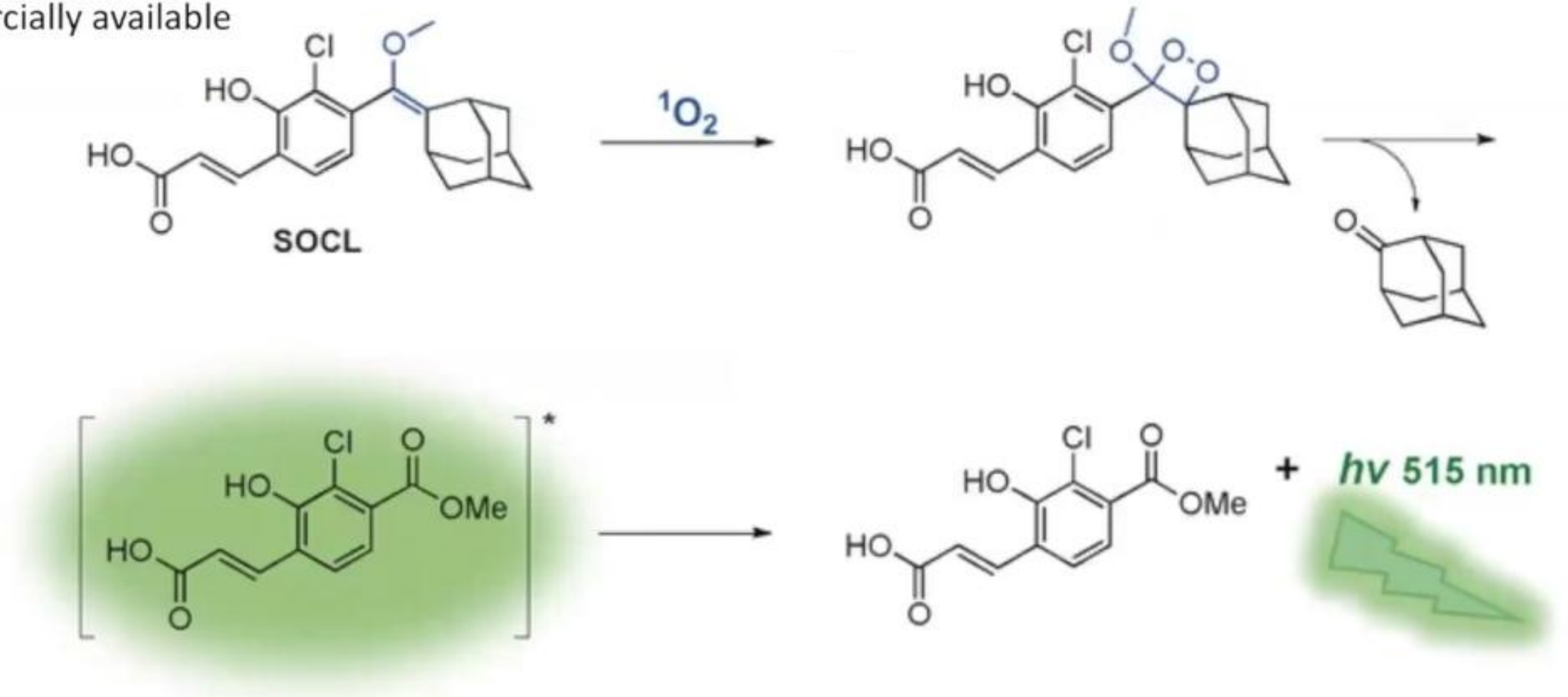
Still under debate!



Scheme 17. Synthesis of antimalarial drug artemisinin in industrial scale.

Photochemistry and Photobiology, **2021**, 97, 1182-1218.

singlet oxygen probe
commercially available



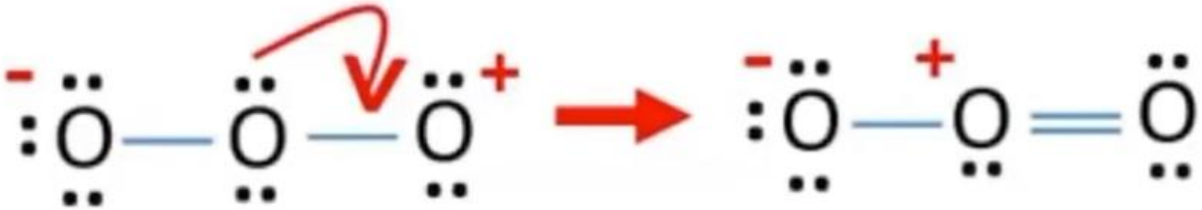
chemiluminescent detection of singlet oxygen!!

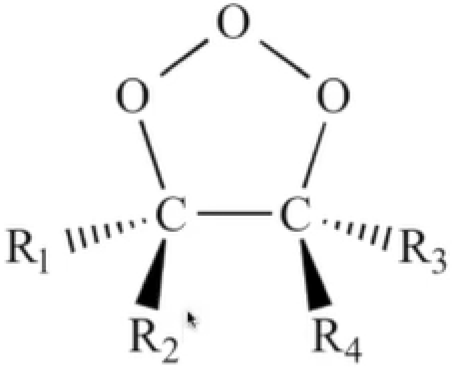
Similarities between ozone and singlet oxygen!

ozone, O_3
(resonance structure)

singlet
oxygen ($^1\Delta_g$)

Similarities between ozone and singlet oxygen!





$^1O_2$ Protecting Us All from Lethal Solar Radiation!

$$^3O_2 + h\nu \rightarrow {}^1O_2$$

$$^1O_2 + {}^3O_2 \rightarrow O_3 + O^\bullet$$

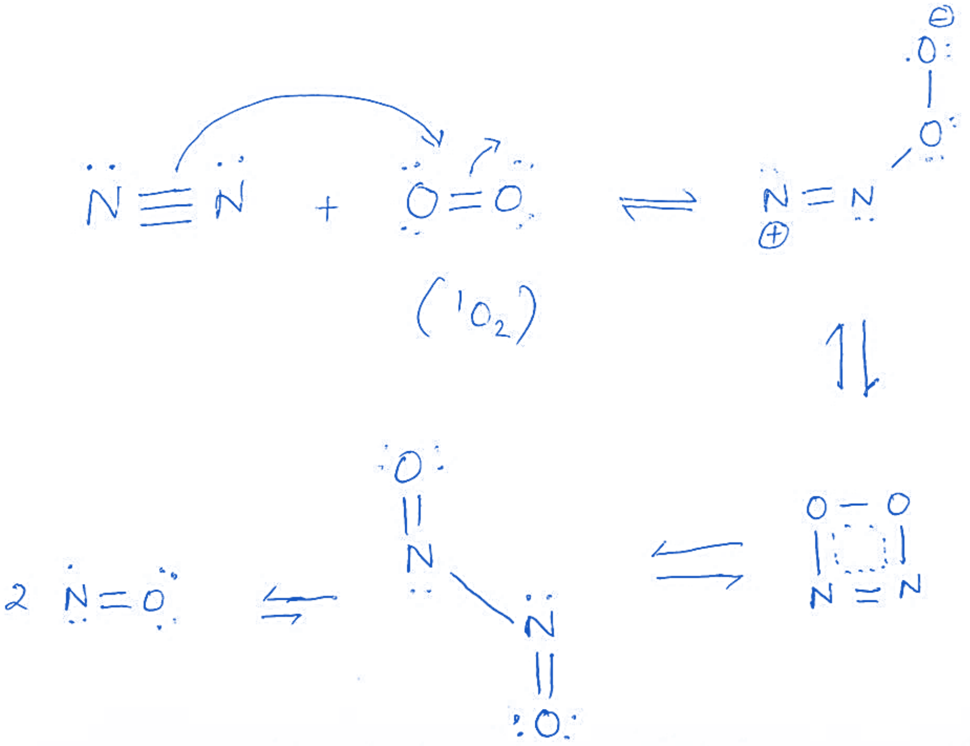
$$O^\bullet + {}^3O_2 \rightarrow O_3$$

$^1O_2$ Fixing N_2: A Possible Solution to Counter Energy and Food Crisis?

$$^3O_2 + h\nu \rightarrow {}^1O_2$$

$$^1O_2 + N_2 \rightarrow 2NO^{\bullet}$$

- The **N≡N bond** in molecular nitrogen is one of the strongest in chemistry (**~941 kJ/mol**).
- **N_2 activation** is slow due to its nonpolar, inert nature.
- Even with catalysts (e.g., FeMo in nitrogenase or Ru-based systems), multi-step electron/proton transfers require **precise control**.



