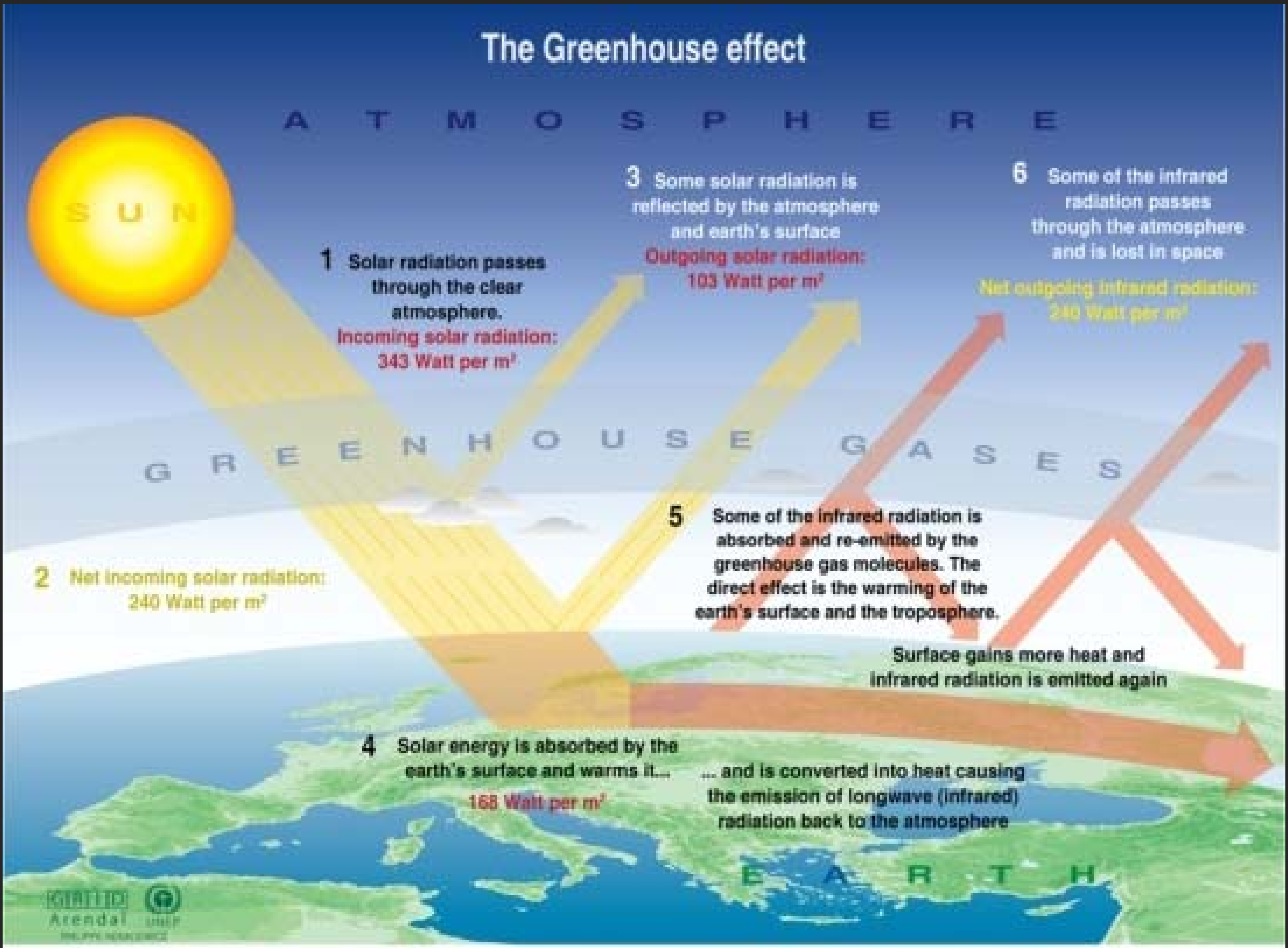
Reading: Boeker & Grondelle, Chaps 1 – 3



Sources: Okanagan university college in Canada, Department of geography, University of Oxford, school of geography; United States Environmental Protection Agency (EPA), Washington; Climate change 1995, The science of climate change, contribution of working group 1 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge university press, 1996.

