Training event “Anthropogenic activities and effects on the living environment and human health.”

Pollutants by anthropogenic activities: mechanism of formation, strategies for reduction

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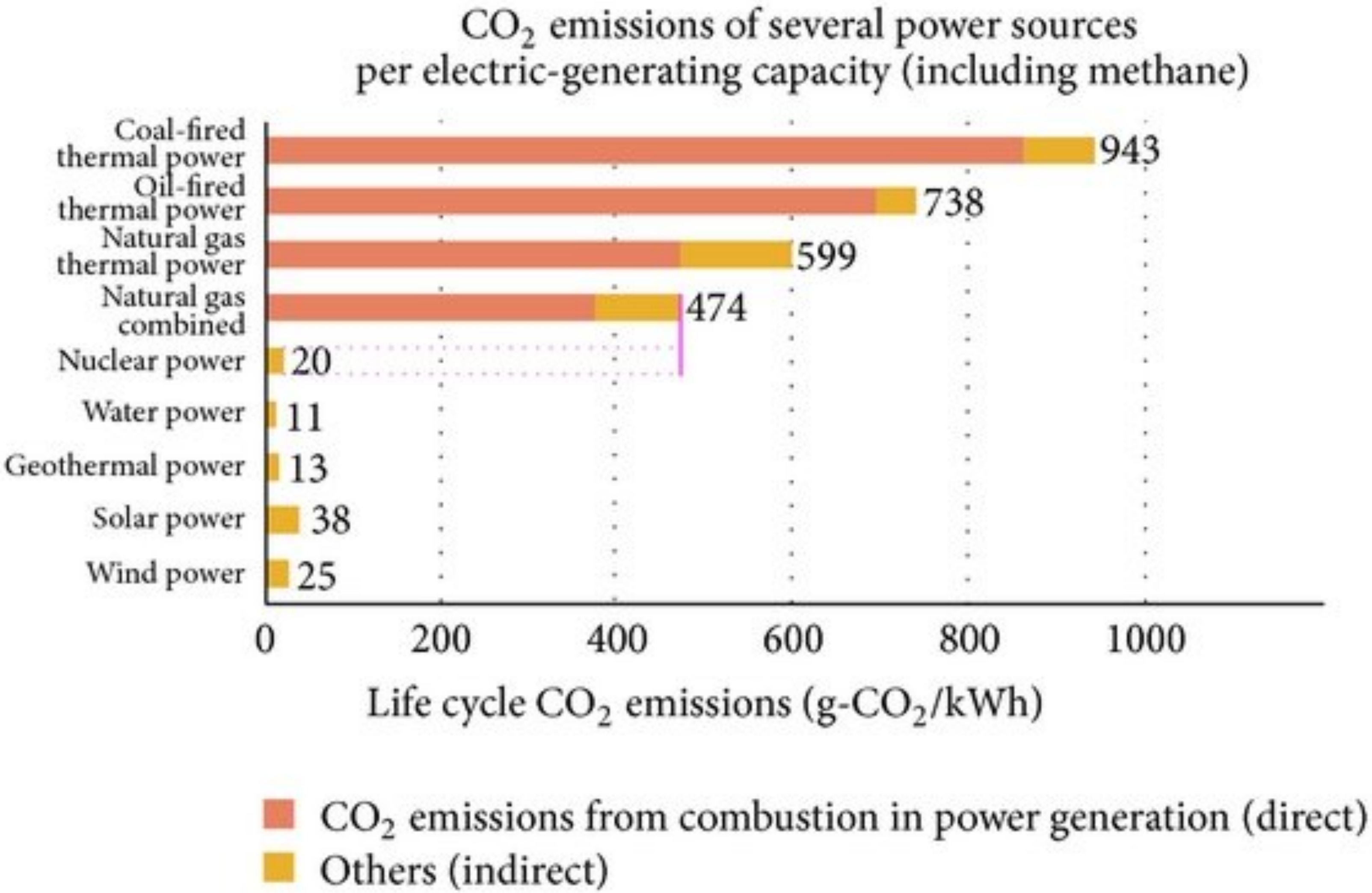
Greenhouse gases and global warming contribution

Gas	Source (natural and anthropogenic)	Estimated Anthropogenic Emission Rate	Preindustrial Global Concentration	Approximate Current Concentration	Estimated Residence Time in Atmosphere	Radiative Forcing Efficiency over 100 years (CO_2 = 1)	Estimated Contribution to radiative Forcing (W/m^2)
Carbon dioxide (CO2)	Fossil fuel combustion, deforestation	38 Gt/yr (10^{12} kg/yr)	280 ppm	390 ppm	50-200 yr	1	1.5-1.8
Methane (CH4)	Anaerobic decay (wetlands, landfills, rice paddies), ruminants, termites, natural gas, coal mining, biomass burning	0.3 Gt/yr	0.8 ppm	1.8 ppm	10 yr	25	0.43-0.53
Nitrous oxide (N2O)	Estuaries and tropical forests, agricultural practices, deforestation, land clearing, low-temperature fuel combustion	0.01 Gt/yr	0.385 ppm	0.32 ppm	140-190 yr	298	0.14-0.18
Chlorofluorocarbons (CFCs)	Refrigerants, air conditioners, foam blowing agents, aerosol cans, solvents	<0.0005 Gt/yr	0	0.0004-0.001 ppm	65-110 yr	4750 (CFC-11)	0.31-0.37
Tropospheric ozone (O3)	Photochemical reactions between VOCs and Nox from transportation and industrial sources	Not emitted directly	NA	0.022 ppm	hours-days	2000	0.25-0.65

GHG emissions from various energy sources



Others air Pollutants

- ✓ Carbon monoxide
- ✓ Hydrocarbons, and VOCs
- ✓ Ground-level Ozone
- ✓ NOx, SO2 and acid deposition
- ✓ Soot and PAHs
- ✓ Air Toxics including Dioxines
- ✓ Particulate Matter (PMx) – primary and secondary PM
- ✓ Ozone

The major pollution issues

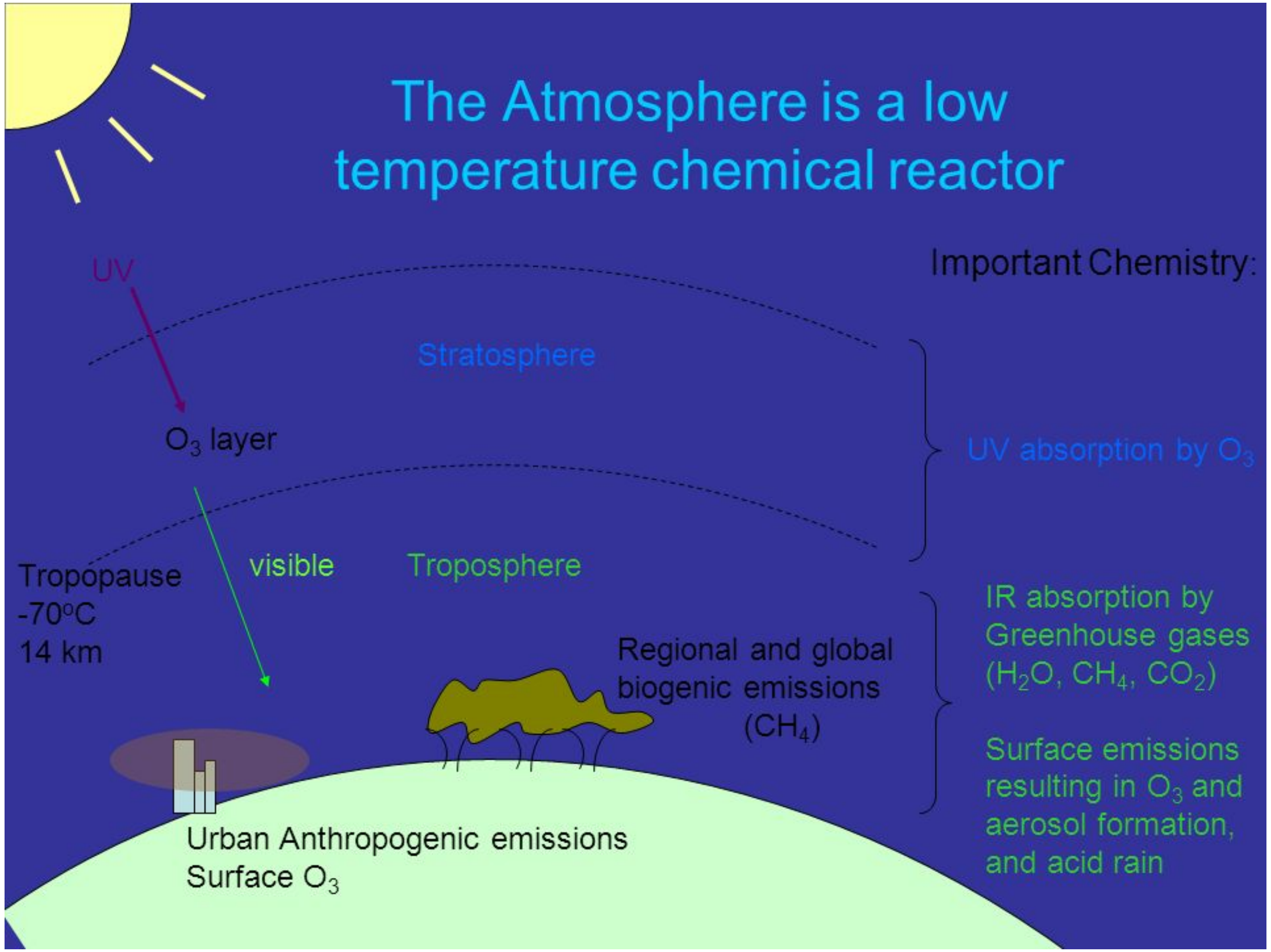
- ✓ The ozone in the troposphere
- ✓ The photochemical smog
- ✓ The ozone in the stratosphere
- ✓ The ozone hole
- ✓ The radiative balance in the atmosphere
- ✓ Global warming: Earth’s albedo
- ✓ Climate change
- ✓ Health effects