Application of $^1O_2$ in Photodynamic Therapy (PDT)

Photodynamic therapy (PDT)

Photodynamic therapy is a minimally invasive therapeutic modality that uses light-activated compounds (photosensitizers) to generate reactive oxygen species, primarily singlet oxygen ($^1O_2$), to kill cancer cells, bacteria, and other pathological targets.

1. **Photosensitizer:** Light-activated compound
2. **Light Source:** Typically visible or near-infrared light
3. **Oxygen:** Present in the biological tissues, converted to singlet oxygen ($^1O_2$)

These three components must be present simultaneously for PDT to be effective.

Photosensitizers Used in PDT

- Porphyrins (e.g., Photofrin)
- Chlorins (e.g., Temoporfin)
- Phthalocyanines
- BODIPY derivatives

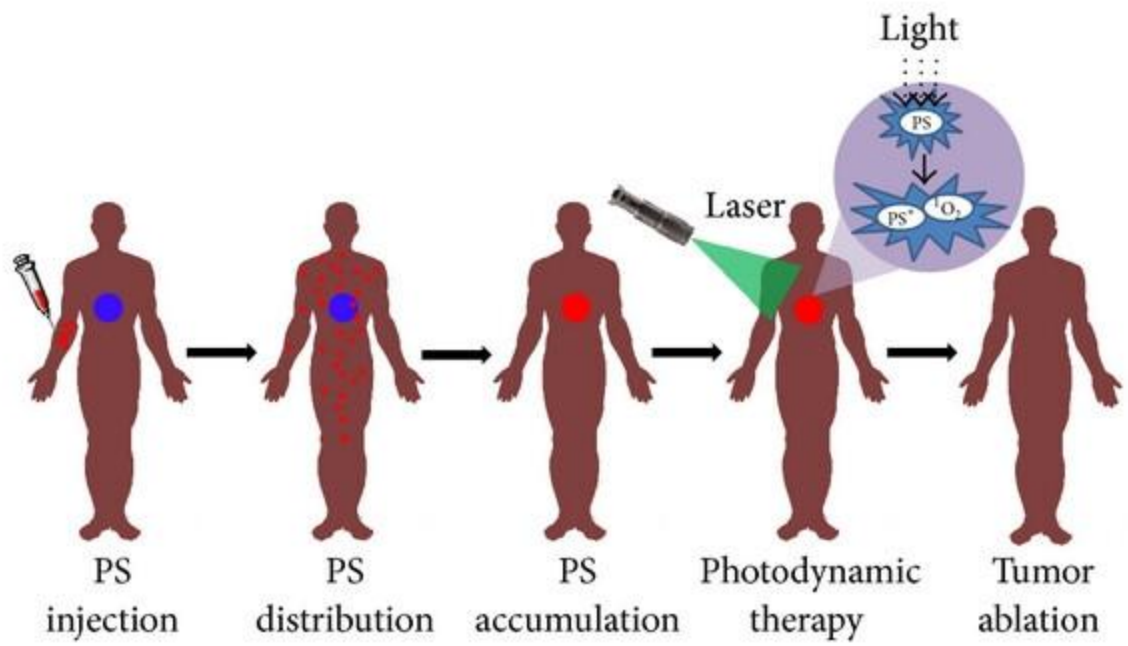
Criteria: High triplet quantum yield, good tissue penetration, selective accumulation in target cells.

Applications of PDT

- Cancer therapy (skin, lung, esophagus, bladder)
- Antibacterial and antifungal treatments
- Age-related macular degeneration (AMD)
- Dermatological conditions (e.g., acne, psoriasis)

$^1O_2$-Assisted PDT: Killing Cancer Cells Locally!

- **Selective Cancer Treatment**
- ***Niels Finsen*** won the **Nobel Prize** for using light to treat **skin diseases like lupus**.
- PDT can use different wavelengths of light to **penetrate tissues to different depths**, allowing treatment of various cancers.
- **Bacteria Killer!** PDT is also used to kill antibiotic-resistant bacteria, making it a promising tool against **superbugs**.
- **No Surgery Needed!** (making recovery faster and less painful)



Advantages and Limitations

Advantages:

- Minimally invasive
- Localized treatment with minimal systemic toxicity
- Repeatable without cumulative toxicity

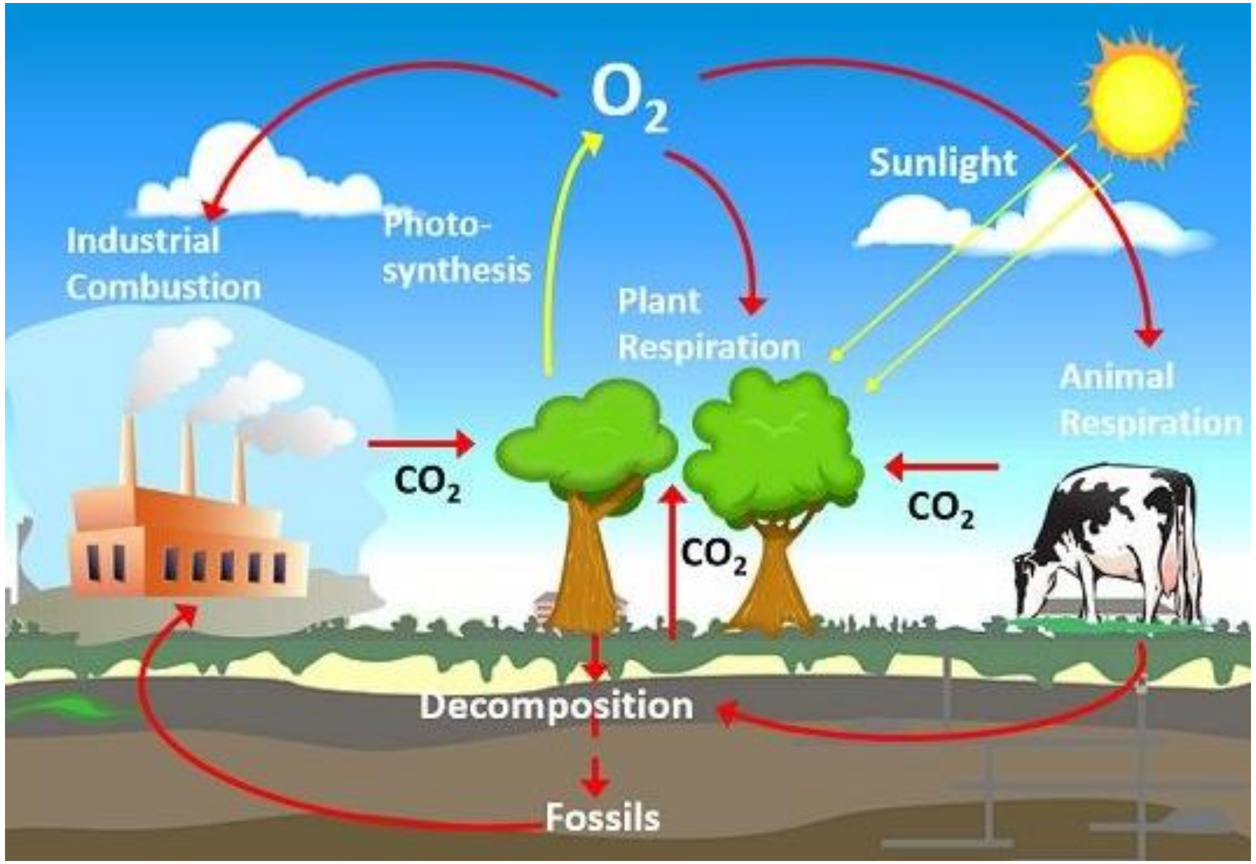
Limitations:

- Light penetration depth
- Oxygen dependency
- Skin photosensitivity post-treatment