20. Molecular physics and Earth's atmosphere

E3/1

A molecule is a bound state of atoms.

- Ionic bond (Na+) (Cl−) ⟷ electric force

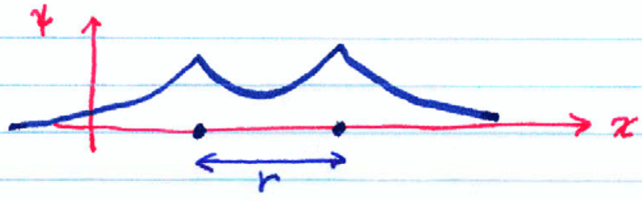
is not relevant to molecules in the atmosphere.

- Covalent bond

e.g., H_2, N_2, O_2, etc.

Molecular Orbitals /quantum theory in chemistry/

(1)

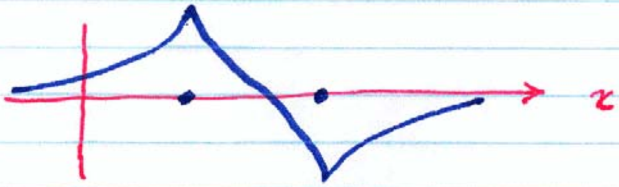


BONDING ORBITAL

$\psi_{n\ell m}(x-r_1) + \psi_{n\ell m}(x-r_2)$

The electron is shared by the two nuclei.

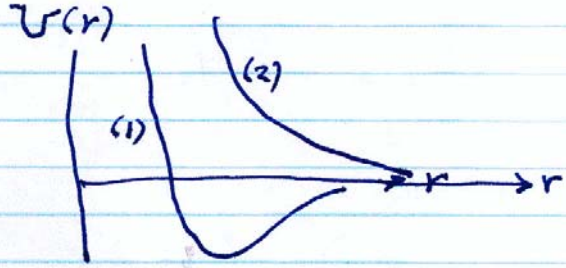
(2)

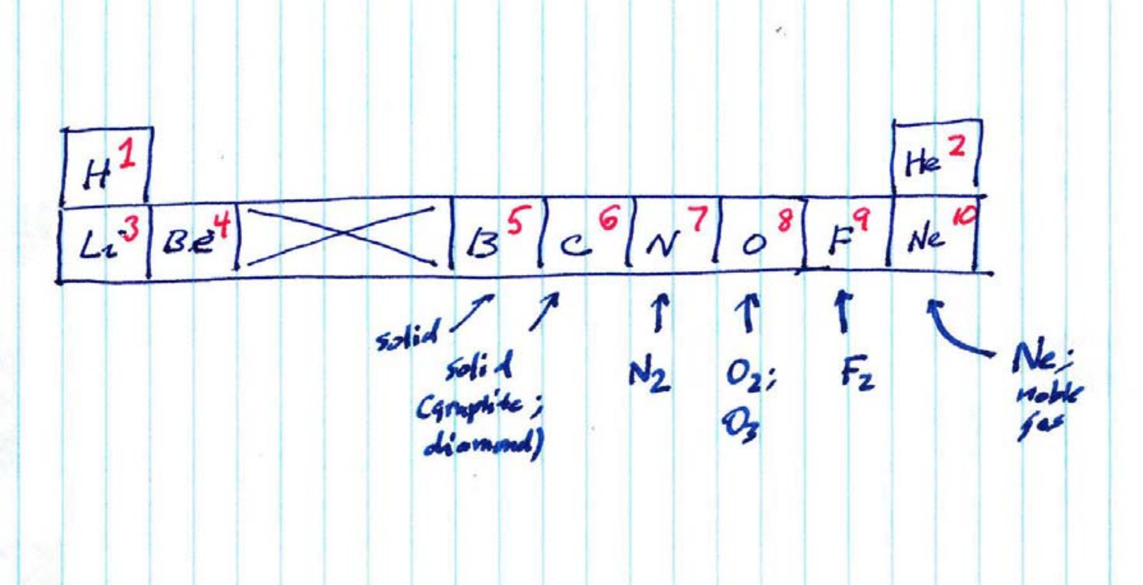


ANTI-BONDING ORBITAL

$\psi_{n\ell m}(x-r_1) - \psi_{n\ell m}(x-r_2)$

The electron density is on the outside.