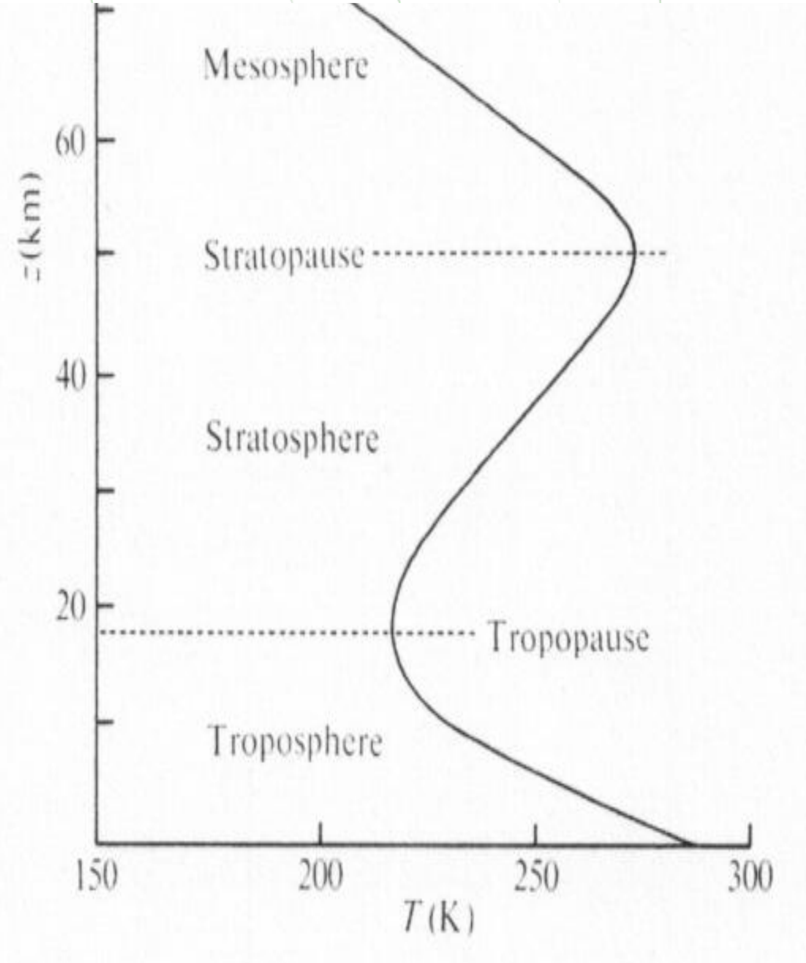
The atmospheric reactor

The atmosphere functions as a massive photochemical reactor, with sunlight serving as the energy source for reactions.

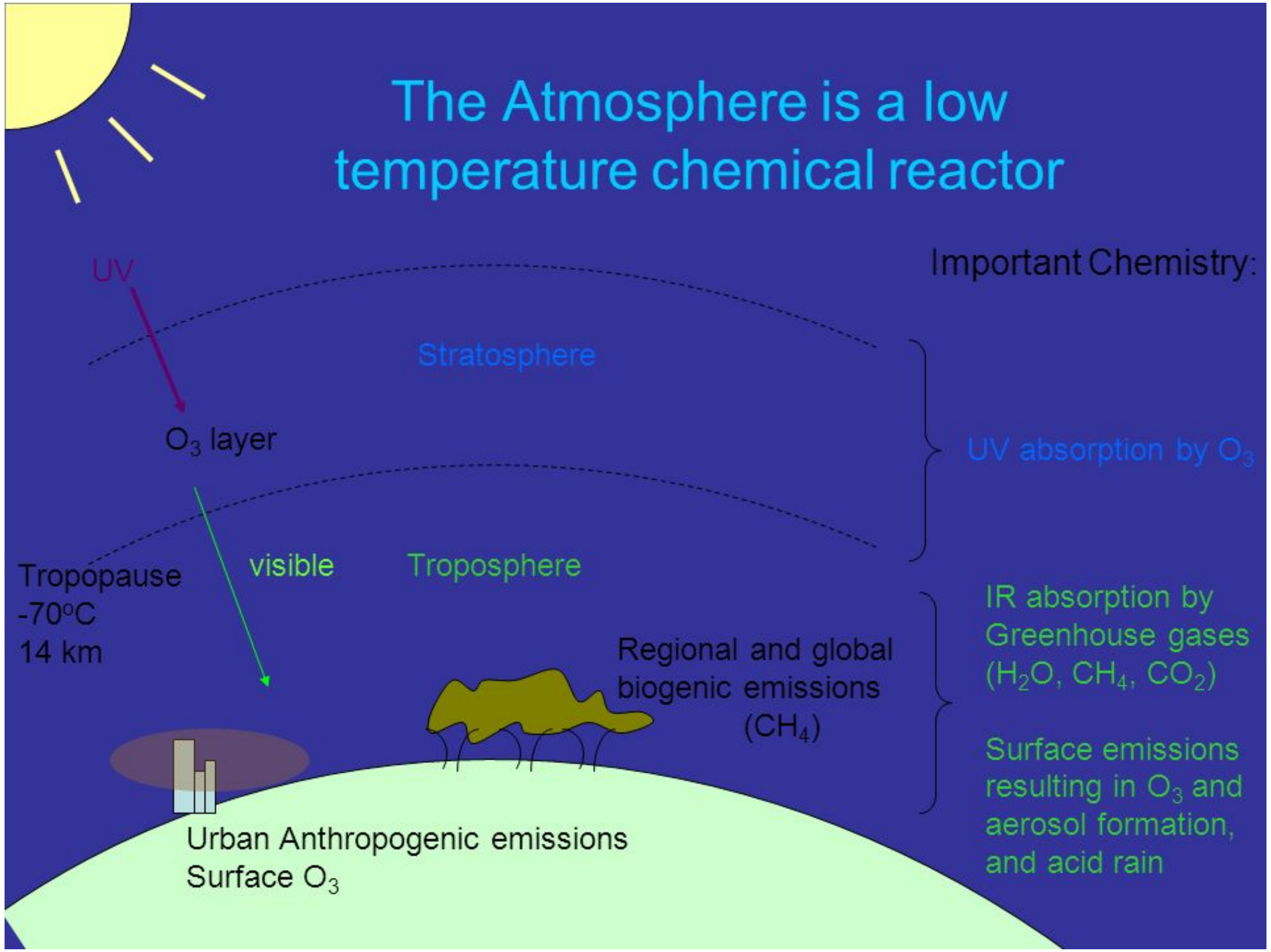
Light radiation, particularly in the visible and ultraviolet regions, has the ability to break down atmospheric constituents to create atoms, radicals, and ions, or to excite the constituents without causing a chemical change, thereby altering their reactivity.

