ChemE 2200 – Chemical Kinetics Lecture 10

Today: Chain Reactions, cont'd.

Photochemical Reactions

"Why is $E_a < 0$ for $O_2 + O \rightarrow O_3$?"

(see Exercise 5 of Calculation Session 11 - *important.*)

Recap: (see Handout)

Chain Reactions

The Rice-Herzfeld Mechanism

for the Dehydrogenation of Ethane

$$CH_3CH_3 \xrightarrow{k_1} \cdot CH_3 + \cdot CH_3 \quad \text{initiation}$$

$$CH_3CH_3 + \cdot CH_3 \xrightarrow{k_2} \cdot CH_2CH_3 + CH_4 \quad \text{initiation}$$

$$\cdot CH_2CH_3 \xrightarrow{k_3} CH_2{=}CH_2 + \cdot H \quad \text{propagation}$$

$$CH_3CH_3 + \cdot H \xrightarrow{k_4} \cdot CH_2CH_3 + H_2 \quad \text{propagation}$$

$$\cdot CH_2CH_3 + \cdot H \xrightarrow{k_5} CH_3CH_3 \quad \text{termination}$$

Initiation: molecule → two radicals

initial radical → propagating radical

Propagation: reactant + propagating radical 1 → product + propagating radical 2

propagating radical 2 (+ reactant 2) → (by)product + propagating radical 1

Termination: two propagating radicals → molecule

2nd Prelim

TOMORROW, April 15, 7:30 – 9:30 p.m.

245 and 128 Olin Hall

Covers –

Classical Thermodynamics

Covers –

Thermodynamics Lectures 1 through 12.
Homework Assignments 5 through 8.
Calculation Sessions 5 through 8.

You may use a hand-written, double-sided reference sheet
and your annotated "Equations of Thermodynamics" lecture handout.

Bring a ruler or straightedge.

Chain Reactions: Additional Reaction Types

Initiation: molecule $\rightarrow$ two radicals

initial radical $\rightarrow$ propagating radical

Propagation: reactant + propagating radical 1 $\rightarrow$ product + propagating radical 2

propagating radical 2 (+ reactant 2) $\rightarrow$ (by)product + propagating radical 1

Termination: two propagating radicals $\rightarrow$ molecule

Retardation: propagating radical 1 + *product* $\rightarrow$ propagating radical 2 + *reactant*

Example: $\cdot CH_2CH_3 + H_2 \rightarrow \cdot H + CH_3CH_3$

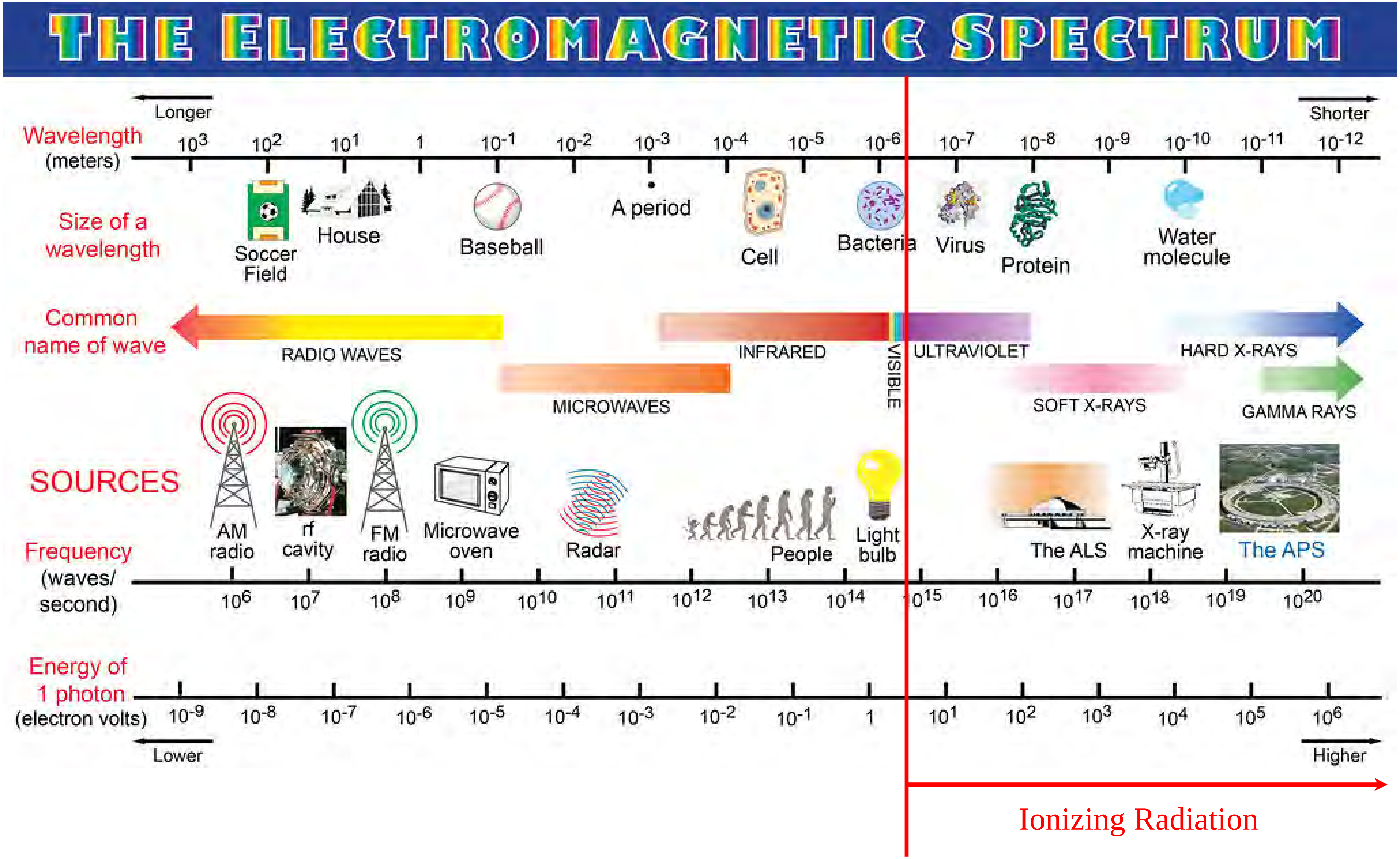
No loss of propagating radicals, but product $\rightarrow$ reactant

Reaction *retards* the forward progress of the overall reaction,
but does not terminate propagation.

Inhibition: radical + spectator $\rightarrow$ by-product   spectator is typically a solvent or an impurity.