H 1
He 2
Li 3
Be 4
B 5
C 6
N 7
O 8
F 9
Ne 10
solid
solid (graphite; diamond)
N2
O2; O3
F2
Ne; noble gas

Examples

- Hydrogen $H = (1s)^1$ atomic configuration

  ↳ H has 1 electron available for bonding; i.e. to go into the bonding orbital.

H_2 2 electrons are in the bonding orbital. They must have spin ↑ and spin ↓ by the Pauli exclusion principle; i.e., $S = 0$.

H—H   Binding energy = 4.5 eV
Bond length = 0.074 nm $0.1 \text{ nm} = 1 \text{ Å}$

- Neon $Ne = \underbrace{(1s)^2(2s)^2(2p)^6}$ atomic configuration

  all electrons are PAIRED (↑ and ↓); not available for bonding orbital unless excited to higher energy level ⇒ unbound

Ne is a "noble gas."

- Fluorine $F = (1s)^2\,(2s)^2\,(2p)^5$ atomic configuration

$$F = \underbrace{(1s)^2\,(2s)^2\,(2p_x)^2(2p_y)^2}_{\text{paired electrons } (\uparrow \text{ and } \downarrow)}\underset{\substack{\uparrow \\ \text{one electron} \\ \text{is available} \\ \text{for bonding}}}{(2p_z)^1}$$

F_2 2 electrons are in the bonding orbital; ↑↓

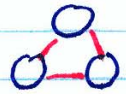
F—F   Binding energy = 1.6 eV
Bond length = 0.142 nm

- Oxygen $O = (1s)^2(2p)^2(2p)^4$

$$= \underbrace{(1s)^2(2s)^2(2p_x)^2}_{\text{Paired electrons}}\underbrace{(2p_y)^1(2p_z)^1}_{\text{2 electrons are available for bonding}}$$

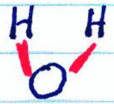
O_2 $O{=}O$ 4 electrons in 2 Bonding orbitals; (↑↓)
(↑↓)