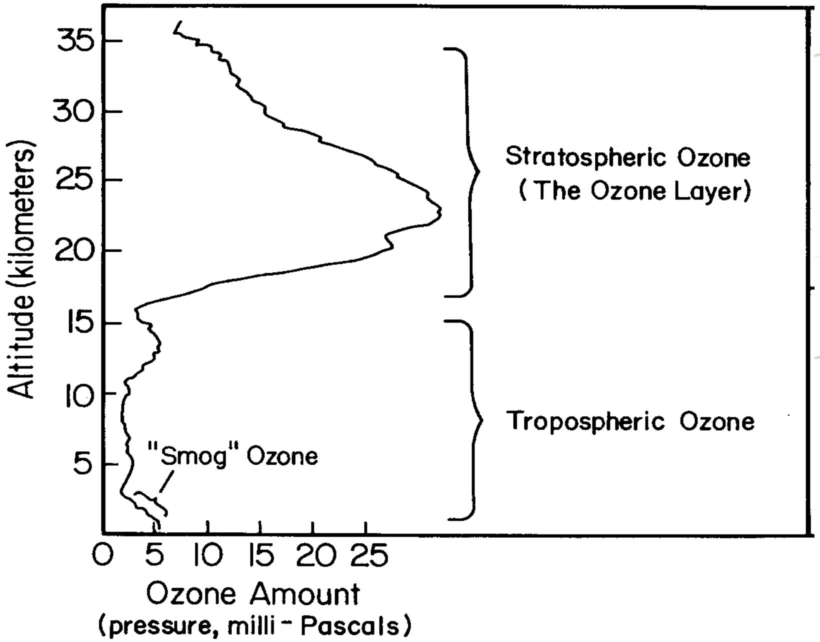
The atmospheric reactor



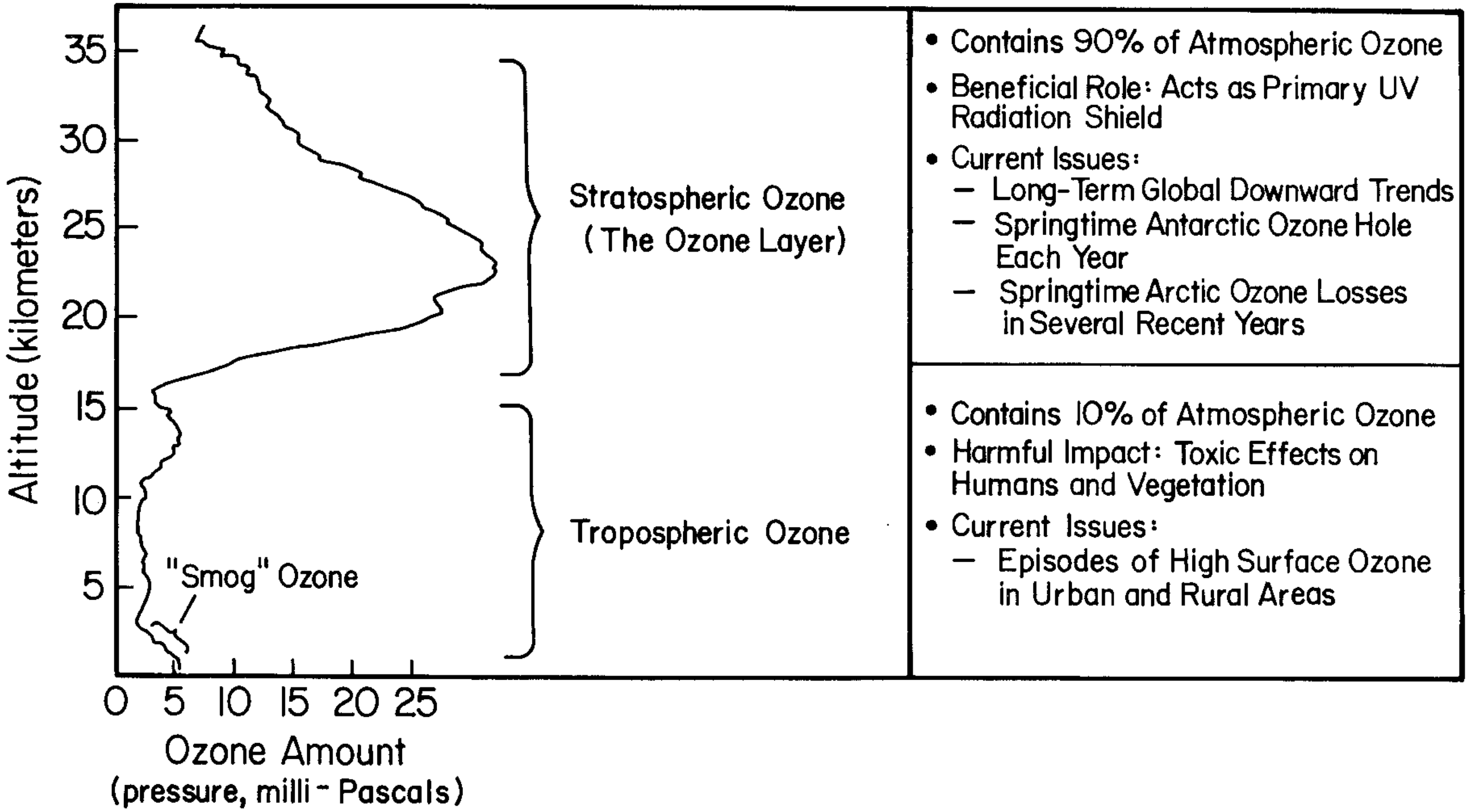


The atmospheric reactor

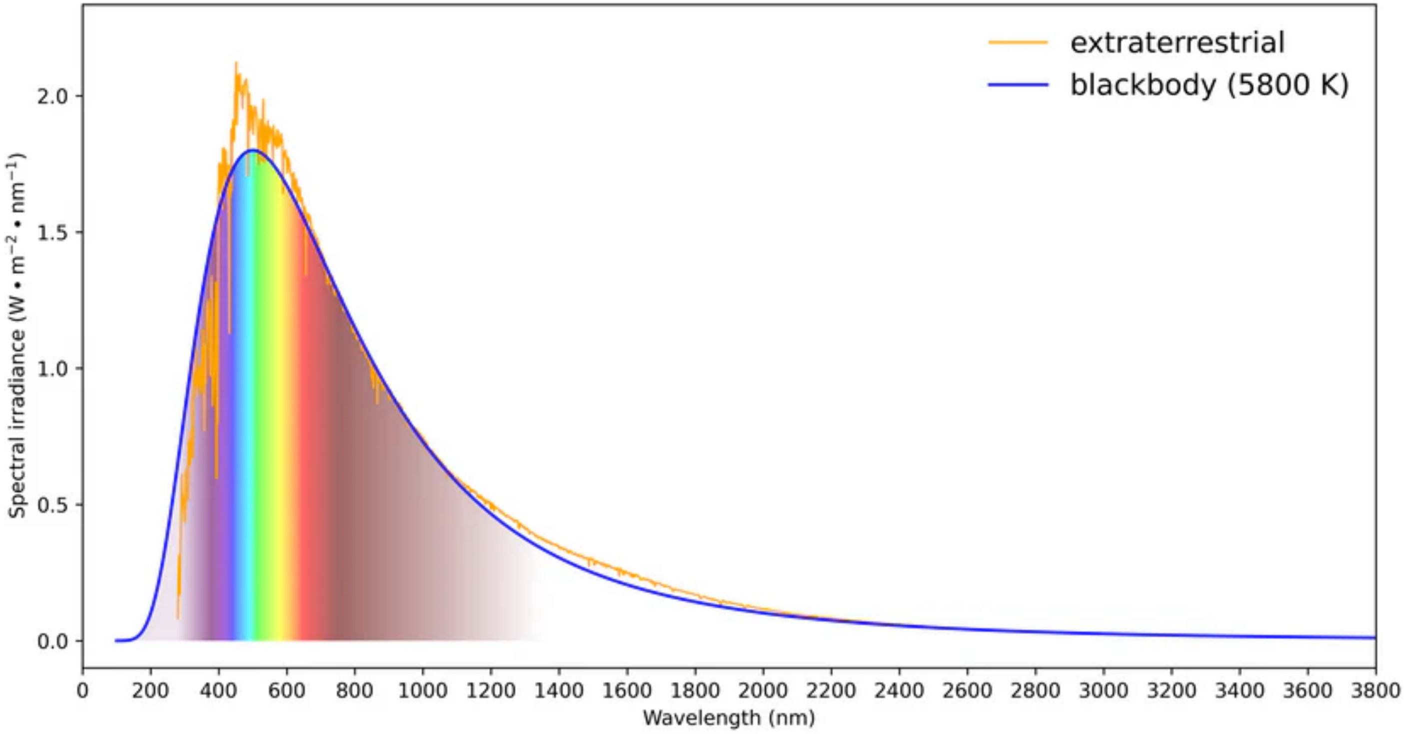




Ozone (O_3) in the atmosphere



The energy source for atmospheric reactions



According to Planck' law, the energy of one photon (***ε***) of frequency ***v*** is ***hv***, where ***h*** is the Planck constant