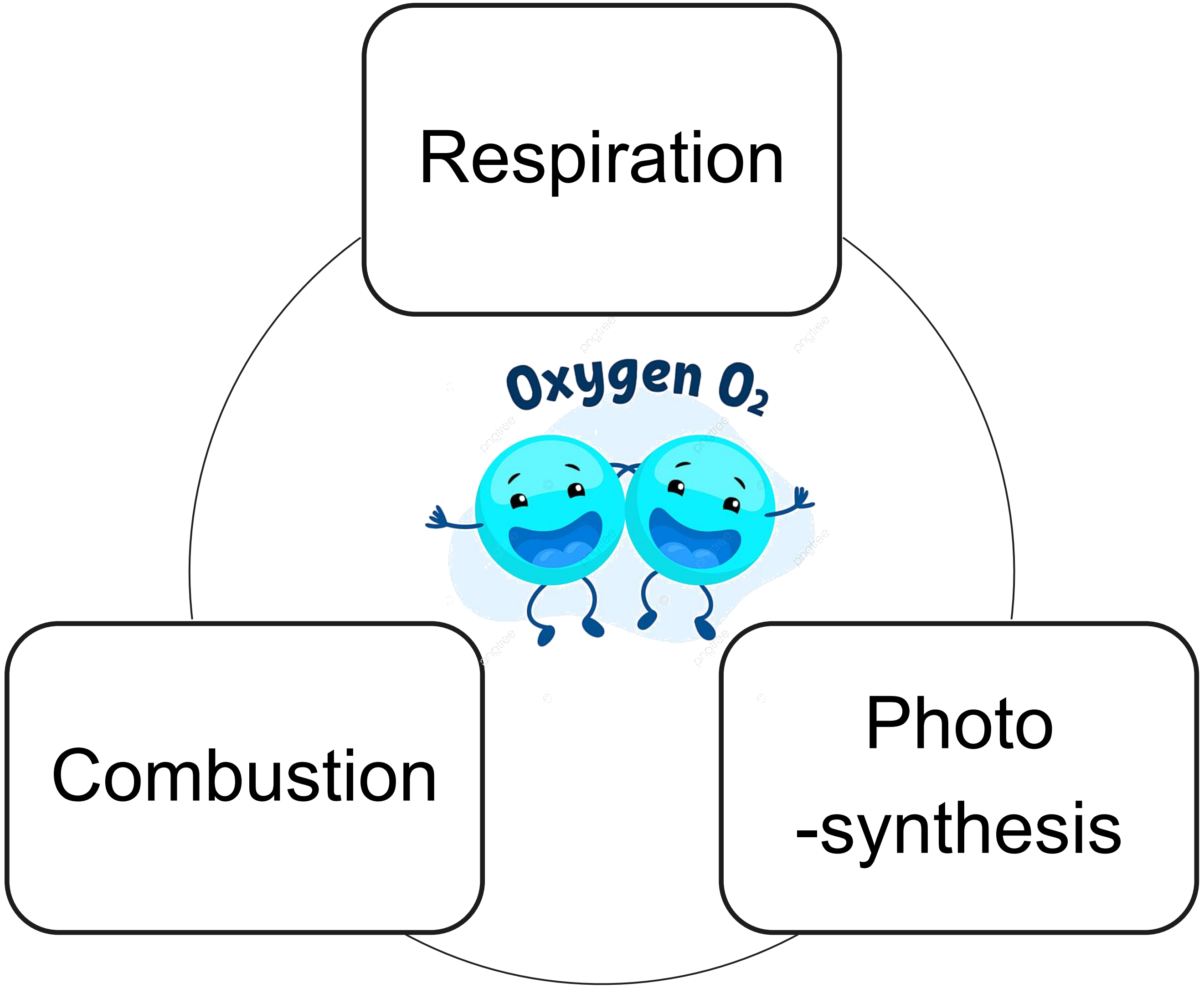
The Oxygen Cycle!

The Oxygen Cycle!

- O in alliance with H and C forms most of the life forms
- With a handful of few more elements the life we know on earth was established

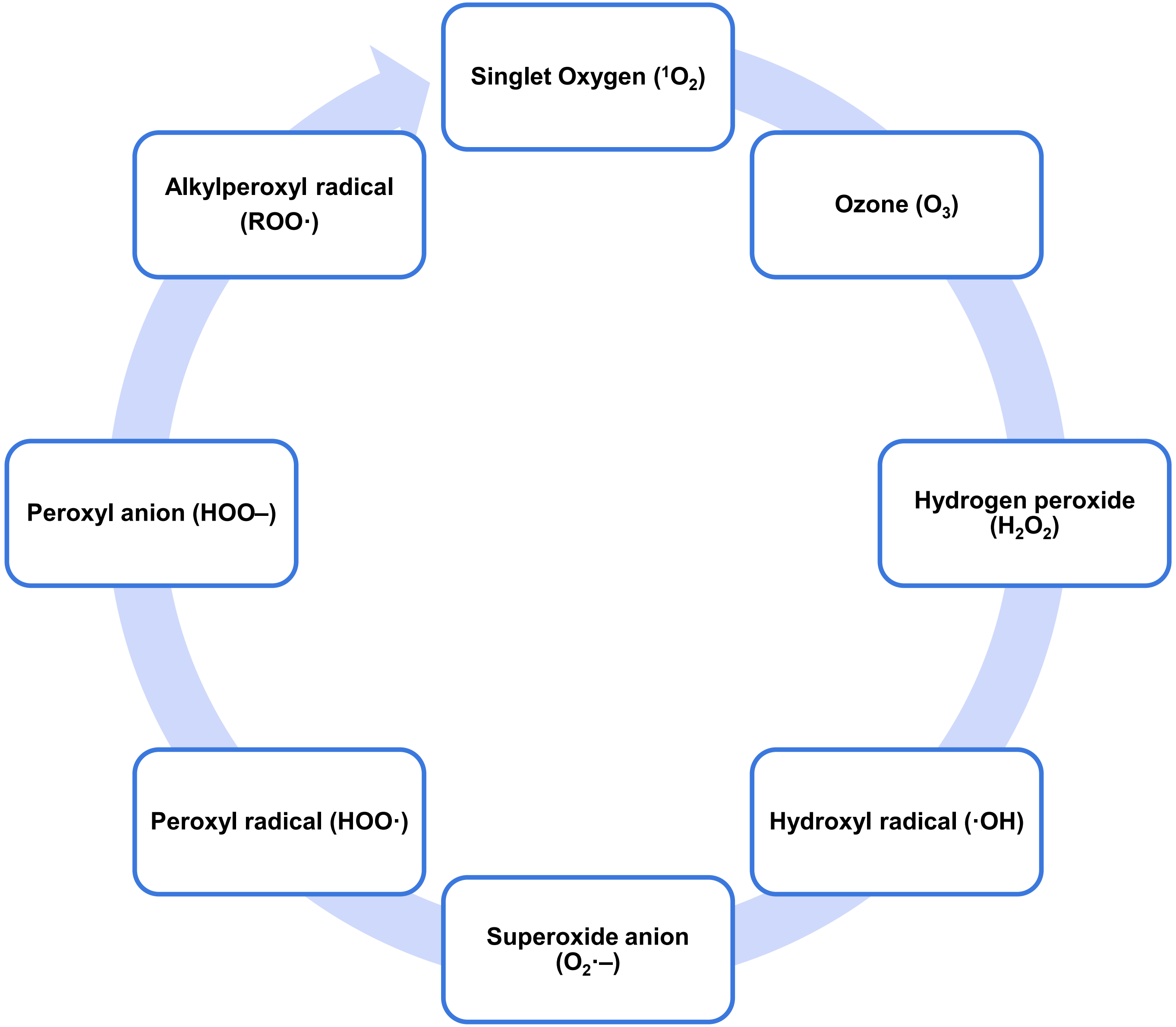


The Inevitability of Oxygen!