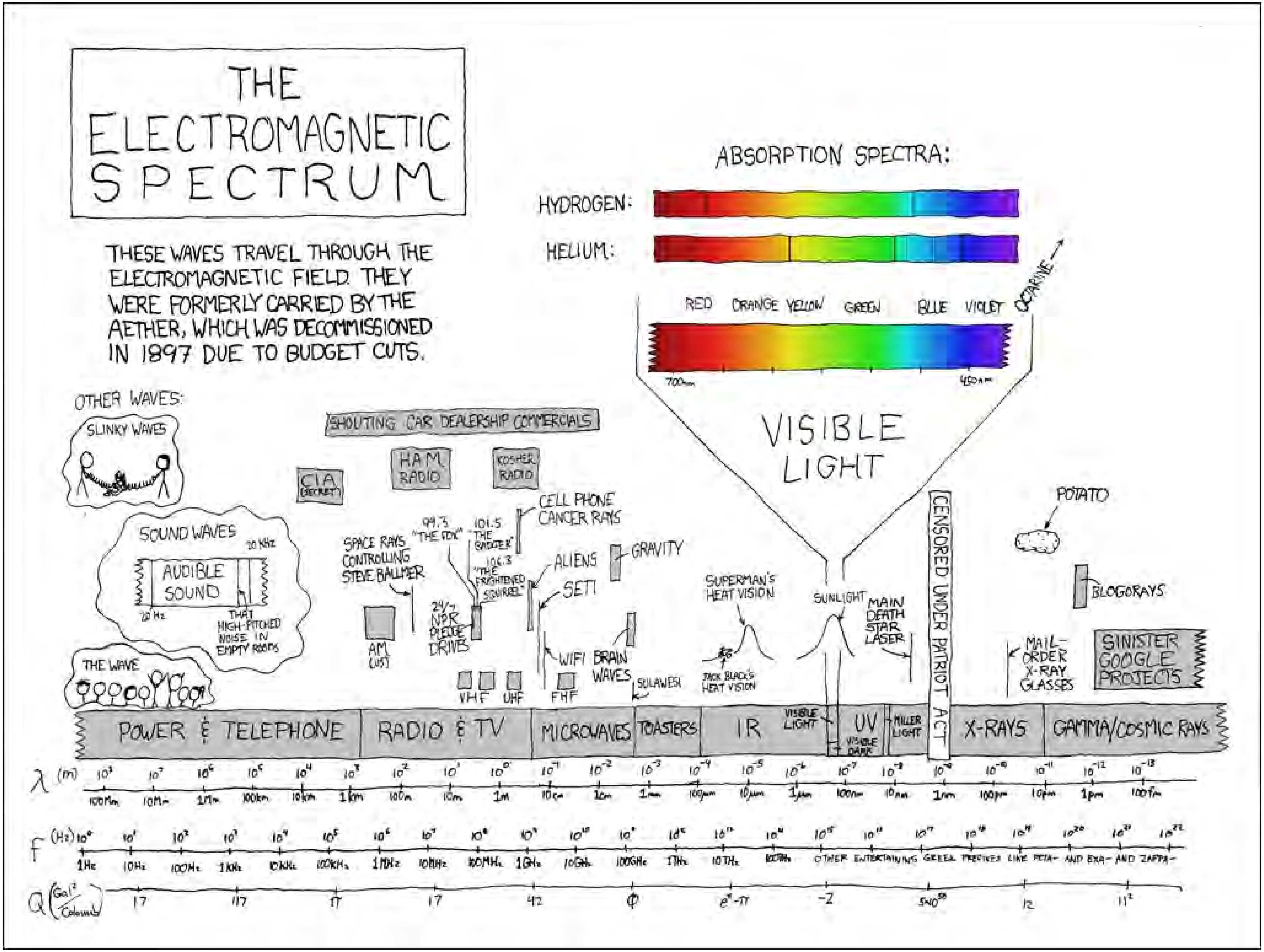
Example: $\cdot H + CO_2 \rightarrow CO + \cdot OH$ supercritical CO_2 is a solvent.

Reaction *inhibits* the forward progress of the overall reaction.
Inhibition is comparable to termination.



ALS = Advanced Light Source at Berkeley National Laboratory
APS = Advanced Photon Source at Argonne National Laboratory

Argonne National Laboratory, 2011



Randall Munroe, xkcd 273, June 6, 2007.

The Ozone Cycle: Converts UV photons into Heat

occurs in stratosphere (> 50 km) stratosphere $T \sim -3^{o}C$

cf. $T \sim -50^{o}C$ at top of troposphere

Reaction		$\Delta\overline{G}^{0}_{rxn}$	E_a
O_2 + UV photon $\rightarrow$ ·O· + ·O· (no k) $E > 5.1$ eV, $\lambda < 240$ nm; triplet O atoms	initiation	+464 kJ/mol	–
·O· + O_2 + M_{cold} $\xrightarrow{k_2}$ O_3 + M_{hot} M_{cold}: dust or ice crystal	propagation	–69	–9.6 for M = Ar
O_3 + UV photon $\rightarrow$ O_2 + ·O· (no k) $E = 3.9$–5.1 eV, $\lambda = 240$–340 nm	propagation	+69	–
·O· + O_3 $\xrightarrow{k_4}$ $2O_2$	termination	–395	+18

sum of propagation reactions:

$$M_{cold} + \text{UV photon} \rightarrow M_{hot}$$

The Ozone Cycle: Elaboration on 1st Propagation Reaction

The 1st propagation reaction is $\cdot O\cdot + O_2 + M_{cold} \xrightarrow{k_2} O_3 + M_{hot}$

Why not simply $\cdot O\cdot + O_2 \xrightarrow{k_2} O_3$?

O_3 is a fragile molecule. The activation energy for dissociation is less than $\Delta\overline{G}^0_{rxn}$

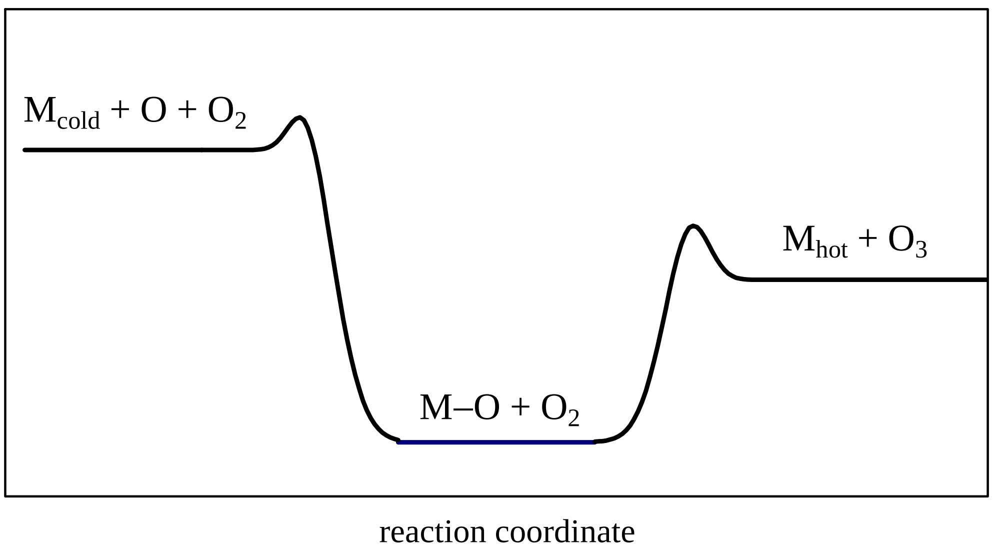
$$\cdot O\cdot + O\!-\!O \rightarrow O\text{-}O\text{-}O^* \rightarrow O\!-\!O + \cdot O\cdot$$

Note: The 1st propagation reaction is not a termolecular collision.

Actual Mechanism:

$M_{cold} + \cdot O\cdot \leftrightarrow M\cdots O$ — O atom adsorbs on M; forms a dative bond

$O_2 + M\cdots O \rightarrow O_3 + M_{hot}$ — M absorbs energy of reaction.



Energy barrier to 2nd reaction is less than ΔG_{rxn}.

Population of M–O + O_2 level decreases as temperature increases.

This leads to an *apparent* negative activation energy for $M_{cold} + O + O_2 \rightarrow M_{hot} + O_3$

See Exercise 5 of Calculation Session 11.