$$\varepsilon = hv$$

and in terms of wavelength of radiation ***λ***

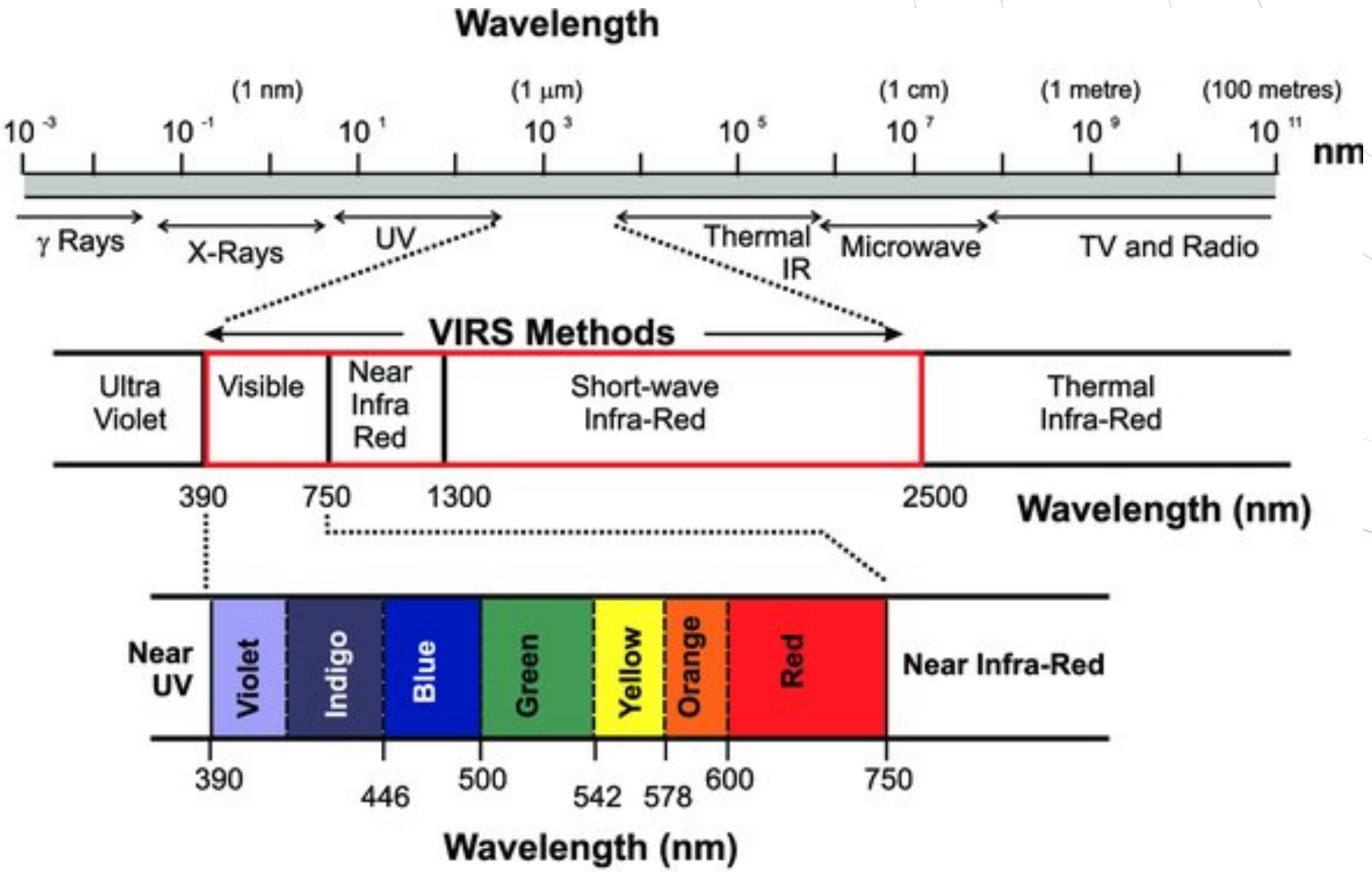
$$v = c/\lambda$$

where ***c*** is the velocity of light

$$\varepsilon = hv = hc/\lambda$$

role of thumb: 300nm = 95.3kcal
300nm = 398.75kJ
300nm = 4.13282eV

The electromagnetic spectrum

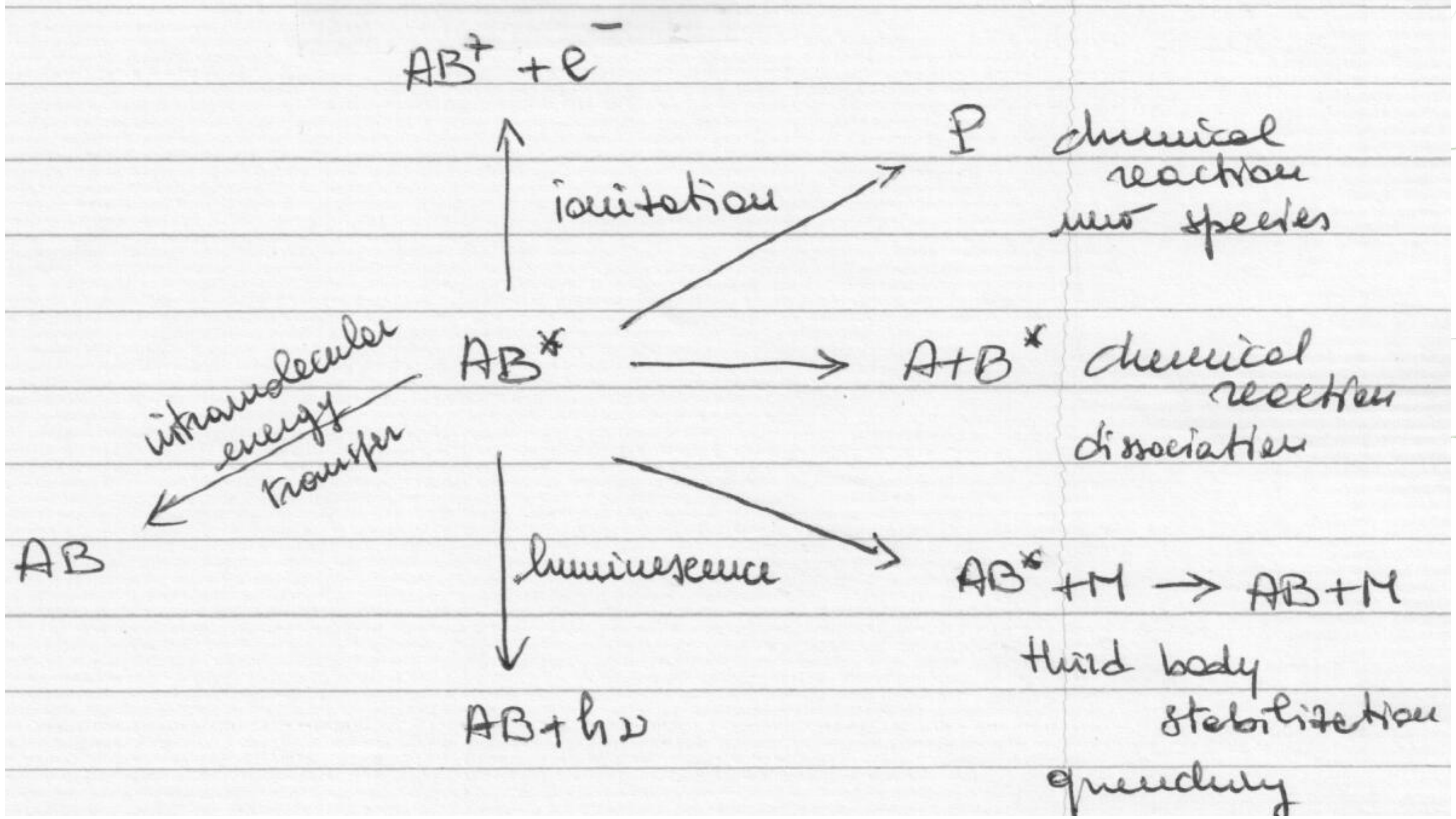


Ionization energies of major species

Species	Ionization energy		Equivalent wavelength (nm)
	eV	kJ mol^{-1}	
Na	5.1	496	241.2
Mg	7.7	738	162.1
NO	9.3	886	135.0
NO_2	9.8	940	127.2
O_2	12.1	1165	102.7
H_2O	12.6	1214	98.7
O_3	12.8	1233	97.0
N_2O	12.9	1246	96.0
SO_2	13.1	1264	94.6
H	13.6	1312	91.2
O	13.6	1314	91.1
CO_2	13.8	1331	89.9
CO	14.0	1352	88.5
N	14.5	1403	85.2
H_2	15.4	1488	80.4
N_2	15.6	1503	79.9

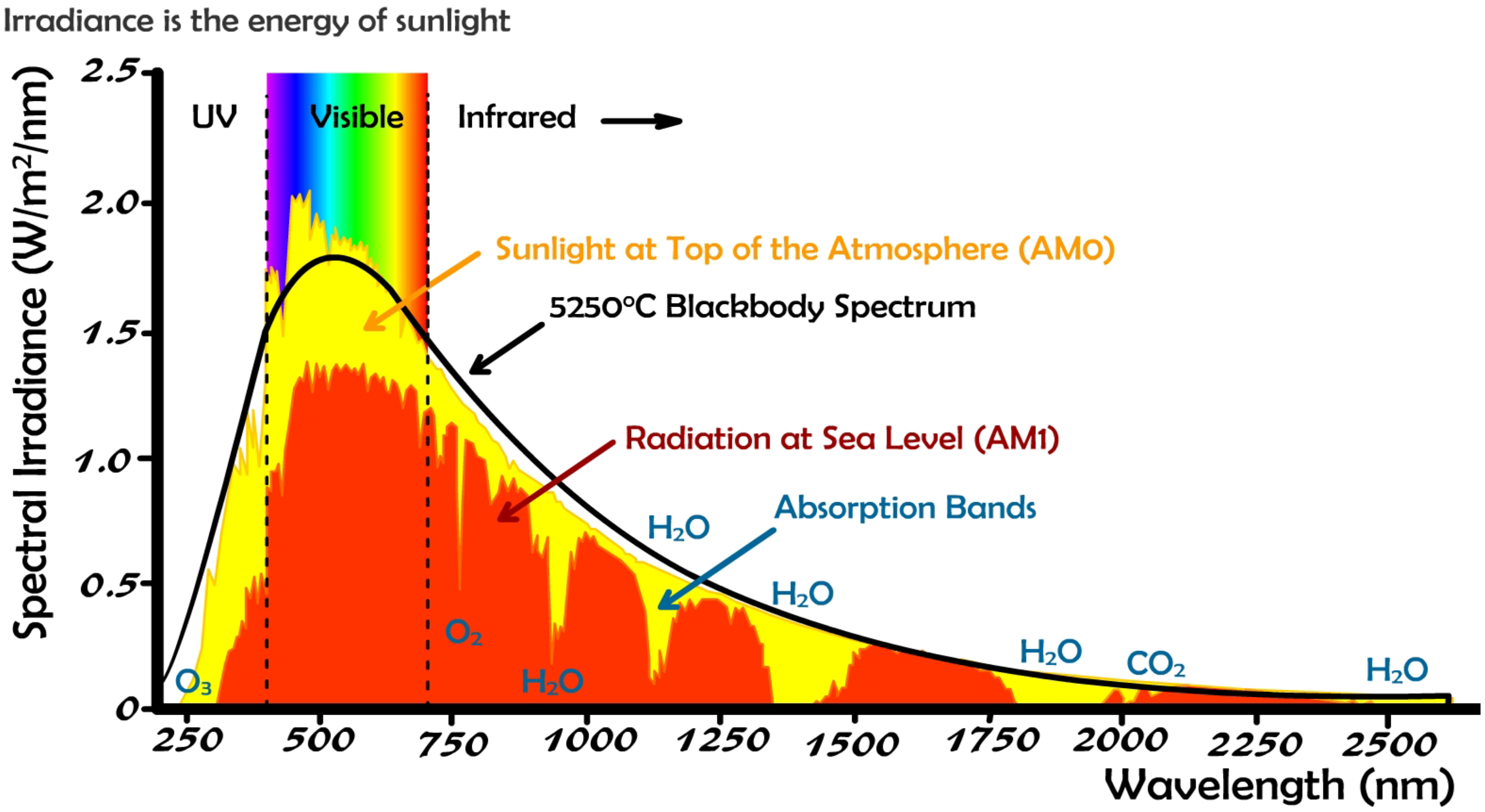
Atmospheric photochemistry

Absorption of a photon of photochemically active radiation leads to electronic excitation: AB + hν → AB*