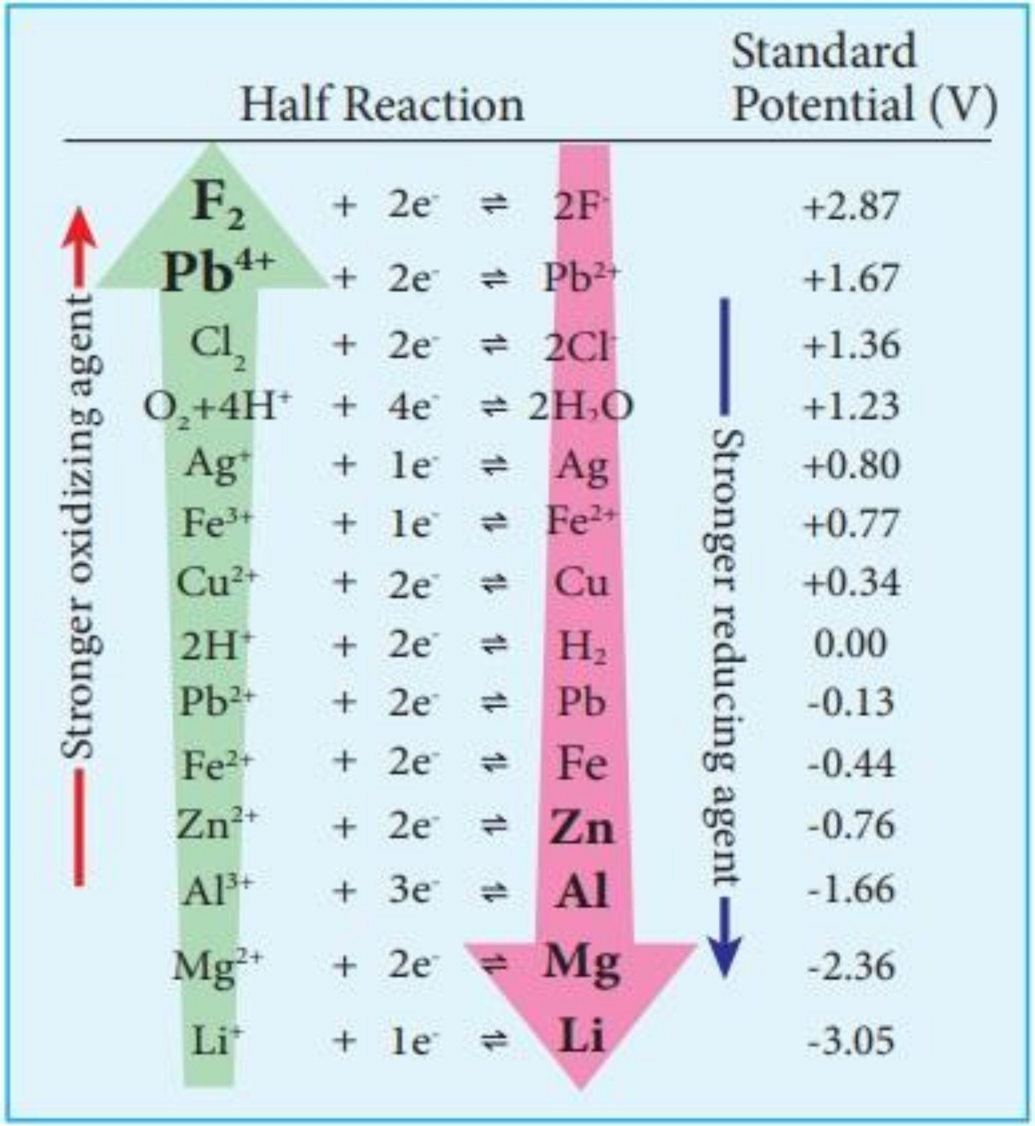
Reactive Oxygen Species (ROS)!

Innocent $^3O_2$ to Hot-headed ROS!



What Makes Them Hot-headed?

- Singlet Oxygen ($^1O_2$)
- Ozone (O_3)
- Hydrogen peroxide (H_2O_2)
- Hydroxyl radical ($\cdot OH$)
- Superoxide anion ($O_2{\cdot}^-$)
- Peroxyl radical ($HOO\cdot$)
- Peroxyl anion (HOO^-)
- Alkyl/Arylperoxyl radical ($ROO\cdot$)



Half Reaction				Standard Potential (V)
F_2	+ $2e^-$	⇌	$2F^-$	+2.87
Pb^{4+}	+ $2e^-$	⇌	Pb^{2+}	+1.67
Cl_2	+ $2e^-$	⇌	$2Cl^-$	+1.36
O_2+4H^+	+ $4e^-$	⇌	$2H_2O$	+1.23
Ag^+	+ $1e^-$	⇌	Ag	+0.80
Fe^{3+}	+ $1e^-$	⇌	Fe^{2+}	+0.77
Cu^{2+}	+ $2e^-$	⇌	Cu	+0.34
$2H^+$	+ $2e^-$	⇌	H_2	0.00
Pb^{2+}	+ $2e^-$	⇌	Pb	-0.13
Fe^{2+}	+ $2e^-$	⇌	Fe	-0.44
Zn^{2+}	+ $2e^-$	⇌	Zn	-0.76
Al^{3+}	+ $3e^-$	⇌	Al	-1.66
Mg^{2+}	+ $2e^-$	⇌	Mg	-2.36
Li^+	+ $1e^-$	⇌	Li	-3.05

The Electrochemical Series

What Makes Them Hot-headed? ROS in the EC Series!

	$E^0 = -\Delta G^0/nF$	E^0/V
Strongly Oxidizing	$O(g) + 2\,H^+ + 2\,e \rightleftharpoons H_2O$	2.421
	$O_3 + 2\,H^+ + 2\,e \rightleftharpoons O_2 + H_2O$	2.076
	$OH + e \rightleftharpoons OH^-$	2.02
	$O_3 + H_2O + 2\,e \rightleftharpoons O_2 + 2\,OH^-$	1.24
	$O_2 + 4\,H^+ + 4\,e \rightleftharpoons 2\,H_2O$	1.229
Both Oxidizing & Reducing	$HO_2^- + H_2O + 2\,e \rightleftharpoons 3\,OH^-$	0.878
	$O_2 + 2\,H^+ + 2\,e \rightleftharpoons H_2O_2$	0.695
Strongly Reducing	$O_2 + H_2O + 2\,e \rightleftharpoons HO_2^- + OH^-$	–0.076
	$O_2 + 2\,H_2O + 2\,e \rightleftharpoons H_2O_2 + 2\,OH^-$	–0.146

What Makes Them Hot-headed? ROS in the EC Series!

Can you Identify the ROS here?