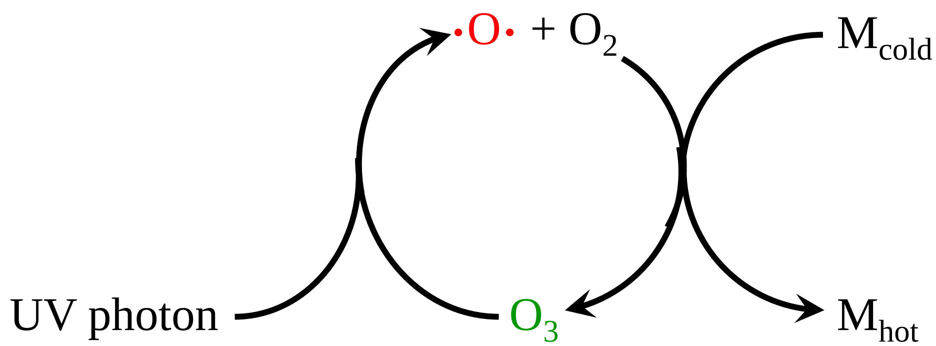
The Ozone Cycle: Propagation Cycle

propagation reactions:

$$\cdot O \cdot + O_2 + M_{cold} \xrightarrow{k_2} O_3 + M_{hot}$$

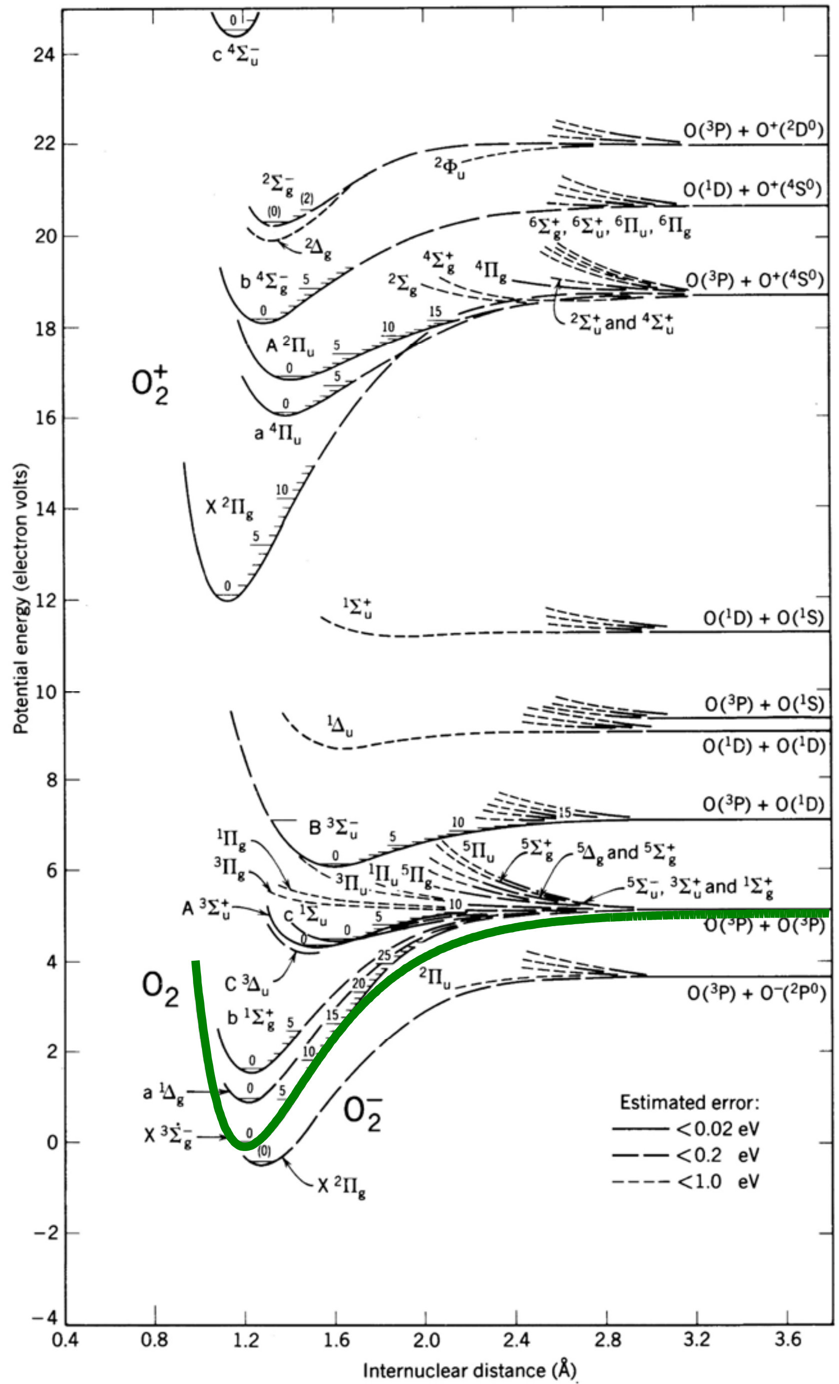
$$O_3 + \text{UV photon} \rightarrow O_2 + \cdot O \cdot$$

overall reaction: $M_{cold} + \text{UV photon} \rightarrow M_{hot}$



The Ozone Cycle: Mechanism of Initiation Reaction

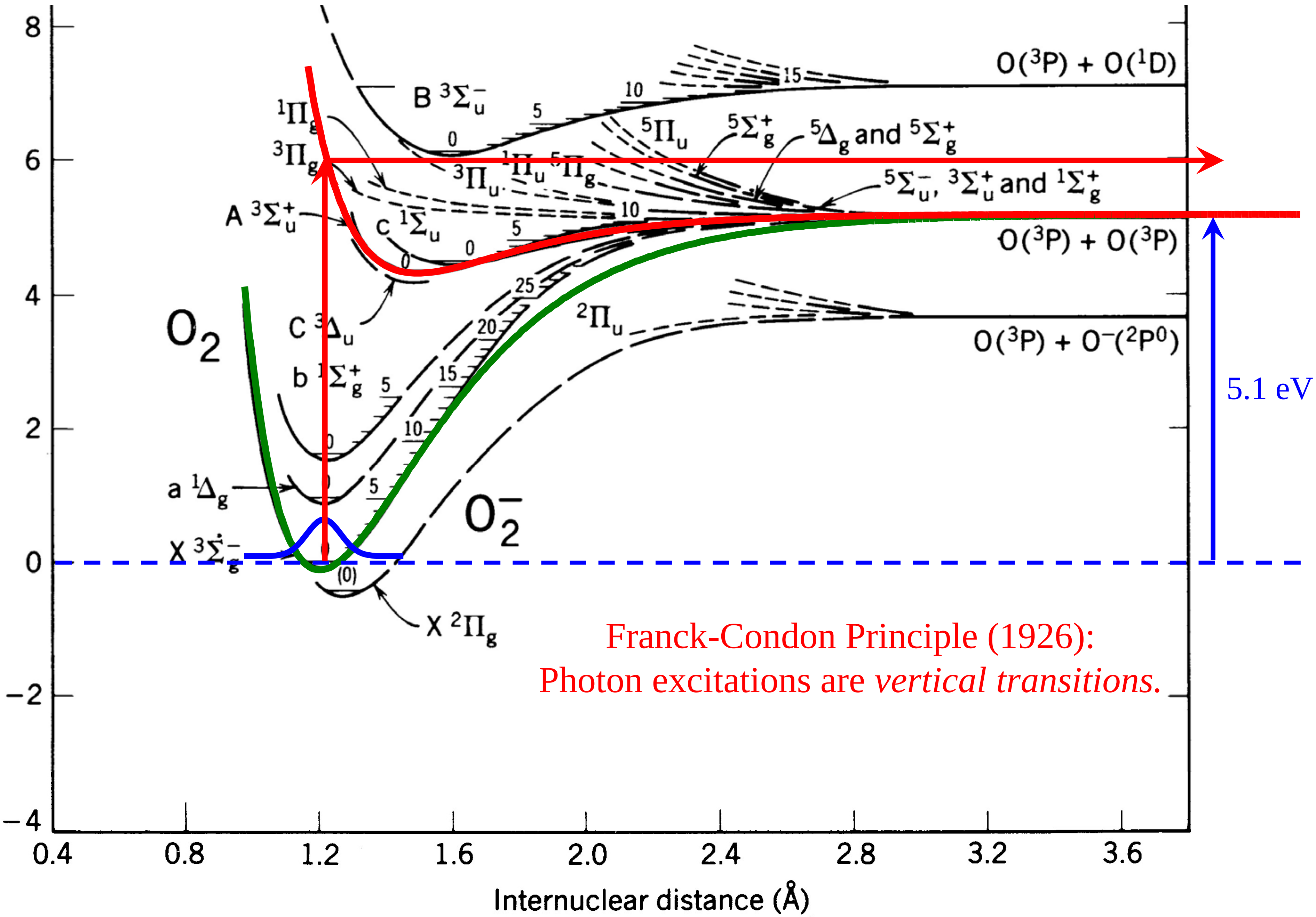
O_2 + UV photon → $\cdot O \cdot$ + $\cdot O \cdot$