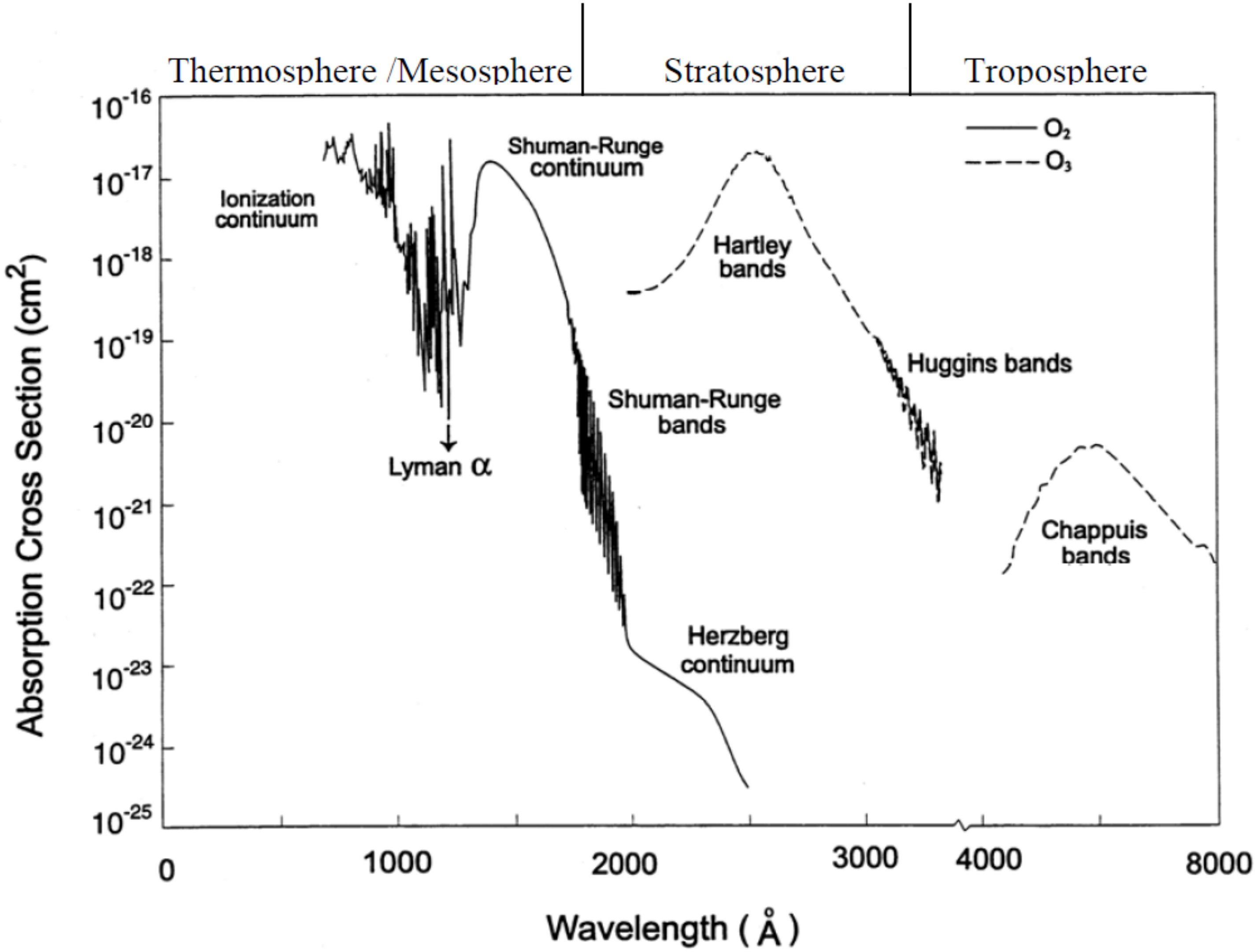


Solar radiation spectrum

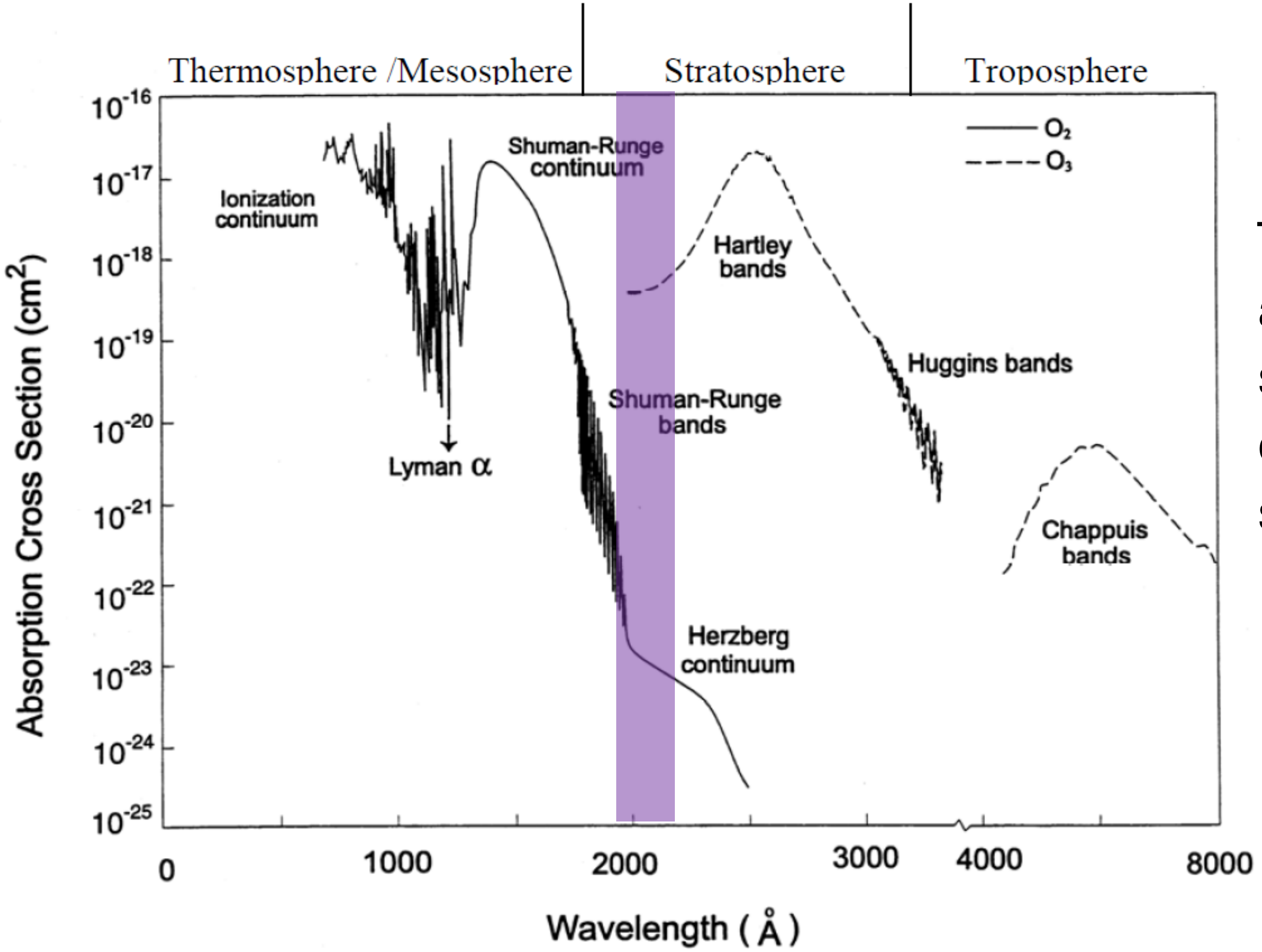
The atmosphere acts as a filter, blocking out short-wavelength radiations