Reaction ($E^0 = -\Delta G^0/nF$)	E^0/V
$O(g) + 2\,H^+ + 2\,e \rightleftharpoons H_2O$	2.421
$O_3 + 2\,H^+ + 2\,e \rightleftharpoons O_2 + H_2O$	2.076
$OH + e \rightleftharpoons OH^-$	2.02
$O_3 + H_2O + 2\,e \rightleftharpoons O_2 + 2\,OH^-$	1.24
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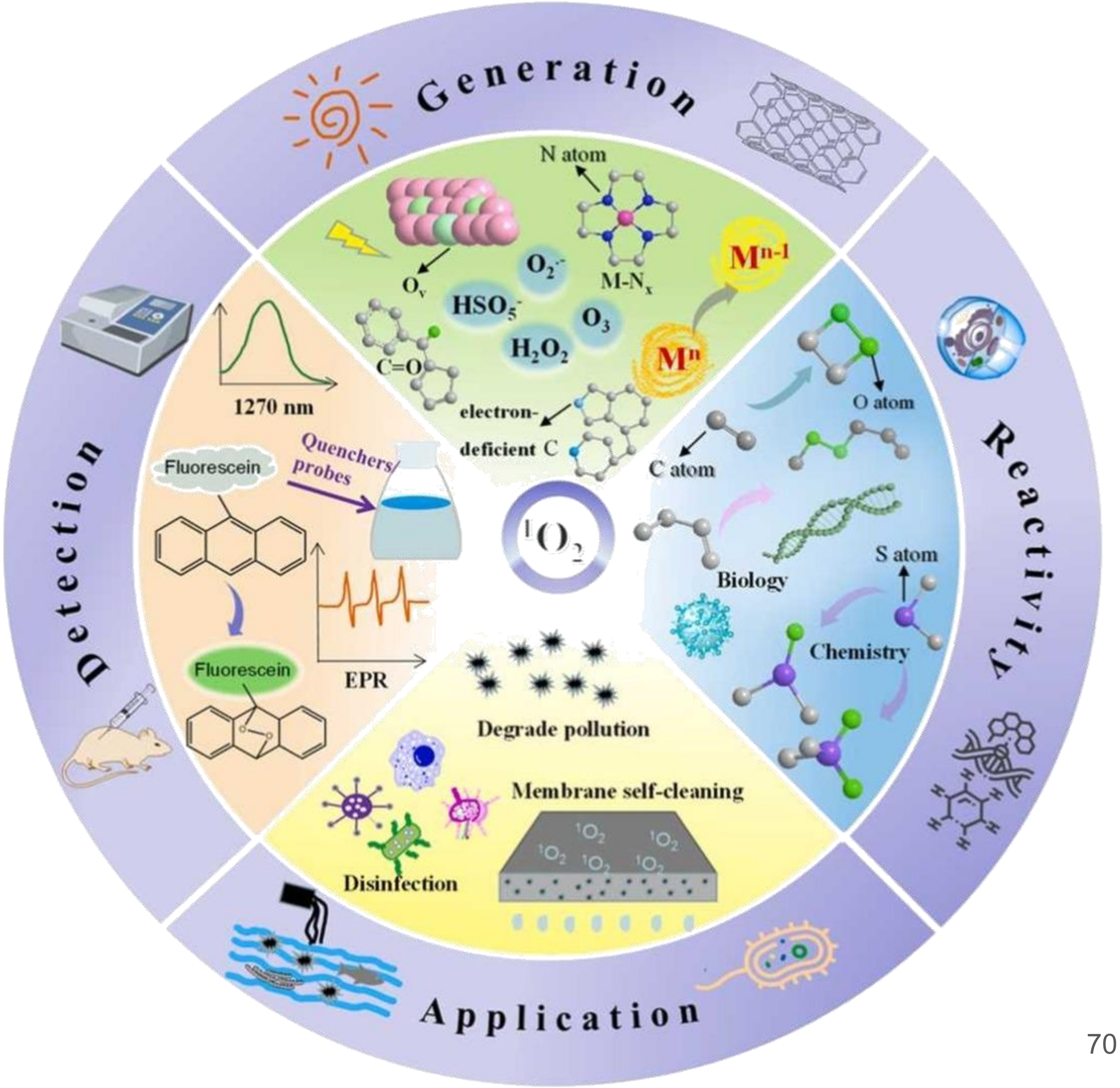
$HO_2^- + H_2O + 2\,e \rightleftharpoons 3\,OH^-$	0.878
$O_2 + 2\,H^+ + 2\,e \rightleftharpoons H_2O_2$	0.695
$O_2 + H_2O + 2\,e \rightleftharpoons HO_2^- + OH^-$	−0.076
$O_2 + 2\,H_2O + 2\,e \rightleftharpoons H_2O_2 + 2\,OH^-$	−0.146

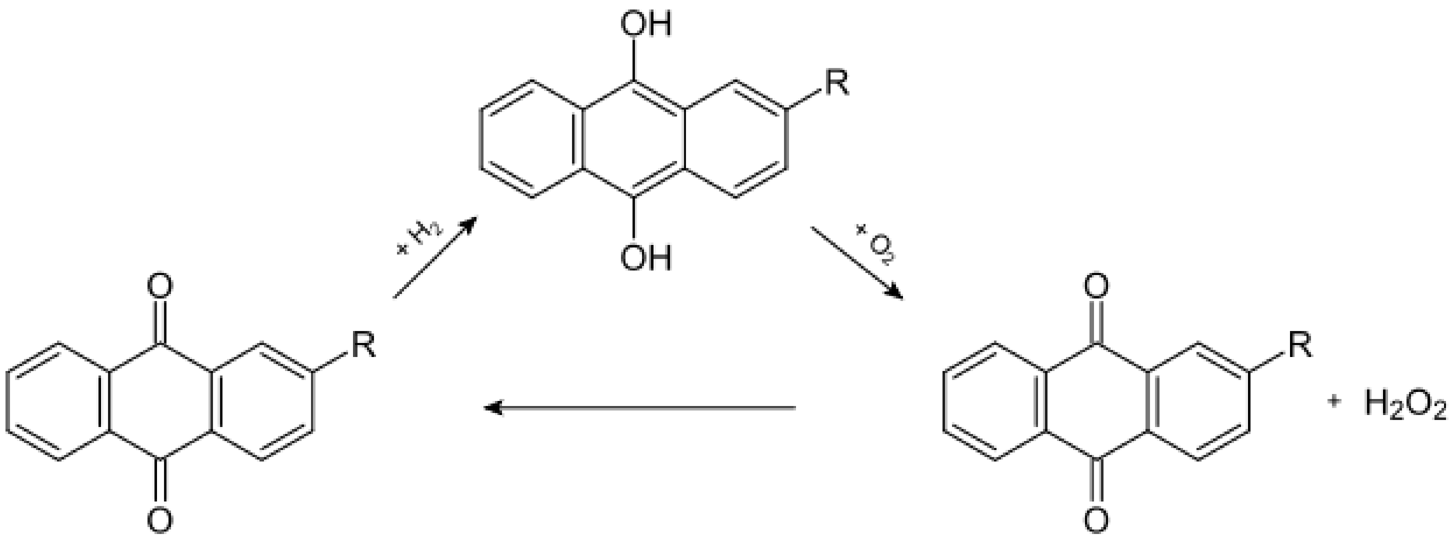
ROS: The Singlet O_2!

Wang and co-workers, Singlet oxygen: Properties, generation, detection, and environmental applications. Journal of Hazardous Materials Volume 461, 5 January **2024**, 132538



ROS: Synthesis of H_2O_2!