F. Gilmore, RAND Corporation Memorandum R-4034-PR, June 1964.

The Ozone Cycle: Mechanism of Initiation Reaction

O_2 + UV photon $\rightarrow$ $\cdot O \cdot$ + $\cdot O \cdot$

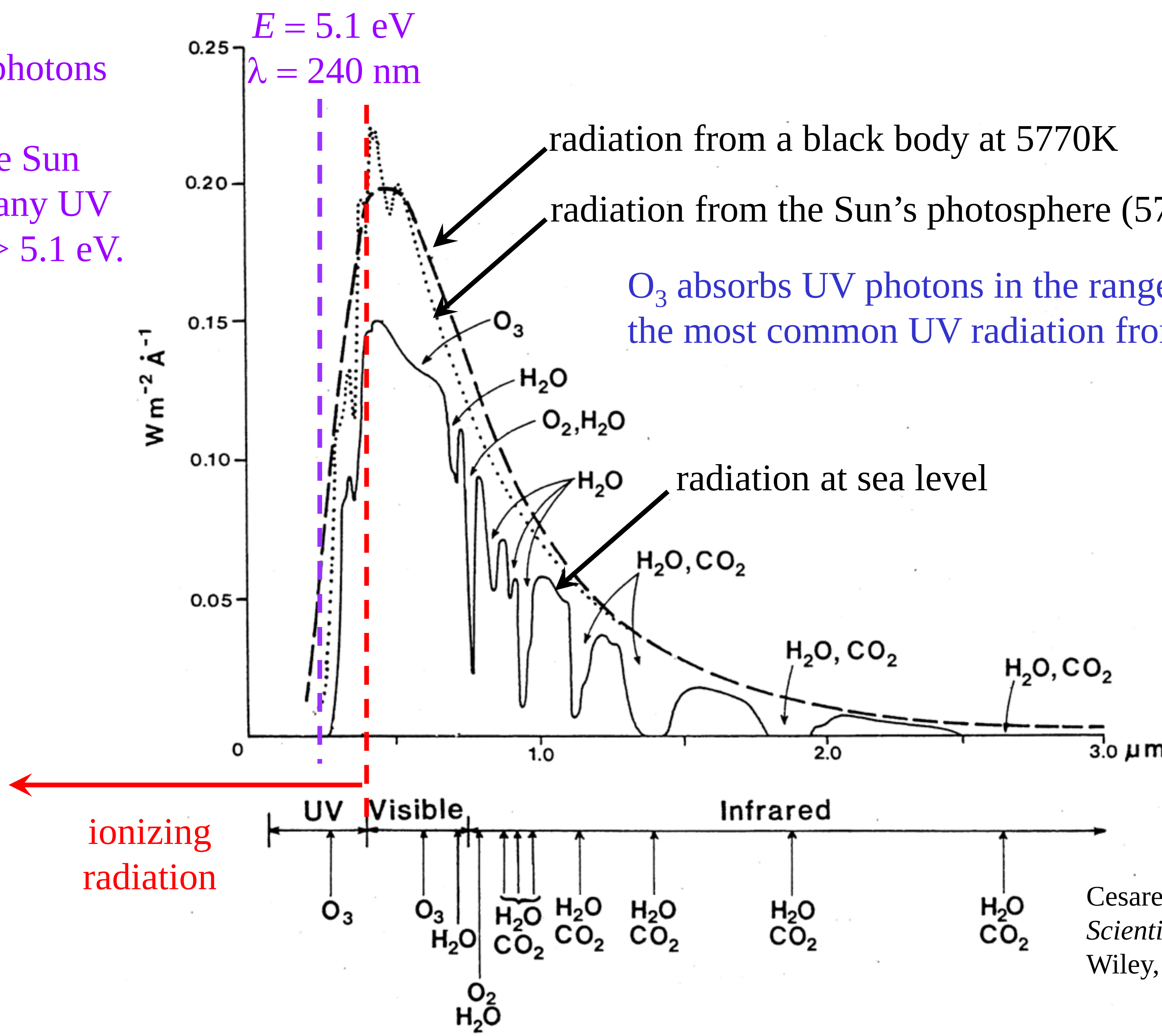


The Ozone Cycle: Why not an Oxygen Cycle?

O_2 absorbs UV photons and there is much more O_2 than O_3.

Why does O_2 not shield us from ionizing radiation? Why do we need an O_3 cycle?

O_2 absorbs UV photons with $E > 5.1$ eV, $\lambda < 240$ nm. The Sun does not emit many UV photons with $E > 5.1$ eV.



O_3 absorbs UV photons in the range 3.9 – 5.1 eV, the most common UV radiation from the Sun.

Cesare Emiliani, *The Scientific Companion*, Wiley, 1995.

Analysis of the Ozone Cycle

rxn 1

$$\text{rate of initiation reaction}: \frac{d[O_2]}{dt} = -\phi_1 I_{abs,1}$$

$$\phi \equiv \text{primary quantum yield} = \frac{\text{number of reactant molecules dissociated}}{\text{number of photons absorbed}}$$

Typically, $\phi \approx 0.01$ to 1. ϕ is obtained by experiment, like rate constants.

$$I_{abs} \equiv \text{photon absorption rate} = \frac{\text{number of photons absorbed}}{\text{L} \cdot \text{sec}}$$

$$I_{abs} = \frac{I_0}{\ell}(1 - e^{-\varepsilon \ell [O_2]})$$ Beer-Lambert Law (1852)

$$I_0 \equiv \text{incident flux of photons} = \frac{\text{number of incident photons}}{\text{m}^2 \cdot \text{sec}}$$

$\varepsilon \equiv$ molar absorption coefficient of O_2 $\quad\varepsilon$ [=] L/(mol·m)

$\ell \equiv$ path length of radiation (thickness of the stratosphere) ~ 10 km

Analysis of the Ozone Cycle, cont'd

rate of UV absorption in the ozone cycle:

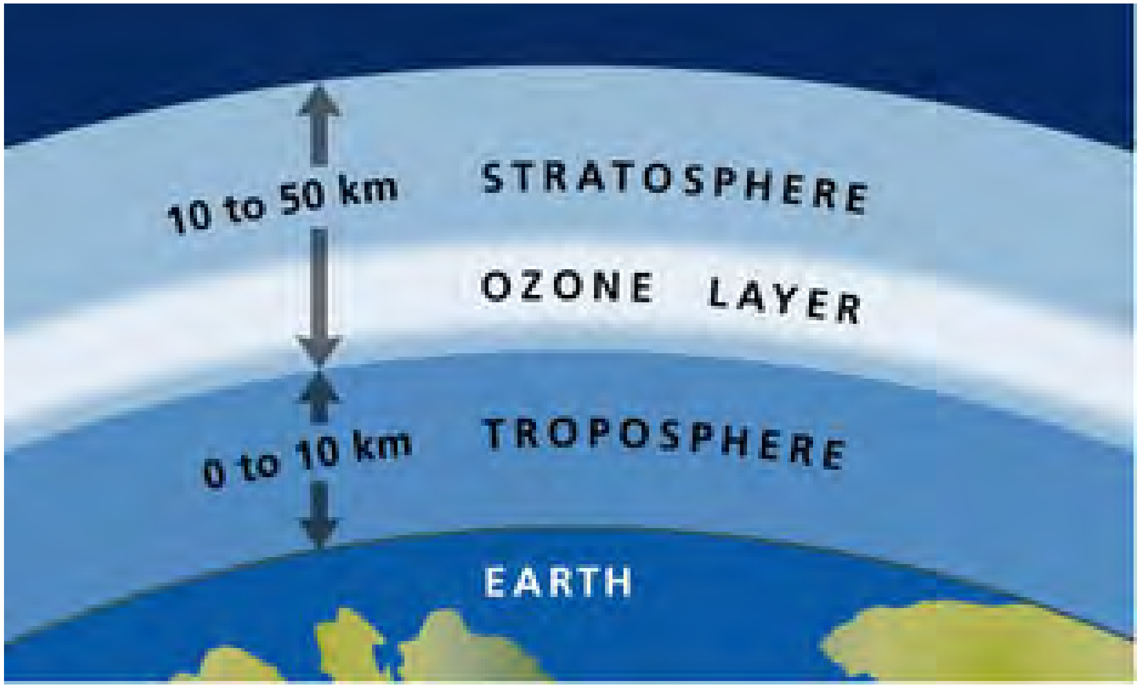
$$\frac{d[\text{UV photons}]}{dt} = -\phi_3 I_{abs,3} = -\phi_3 \frac{I_0}{\ell}(1 - e^{-\varepsilon \ell [O_3]})$$

Because the fractional absorption is small, ~ 20%

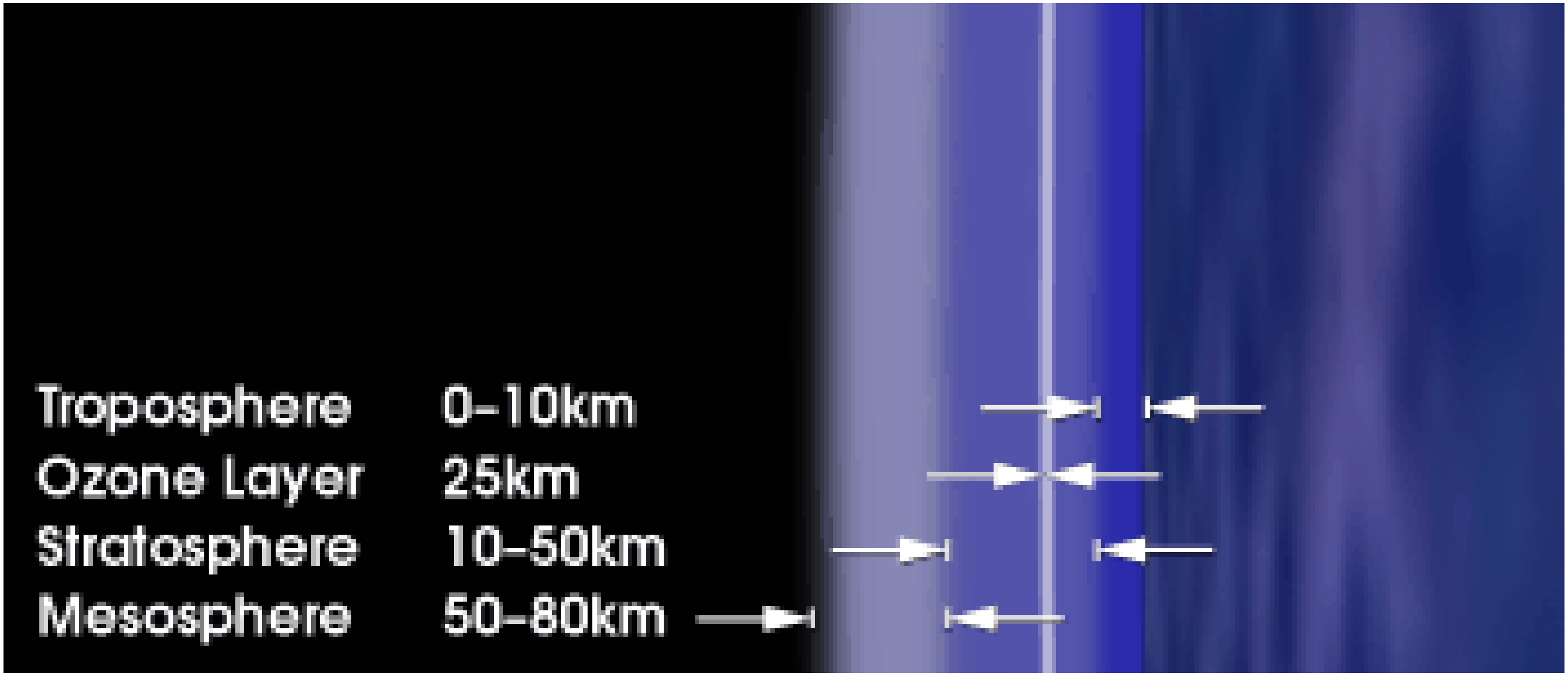
$$e^{-\varepsilon \ell [O_3]} \approx 1 - \varepsilon \ell [O_3]$$

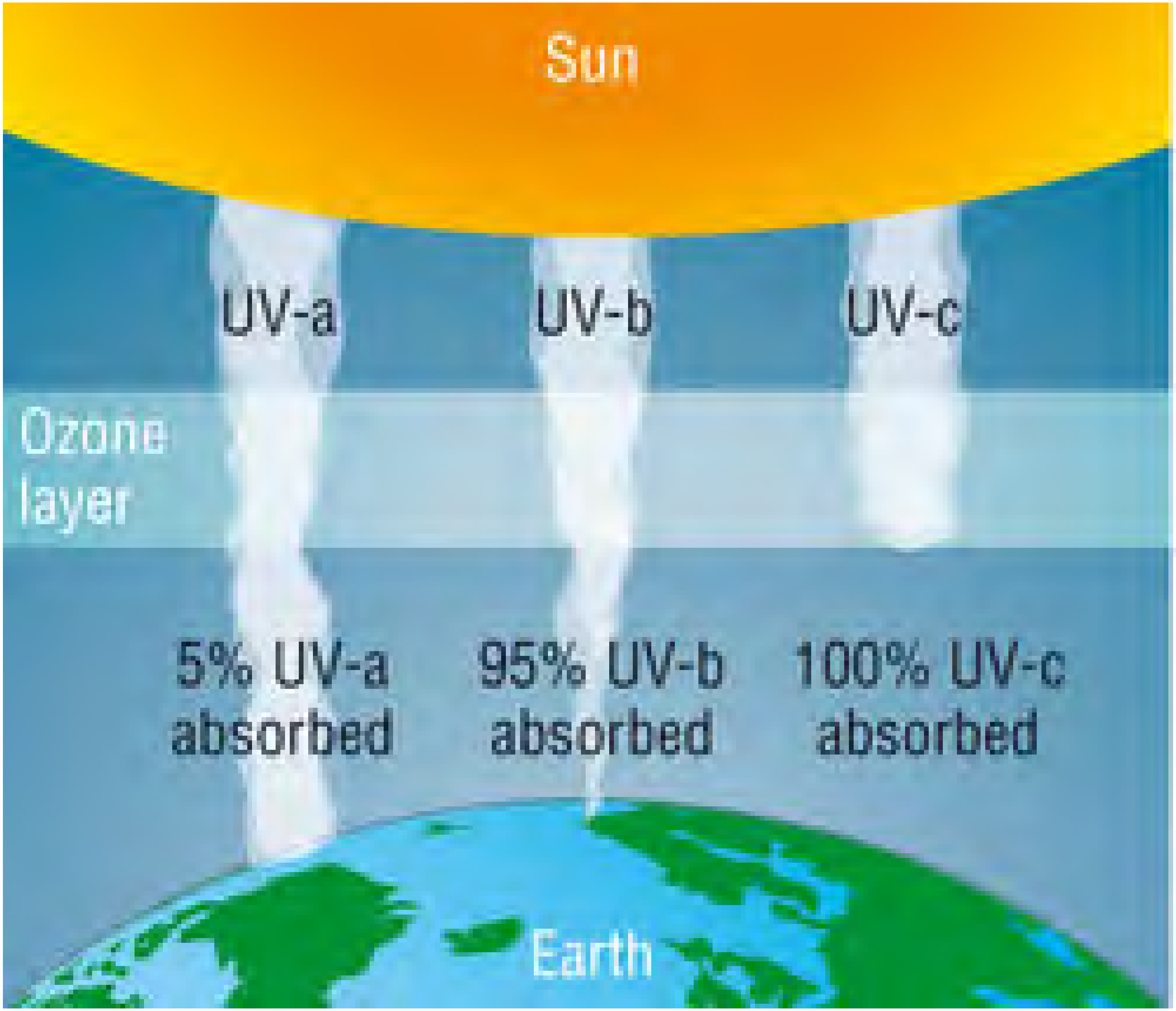
$$\frac{d[\text{UV photons}]}{dt} \approx -\phi_3 \frac{I_0}{\cancel{\ell}}(\varepsilon \cancel{\ell} [O_3]) \approx -\phi_3 I_0 \varepsilon [O_3]$$