Spectral absorption cross-sections

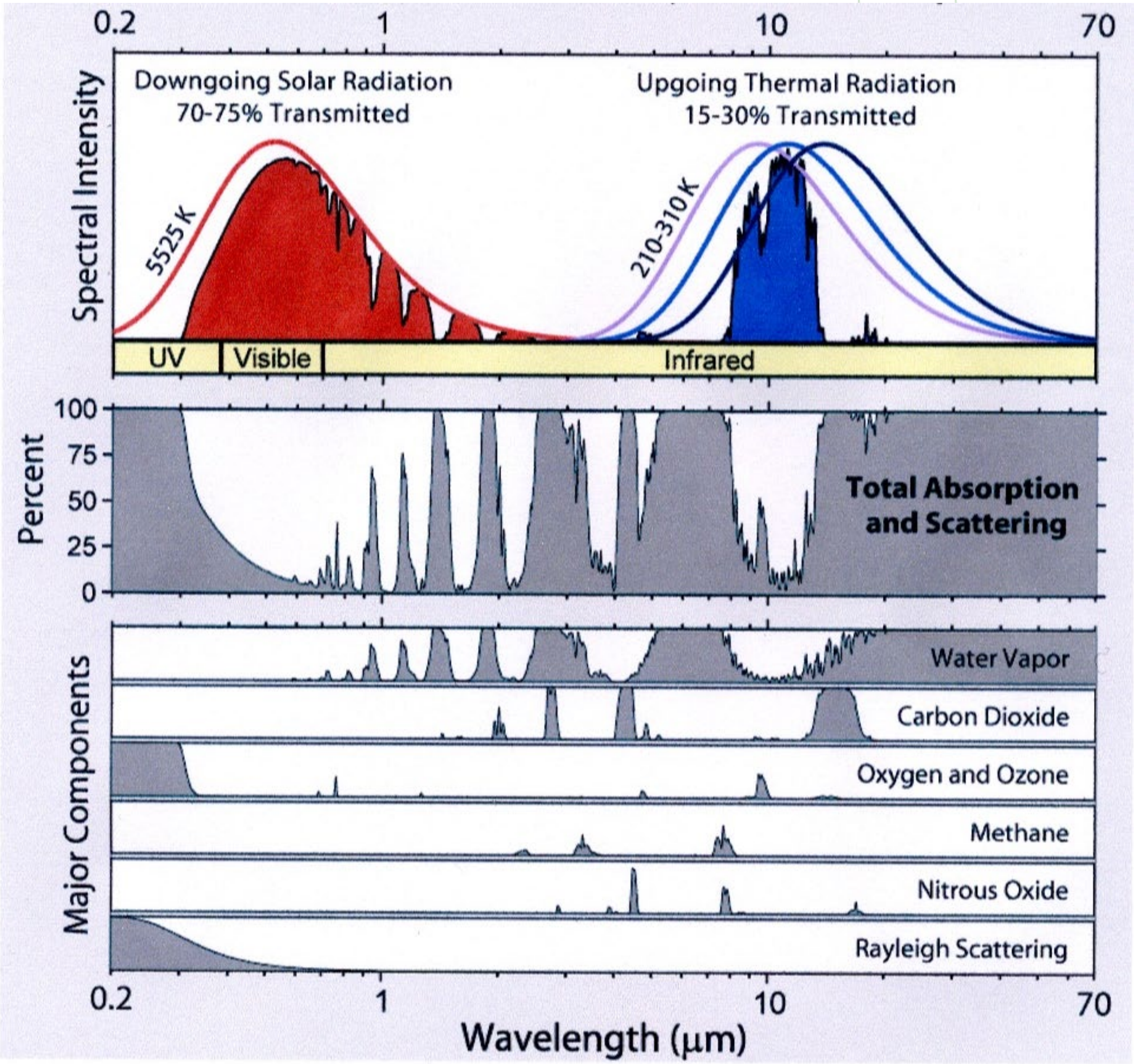


Spectral absorption cross-sections



There is a gap in the two absorption spectra that strongly affects the chemistry of the stratosphere.

Transmitted Radiation (by the Atmosphere)



Major anthropogenic pollutants

The five principal classes of pollutants emitted human activities involving combustion are

- carbon monoxide
- nitrogen oxides
- sulfur oxides
- organic compounds (unburned and partially burned hydrocarbons)
- particulates (soot, flyash, aerosols)

Major anthropogenic pollutants

Emission estimates

Sources	SO_2	NO_x[a]	CO	VOC[b]	PM_{10}	$PM_{2.5}$
Electric power and heat production	49	31	6.5	0.7	4.9	3
Oil refineries	1.7	0.9	0.5	2.1	<0.1	<0.1
Other industrial sources	31	19.2	137.9	63.4	16.3	10.1
Waste and wastewater treatment	0.1	0.2	0.1	2.6	0.2	0.1
Residential, commercial, and institutional sector	8.2	6.2	232.5	36	30.2	18.2
Agriculture	0.4	6	75	4.4	10	8.3
On-road transportation	0.8	27	170	25.4	0.9	0.9
Aviation	0.3	2.9	0.5	0.1	<0.1	<0.1
Maritime shipping	11	17	5.3	1.2	1.9	1.8
Other modes of transportation	0.1	1.9	0.6	0.2	0.3	0.3
Sub-total of anthropogenic sources	103	112	629	136	65	43
Biomass fires[c]	3	25	413	251	49	36
Natural sources	19	53	140	1000	1690	460
Total	**125**	**190**	**1182**	**1387**	**1804**	**539**

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Hydrocarbon oxidation chemistry

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C_xH_y is the general formula for an hydrocarbon molecule

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \rightarrow x\,CO_2 + \frac{y}{2}H_2O$$

it is not an elementary reaction but it includes some elementary steps with some intermediates of reactions

Hydrocarbon oxidation chemistry

Let first individuate an initiation reaction :

$$C_xH_y \xrightarrow[\text{or } H]{h\nu} C_xH^{\bullet}_{y-1} + H^{\bullet}$$

it may be photo- ($h\nu$) or collision-activated (M)

Hydrocarbon oxidation chemistry

At high temperatures, i.e. higher than 1100K, the most active reaction is β-decomposition of the alkylradical $C_xH_{y-1}^{\bullet}$

$$C_xH_{y-1}^{\bullet} \longrightarrow CH_3^{\bullet} + \left(\frac{x-1}{2}\right) C_2H_4 \quad \text{if } x \text{ is odd}$$

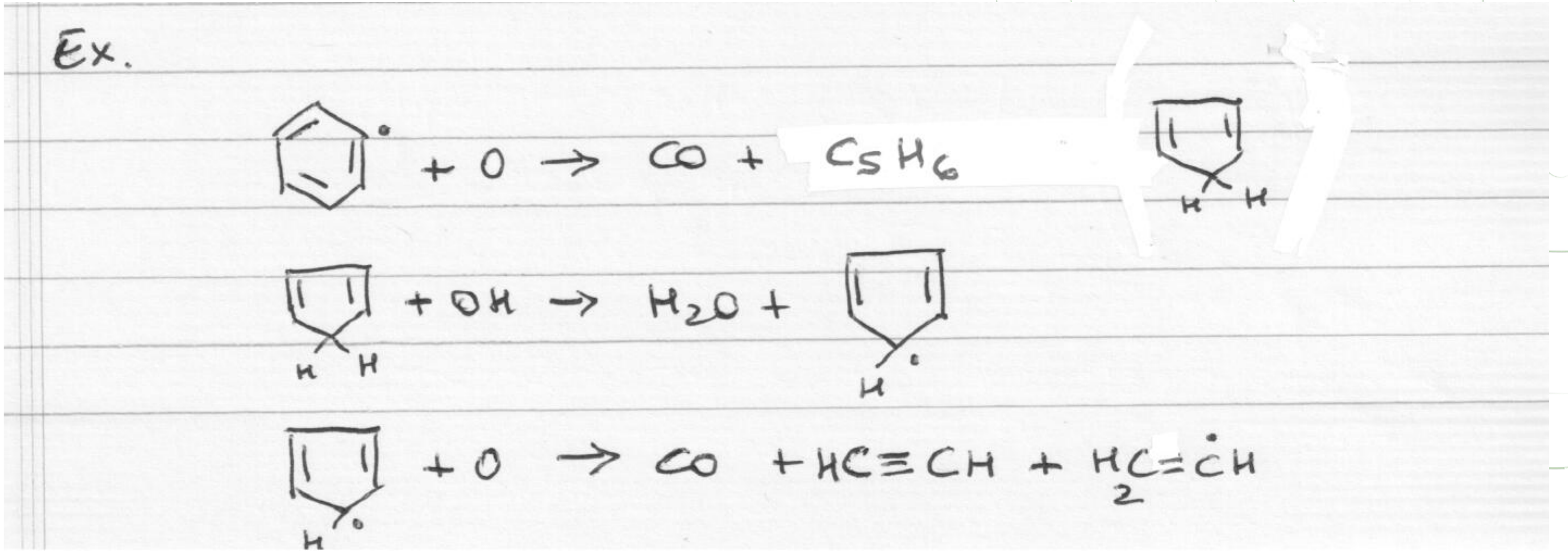
$$\longrightarrow C_2H_5^{\bullet} + \left(\frac{x-2}{2}\right) C_2H_4 \quad \text{if } x \text{ is even}$$

Hydrocarbon oxidation chemistry

it is a propagation reaction that transforms the hydrocarbon (also a complex one) in C_2H_4, $CH_3^{\bullet}$ and $C_2H_5^{\bullet}$

it is valid for aliphatic hydrocarbons
for aromatics there are some complications but also the process continues trough small species (low C number) and radicals

Hydrocarbon oxidation chemistry



Hydrocarbon oxidation chemistry

Thus the oxidation of hydrocarbons at high temperatures is the oxidation of C_2 and C species

Hydrocarbon oxidation chemistry

the H atom formed by the initiation reaction can react with O_2 in the well-known branching cycle of the H_2/O_2 system