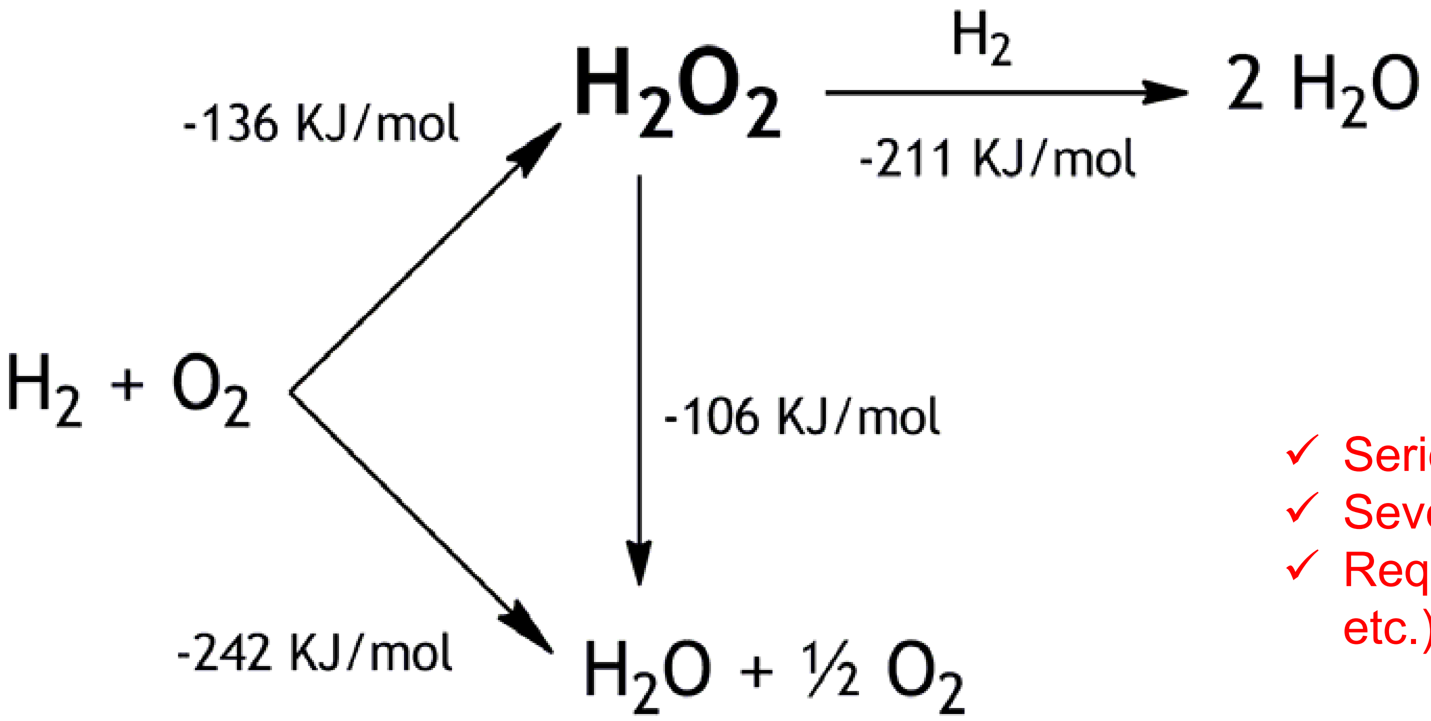
The anthraquinone process



- ✓ Uses carcinogenic chemicals
- ✓ Requires phase transfer catalysts
- ✓ Can only be carried out in batches
- ✓ Always result in dangerously concentrated H_2O_2 solution (>80% by volume)

ROS: Synthesis of H_2O_2!

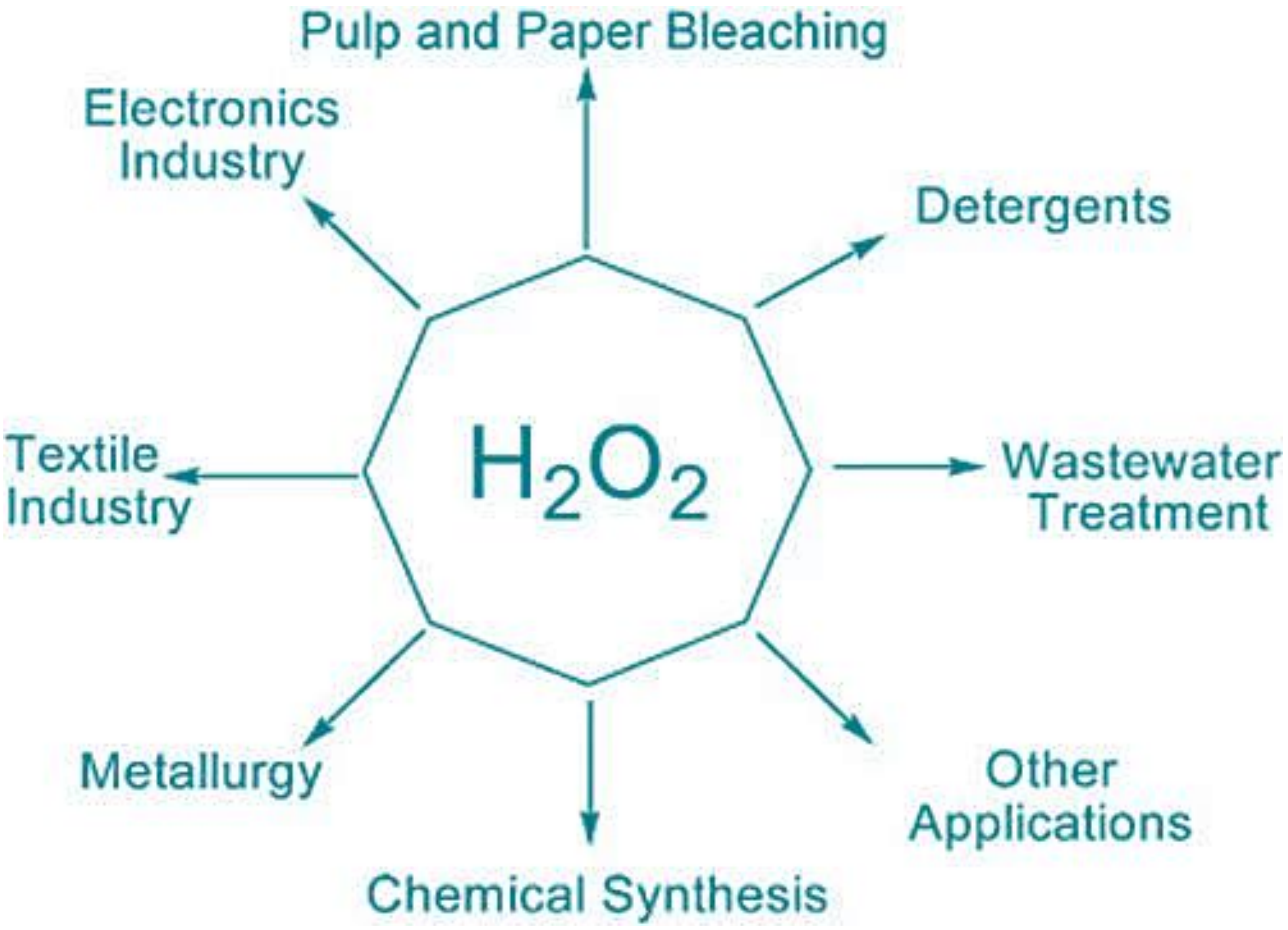
Direct Synthesis of H_2O_2



- ✓ Serious explosion hazard
- ✓ Severe loss of H_2O_2
- ✓ Requires noble metals (Pt, Pd, Au, Ag etc.) as catalysts

ROS: Uses of H_2O_2!

- Universal Oxidant
- The **GREENEST** Oxidant
- Produces just H_2O/O_2 as byproduct