The rate of absorption of UV photons by the ozone cycle is proportional to $[O_3]$.

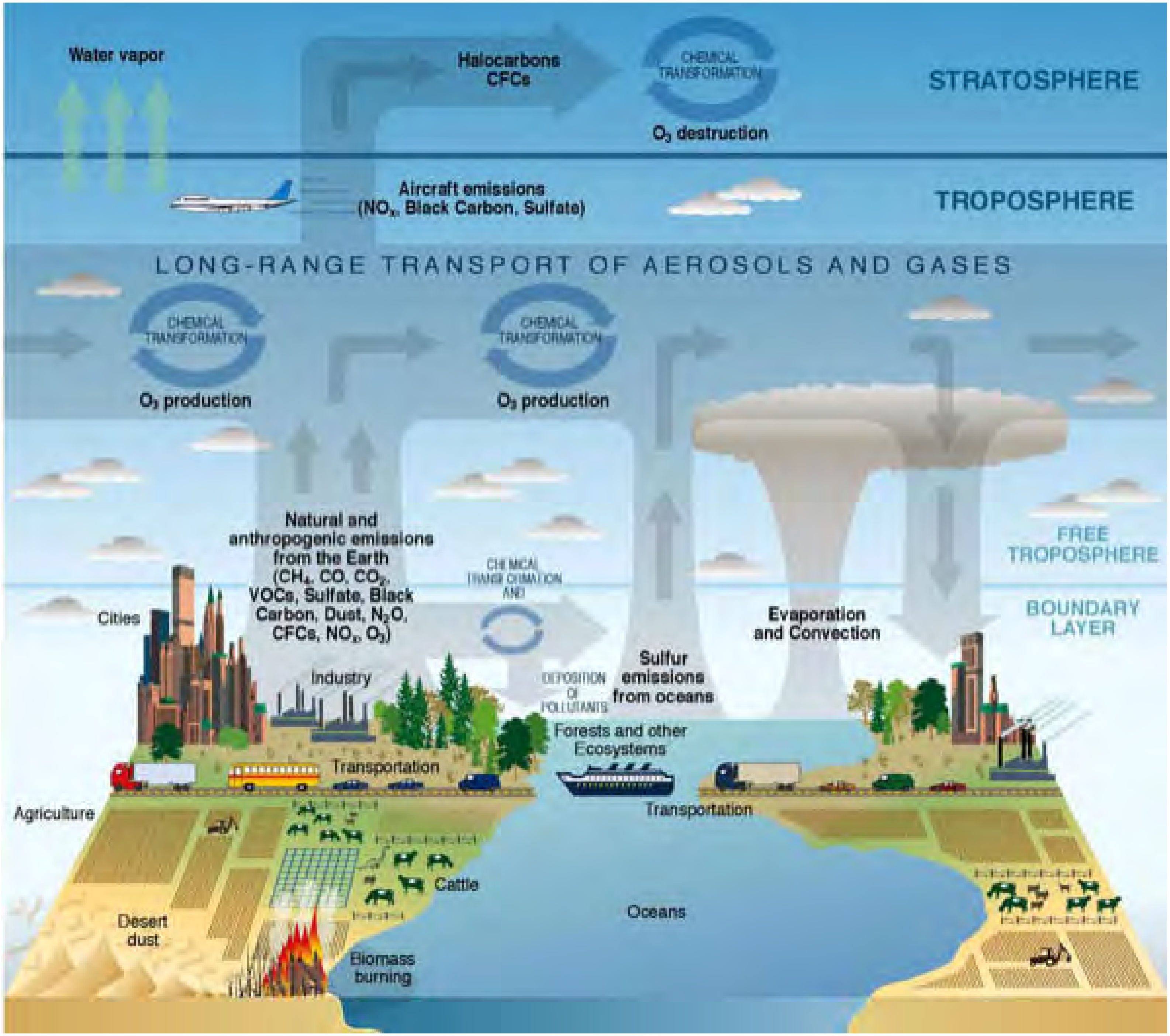


NASA's Earth Laboratory:
https://earthobservatory.nasa.gov/
features/Ozone/ozone_2.php





NASA’s Earth Laboratory:
https://earthobservatory.nasa.gov/features/Ozone/ozone_3.php



http://www.home-air-purifier-expert.com/ozone.html

The Chlorofluorocarbon (CFC) Cycle in the Stratosphere

no k

CF_2Cl_2 + UV photon → $\cdot CF_2Cl$ + $\cdot Cl$ initiation

freon 12 E = 5.1–6.8 eV

λ = 180–240 nm

inhibition of the ozone cycle:

$\cdot Cl + O_3 \xrightarrow{k_2} \cdot ClO + O_2$ propagation

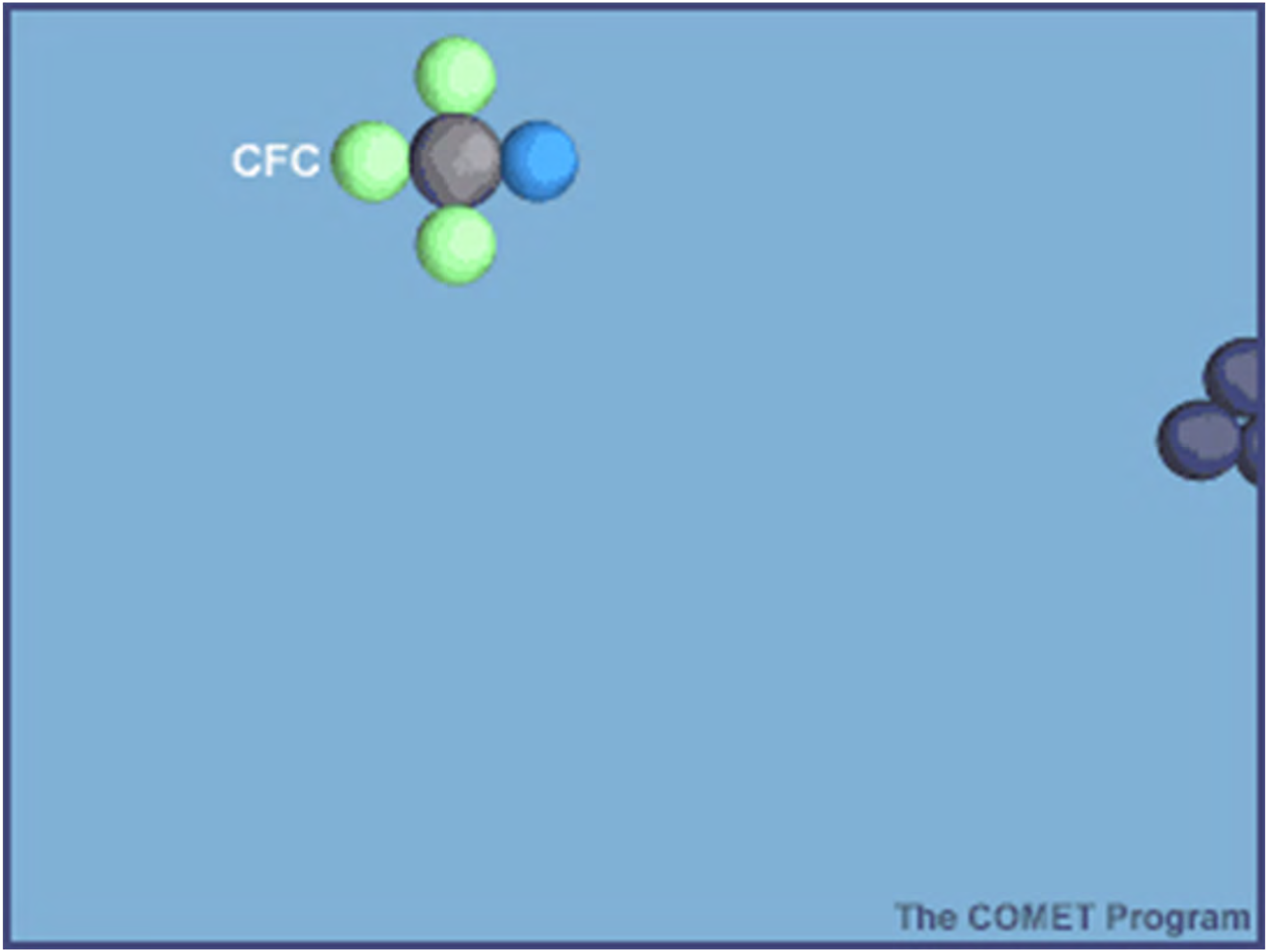
$\cdot ClO + \cdot O \cdot \xrightarrow{k_3} \cdot Cl + O_2$ propagation

$\cdot Cl + CH_4 \xrightarrow{k_4} HCl + \cdot CH_3$ inhibition (of the CFC cycle)

sum of propagation rxns: $\cdot O \cdot + O_3 \rightarrow 2O_2$

like termination – loss of a propagating radical.

The CFC cycle consumes the propagators of the ozone cycle!



http://www.ucar.edu/learn/1_6_2_25t.htm

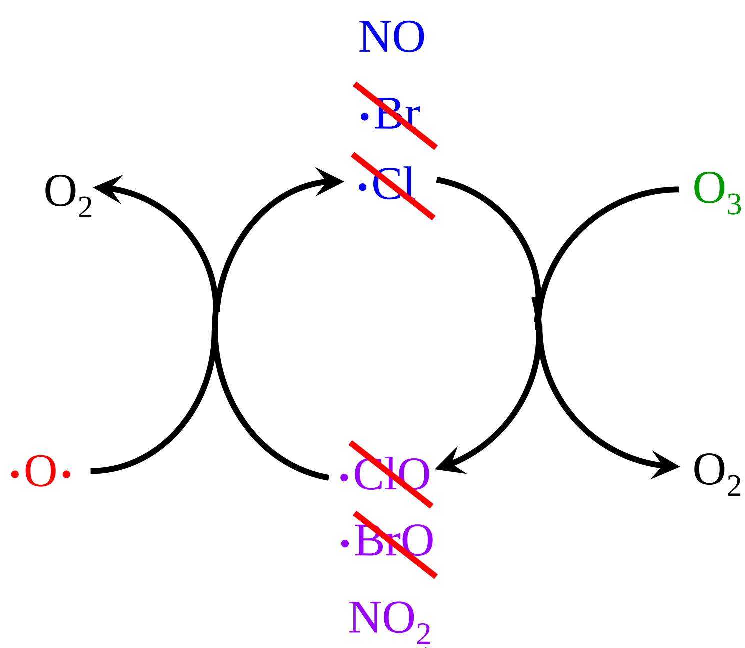
The Chlorofluorocarbon (CFC) Cycle: Propagation Cycle

propagation reactions:

$$\cdot Cl + O_3 \xrightarrow{k_2} \cdot ClO + O_2$$

$$\cdot ClO + \cdot O\cdot \xrightarrow{k_3} \cdot Cl + O_2$$

overall reaction: $\cdot O\cdot + O_3 \rightarrow 2O_2$



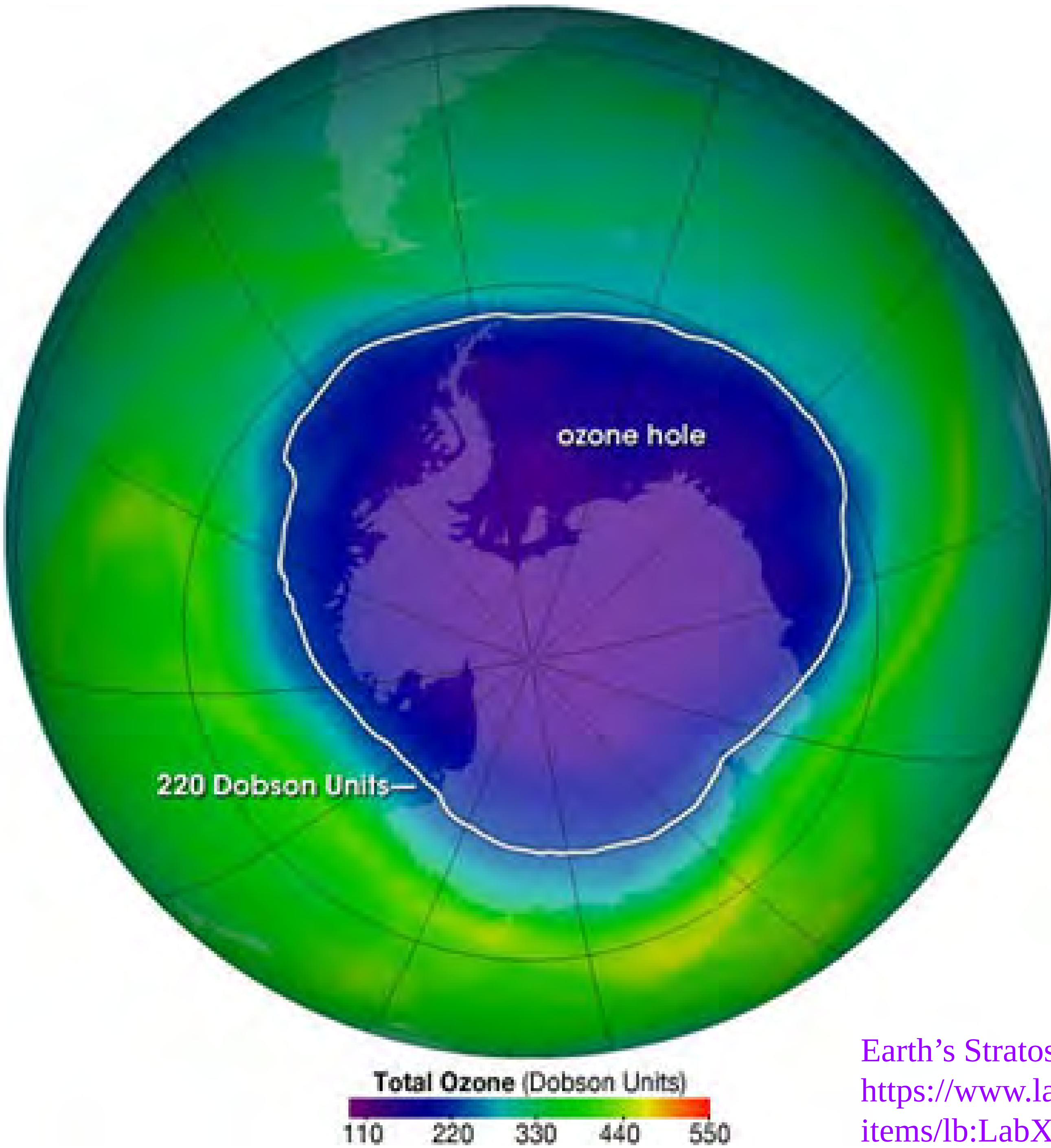
·Br in the stratosphere is ~20-60 times more efficient at destroying O_3.