Rx1 $H + O_2 \rightarrow OH + O$

Rx3 $O + CH_3^{\bullet} \rightarrow CH_3-O^{\bullet}$

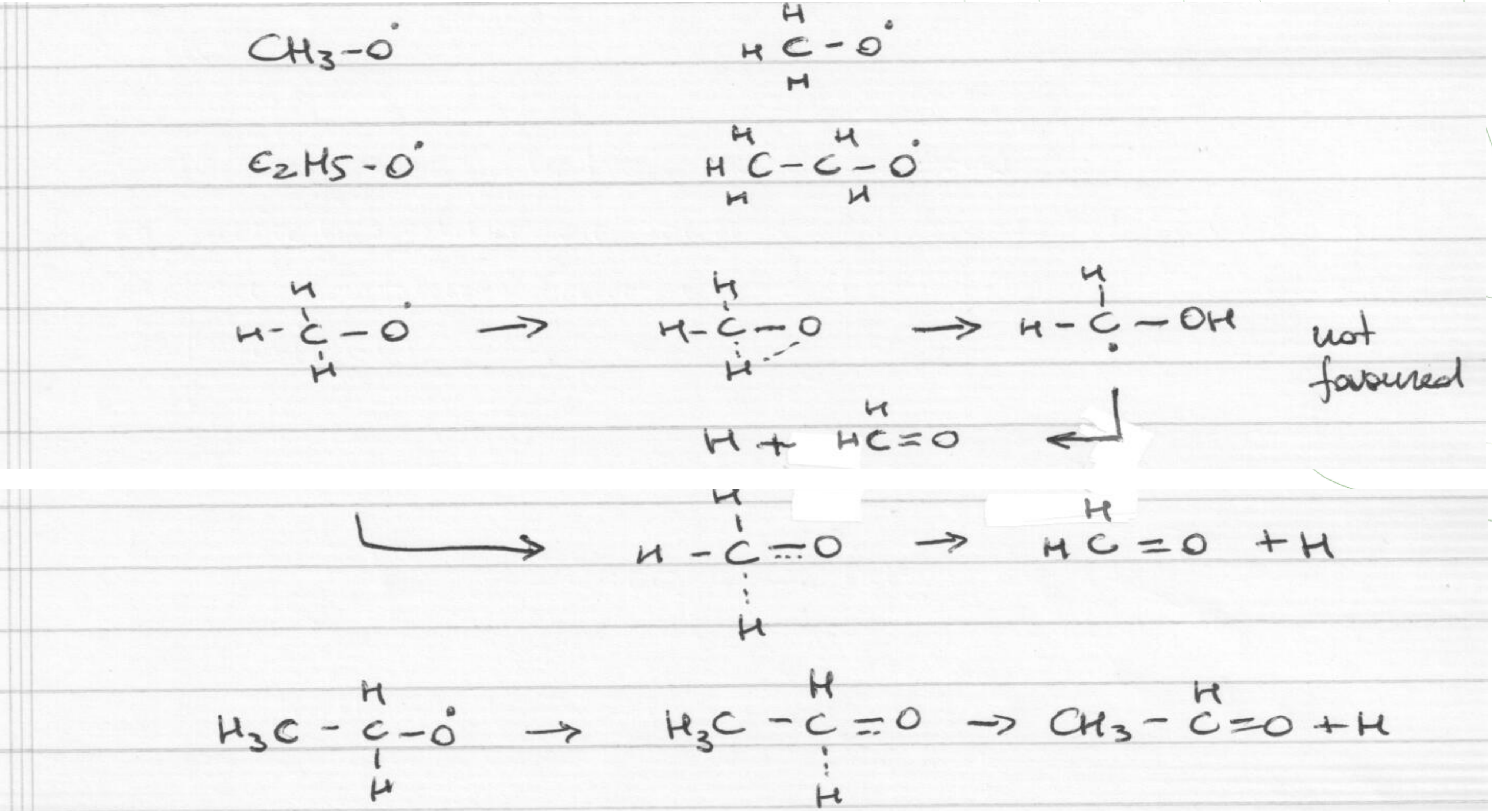
Rx2 $O + C_2H_4 \rightarrow OH + C_2H_3^{\bullet}$

Rx4 $O + C_2H_5^{\bullet} \rightarrow C_2H_5-O^{\bullet}$

Rx1 and 2 are branching reactions

Rx3 and 4 are propagation reactions

Hydrocarbon oxidation chemistry



Hydrocarbon oxidation chemistry

the formation of aldehydes is the favourite process
it is a propagation reaction

A lot of H atoms and aldehydes with 1 or 2 Carbons are formed.

H atoms can react with O_2 with the well-known branching reaction

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Aldehydes are very active species due to the double bond of oxygen with carbon. Indeed being O more electronegative than C, electrons of the double bond are localized more on O than on C.
Also the other electron of the C atom are pulled towards O making the C–H bond weaker by some kcal. Therefore the C–H bond is weaker and easily attacked by H atoms

$$H\overset{H}{C}=O + H \rightarrow H\text{–}\overset{H\cdots H}{C}=O \rightarrow H\dot{C}=O + H_2$$

$$H\dot{C}=O + H \rightarrow \overset{H}{H}\cdots C=O \rightarrow C=O + H_2$$

$$H\dot{C}=O \rightarrow CO + H$$

Hydrocarbon oxidation chemistry

Similarly

$$CH_3-CH=O + H \rightarrow CH_3-\dot{C}=O + H_2$$

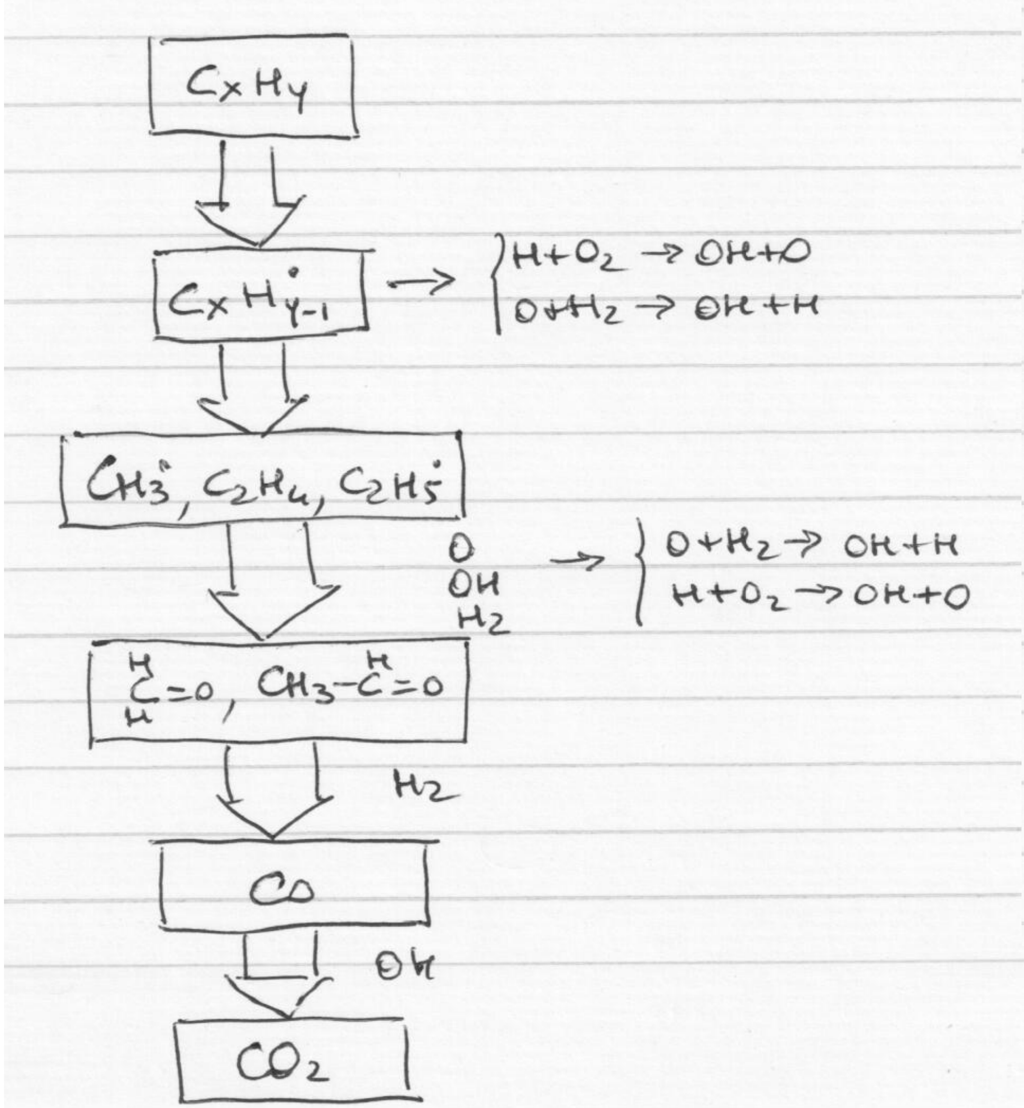
$$CH_3-\dot{C}=O \rightarrow CH_3^{\cdot} + CO$$

The product CO is formed.

$$CO + OH \rightarrow CO_2 + H$$

it is the most important (energetically) reaction that forms the product of C-atoms oxidation

Hydrocarbon oxidation chemistry



Summarizing and using RH to indicate the C_xH_y hydrocarbon:

$$RH \rightarrow R^{\circ} + H$$
$$R^{\circ} \rightarrow R' + C_2H_4$$
$$R' + O \rightarrow R\text{-}O^{\circ}$$
$$R' + OH \rightarrow R\text{-}OH$$
$$R\text{-}O^{\circ} \rightarrow RCHO + H$$
$$RCHO + H\ (O,\ OH) \rightarrow R\dot{C}{=}O + H_2\ (OH,\ H_2O)$$
$$R\dot{C}{=}O \rightarrow R^{\circ} + CO$$
$$CO + OH \rightarrow CO_2 + H$$

Hydrocarbon oxidation chemistry

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RH represents the parent hydrocarbon fuel

$R^{\bullet}$ is a hydrocarbon radical produced by removing a H-atom from the fuel molecule

The rate at which CO is oxidised to CO_2 is relatively slow compared to the CO formation rate

This has a strong effect in determining intermediates in the hydrocarbon oxidation process

Hydrocarbon oxidation chemistry

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Indeed during the progress of reaction, CO is firstly formed (faster oxidation rate) and only when there are no more hydrocarbons to be oxidized, CO is oxidized to CO_2 by OH.