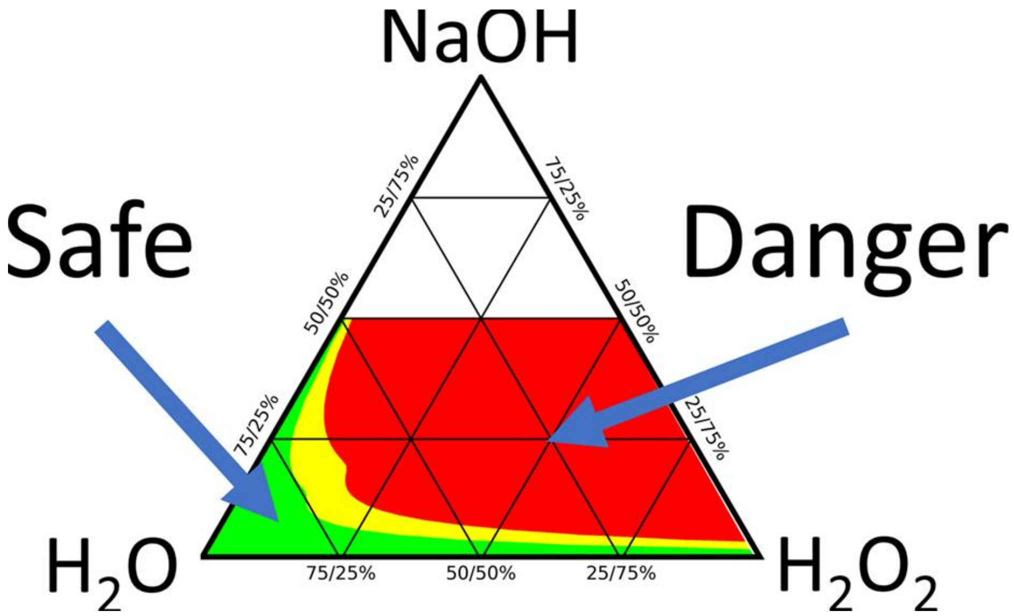


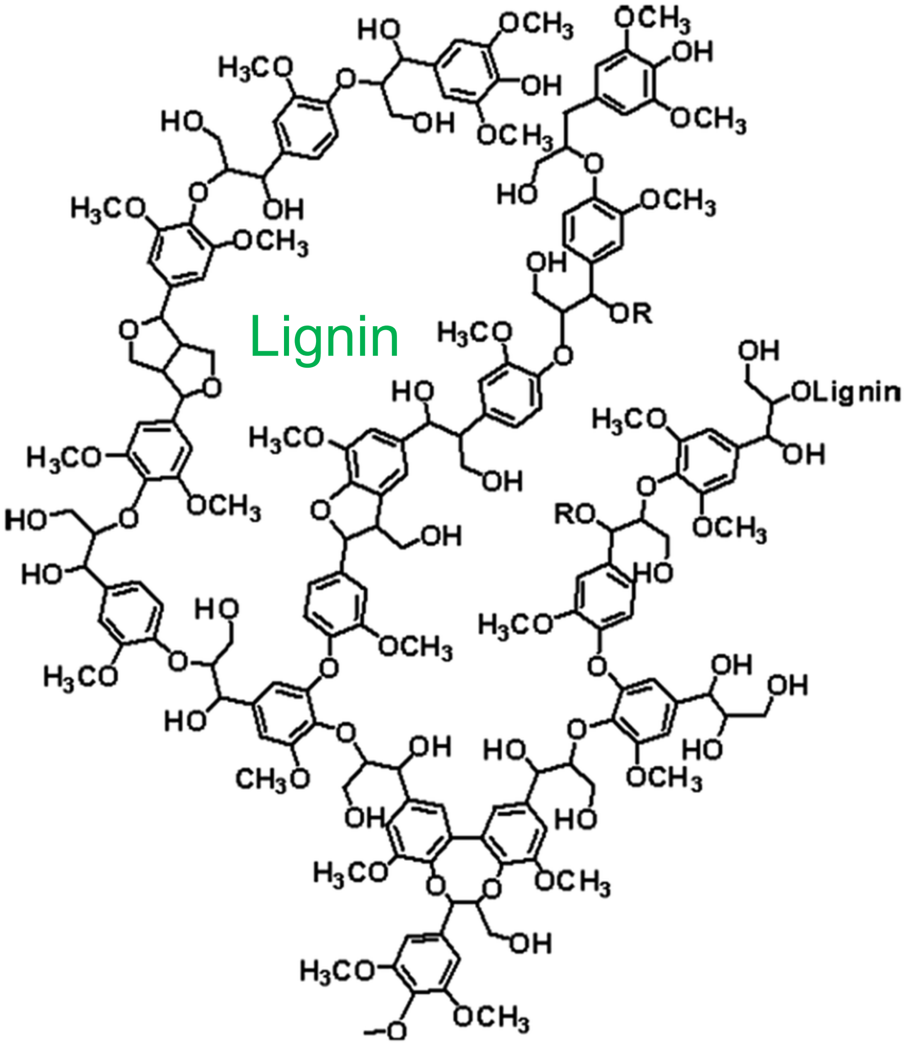
ROS: Uses of H_2O_2 => Industrial Bleaching!

- H_2O_2 breaks down **lignin**
- Lignin gives the structural integrity and the color to wood.
- H_2O_2 is usually activated by using NaOH

ROS: Uses of H_2O_2 => Industrial Bleaching!

- NaOH activation of H_2O_2





ROS: Uses of H_2O_2 => Water Treatment!

- Disinfection
- Oxidizing organic and inorganic compounds
- Dechlorination
- Cyanide removal
- VOC removal

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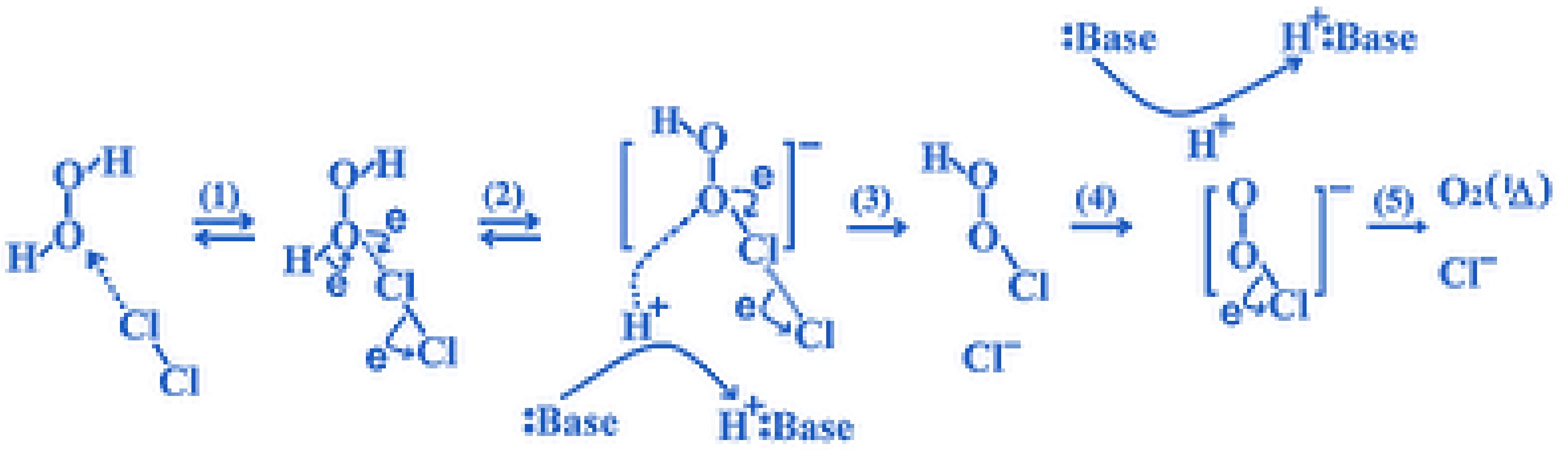


$$H_2O_2 + Cl_2 + 2\,{:}Base = O_2(^1\Delta)\uparrow + 2Cl^- + 2H^+{:}Base$$

$$({:}Base = C_5H_5N,\ CH_3COO^-,\ HCOO^-,\ F^-)$$

ROS: Uses of H_2O_2 => Water Treatment!

- Disinfection
- Oxidizing organic and inorganic compounds
- Dechlorination
- Cyanide removal
- VOC removal

$$Me(CN)_x^{y} \xrightarrow{h\nu} Me(CN)_x^{y\,*}$$

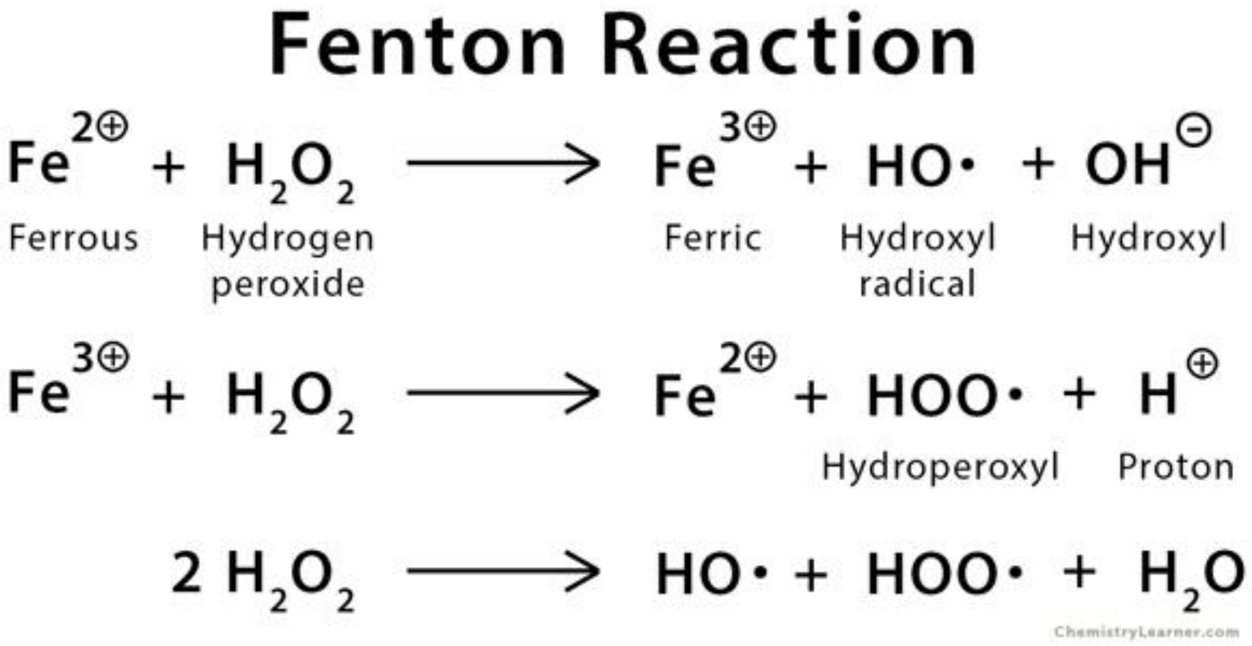
$$Me(CN)_x^{y-\,*} + H_2O_2 \longrightarrow x\,CNO^- + Me(OH)_z$$