Source is CH_3Br – a soil fumigant and product of burning biomass – forest fires.

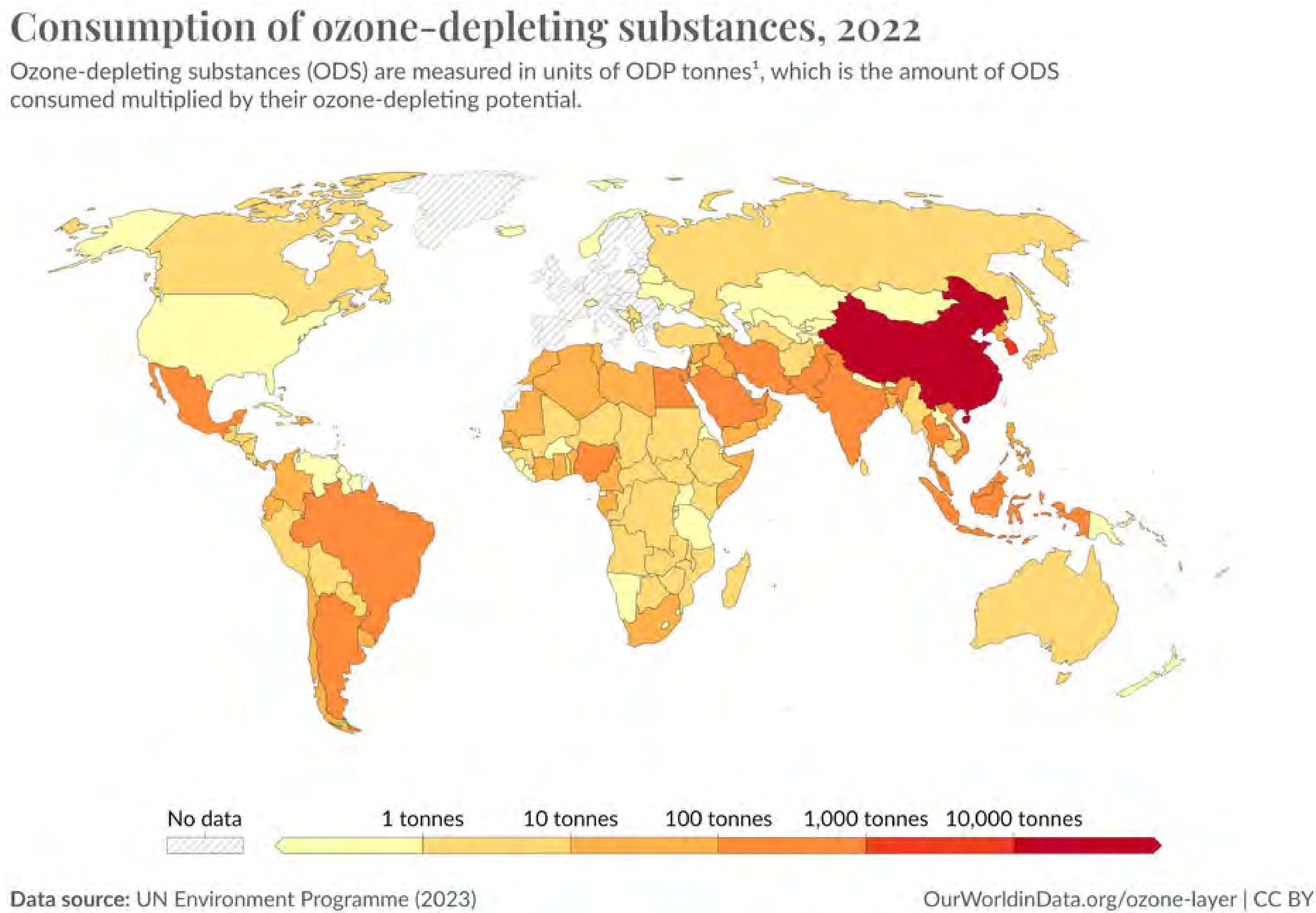
See Exercise 7 of Calculation Session 12

NO in the stratosphere comes from N_2O produced by bacteria in the soil and supersonic transports.

The Ozone Hole over Antarctica



Earth's Stratospheric Ozone Layer,
https://www.labxchange.org/library/items/lb:LabXchange:0bc70396:html:1



The Amazing World of Science with Mr. Green,
https://www.mrgscience.com/ess-subtopic-64-stratospheric-ozone.html

Analysis of the Chlorofluorocarbon (CFC) Cycle

$$\text{rate of } O_3 \text{ loss} = \frac{d[O_3]}{dt} = -k_2[\cdot Cl][O_3]$$

Need an expression for [·Cl]. Because this is a chain reaction,

$$\text{rate of initiation} = \text{rate of inhibition}$$

$$\phi_1 I_{abs,1} = k_4[\cdot Cl][CH_4]$$

$$[\cdot Cl] = \frac{\phi_1 I_{abs,1}}{k_4[CH_4]}$$

Substitute into the rate equation for O_3 loss.

$$\frac{d[O_3]}{dt} = -k_2 \frac{\phi_1 I_{abs,1}}{k_4[CH_4]}[O_3]$$

$$\frac{d[O_3]}{dt} = -\phi_1 \frac{k_2}{k_4} \frac{[O_3]}{[CH_4]} I_{abs,1}$$

$$\frac{d[O_3]}{dt} = -\Phi I_{abs,1} = -\Phi \frac{I_0}{\ell}\left(1 - e^{-\varepsilon \ell [CF_2Cl_2]}\right) \approx -\Phi I_0 \varepsilon [CF_2Cl_2]$$

$$\Phi \equiv \text{total quantum yield} = \frac{\text{number of product molecules}}{\text{number of photons absorbed}}$$

If no chain reaction, $\Phi = \phi$ or $\Phi = 2\phi$ for dissociation

If chain reaction, $\Phi = 100\phi$ to $10^6\phi$

Photochemistry

Photons are reactants.
Monochromatic photons (photons from lasers)
are expensive – about $100/mol.
Compare to hydrocarbons – $0.01/mol to $1/mol.

But the cost of monochromatic photons
can be justified by improved selectivity:
reduced consumption of reactants and
reduced costs of separating product(s) from by-product(s).