It means that all the C atoms of the hydrocarbons are first transformed in aldehydes, then aldehydes form CO and only when all the hydrocarbons have been transformed to CO, then CO is oxidized in CO_2
(it is a schematic view, in the reality processes are sometimes overlapped)

Hydrocarbon oxidation chemistry

At temperatures lower than 1100K, the oxidation process modifies.

The most important difference relies in the β-scission reaction that is no more active in this temperature range.

It follows that the oxidation process is fuel-dependent. Each reaction is strongly influenced by the chemical structure of the parent hydrocarbon

Hydrocarbon oxidation chemistry

$$R\text{-}H + O_2 \rightarrow R^{\bullet} + HO_2^{\bullet}$$

$$R^{\bullet} + O_2 \rightleftharpoons RO_2^{\bullet}$$ formation of a peroxy radical

Peroxy radicals are unstable species and they decompose to $R^{\bullet}$ and O_2 as temperature increases

The equilibrium shifts towards reactants at higher temperatures

Pollutant formation (CO, VOC, SVOC)

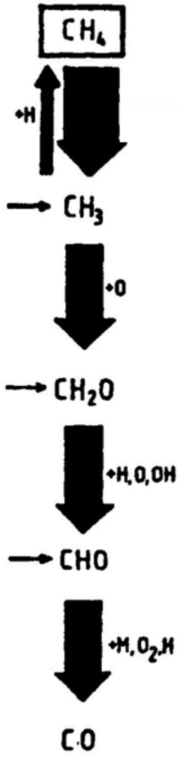
CO_2 is the product of the oxidation of hydrocarbons (complete oxidation)

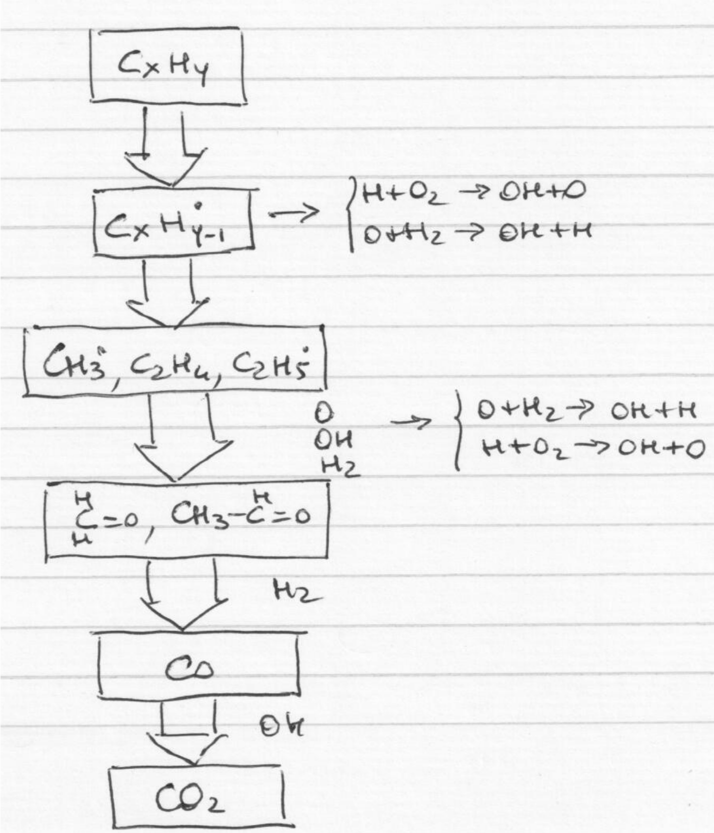
the best combustion processes form CO_2 as product at high temperature

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow x\,CO_2 + \frac{y}{2}\,H_2O$$

Let us follow the complete oxidation process for methane, the simplest hydrocarbon fuel

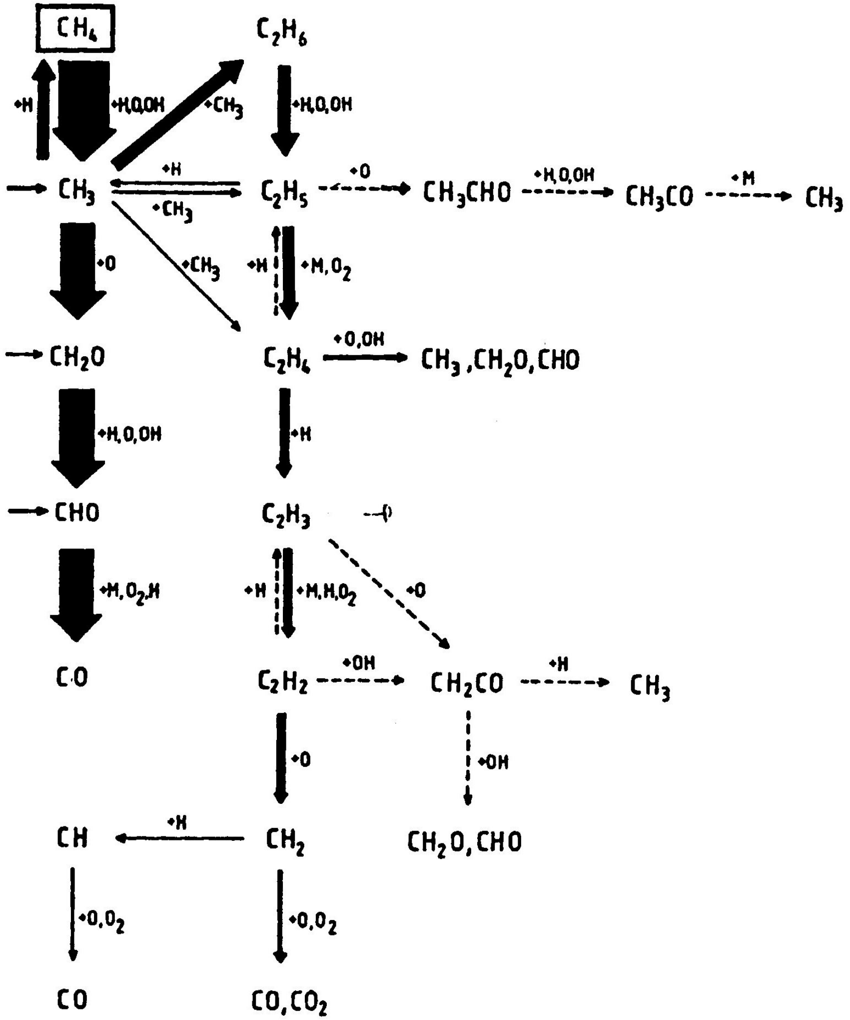
Pollutant formation (CO, VOC, SVOC)



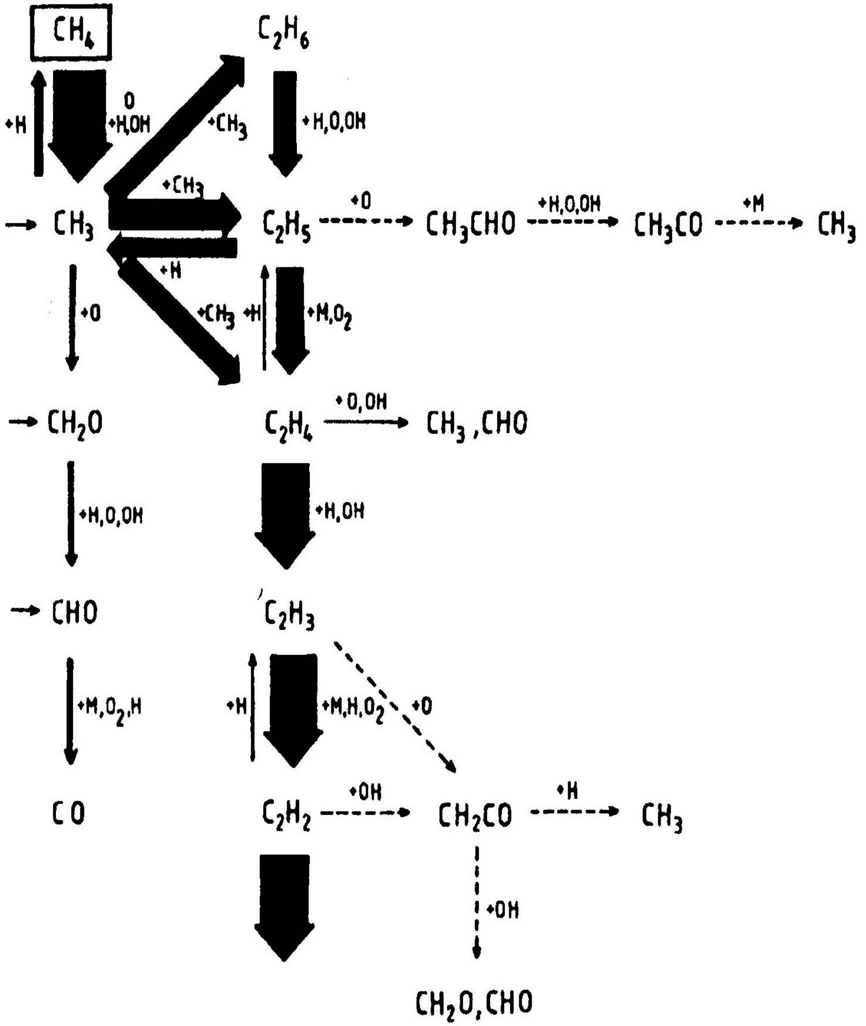


the process here skematized is valid in stoichiometric conditions, i.e. one CH_4 molecule surrounded by two O_2 molecules (premixed conditions)

Pollutant formation (CO, VOC, SVOC)



stoichiometric



fuel-rich

Pollutant formation (CO, VOC, SVOC)