$$H_2O_2 \xrightarrow{h\nu} 2\,HO^\bullet$$

$$CN^- + 2\,HO^\bullet \longrightarrow CNO^- + H_2O$$

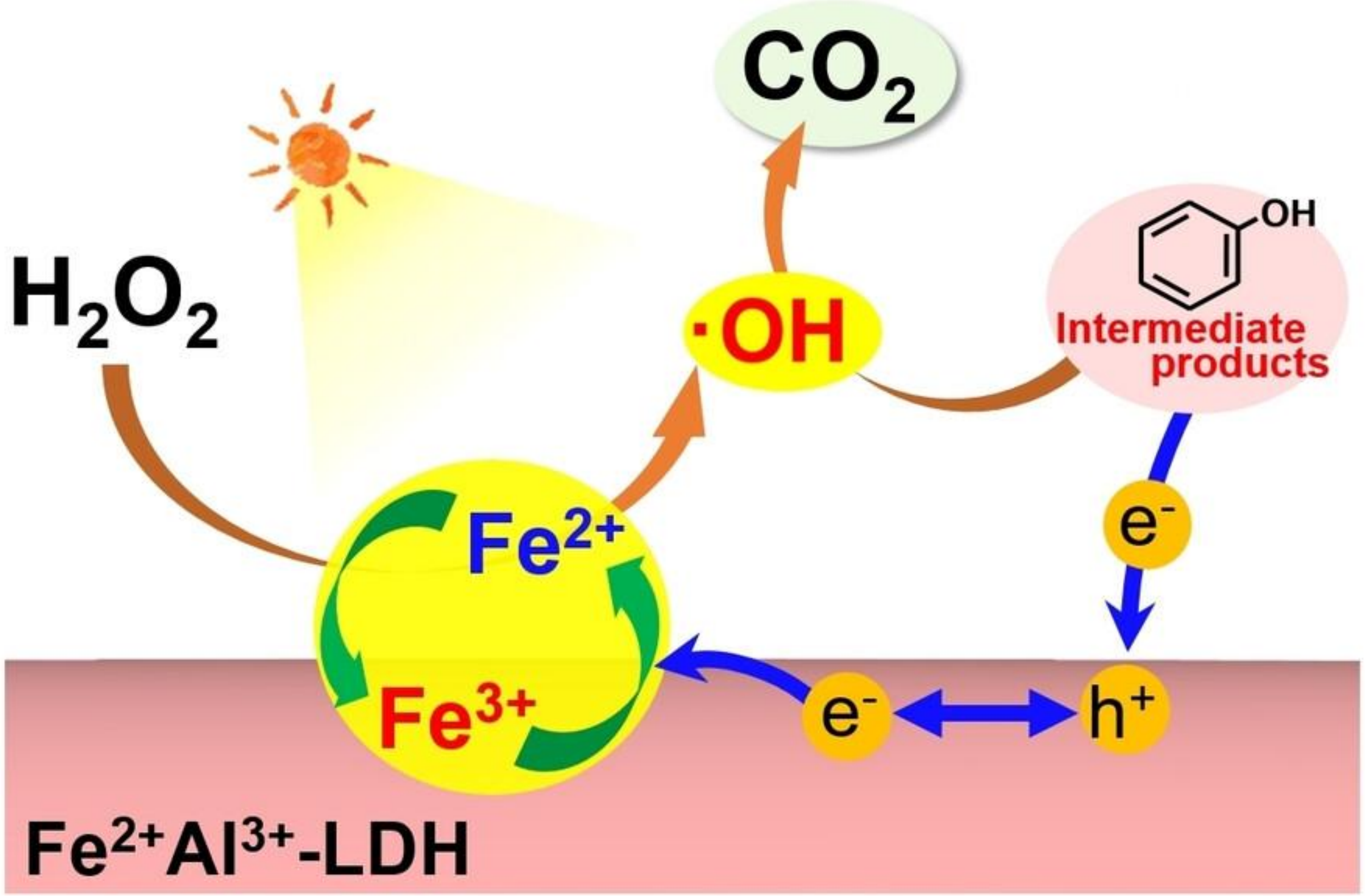
Water Treatment: The Fenton Process!

- Disinfection
- Oxidizing organic and inorganic compounds
- Dechlorination
- Cyanide removal
- VOC removal



Water Treatment: The Photo-Fenton Process!

- Disinfection
- Oxidizing organic and inorganic compounds
- Dechlorination
- Cyanide removal
- VOC removal



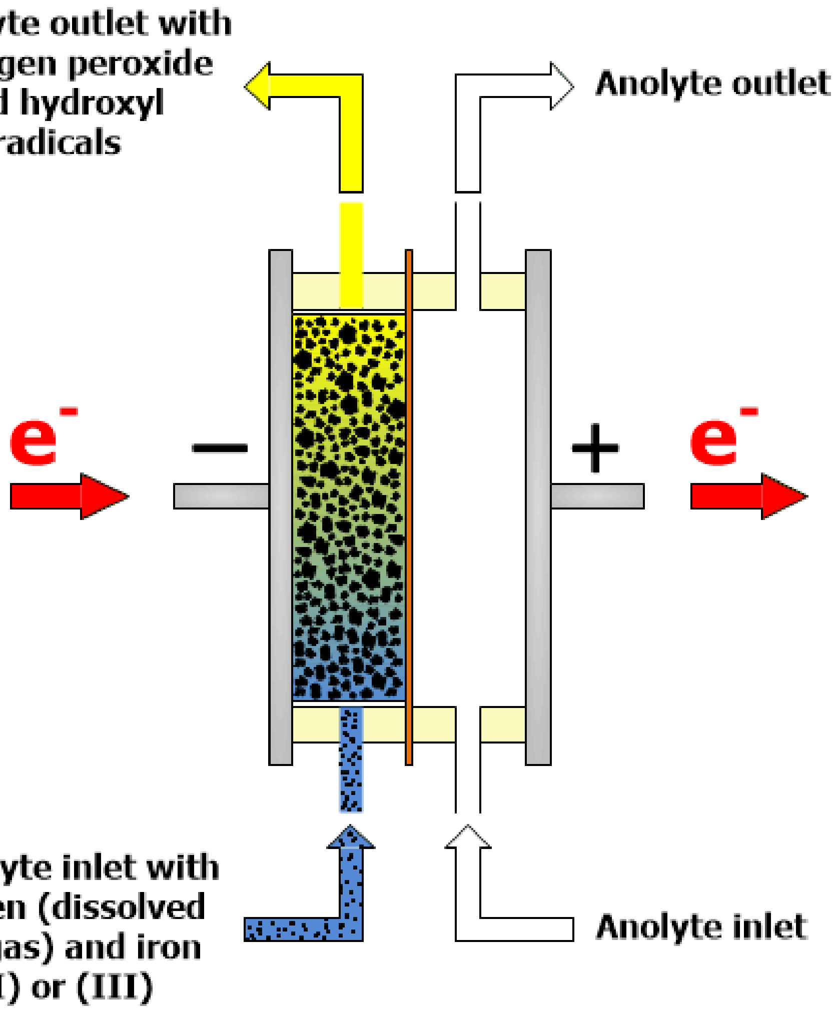
Water Treatment: The Electro-Fenton Process!

Cathodic reactions:

$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$

$H_2O_2 + Fe^{2+} \longrightarrow {}^{o}OH + Fe^{3+} + OH^-$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$



Anodic reactions:

$H_2O \longrightarrow ½\,O_2 + 2H^+ + 2e^-$