O_3



6 electrons in 3 bonding orbitals

H_2O



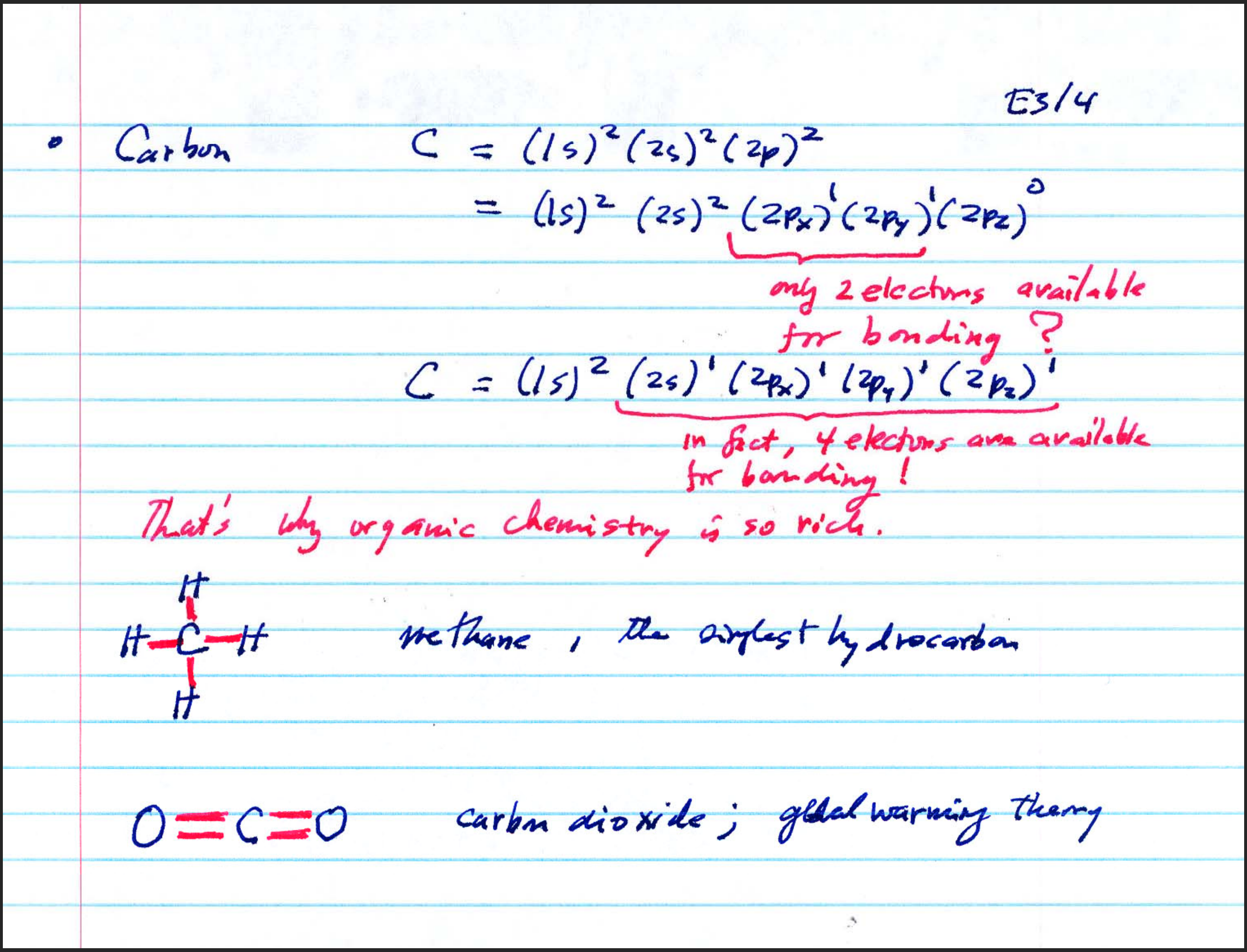
- Nitrogen $N = (1s)^2(2s)^2(2p)^3$

$$= \underbrace{(1s)^2(2s)^2}_{\text{paired}}\underbrace{(2p_x)^1(2p_y)^1(2p_z)^1}_{\text{3 electrons available for bonding}}$$

N_2 $N \equiv N$ 6 electrons in 3 bonding orbitals

N_2 is very strongly bound;
∴ chemically inactive compared to O_2

	B [ev]	R_0 [nm]
H_2	4.5	0.074
F_2	1.6	0.142
O_2	5.1	0.12
N_2	9.8	0.11

 E3/4

- Carbon $C = (1s)^2(2s)^2(2p)^2$

$$= (1s)^2(2s)^2\underbrace{(2p_x)^1(2p_y)^1}_{\text{only 2 electrons available for bonding ?}}(2p_z)^0$$

$$C = (1s)^2\underbrace{(2s)^1(2p_x)^1(2p_y)^1(2p_z)^1}_{\text{in fact, 4 electrons are available for bonding!}}$$

That's why organic chemistry is so rich.

$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

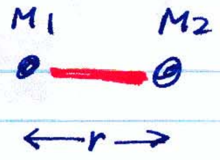
methane, the simplest hydrocarbon

$O=C=O$ carbon dioxide; global warming theory

Burning hydrocarbons releases CO_2 into the atmosphere: E.g.,

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

Molecular Spectroscopy



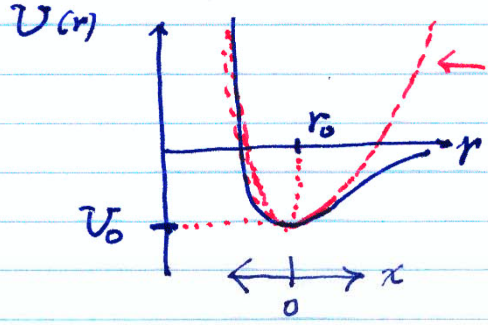
$$E = E_{\substack{\text{electrons}\\ \text{states}}} + E_{\text{vibration}} + E_{\text{rotation}}$$

transition energies ~ 1 eV or higher (visible light photons)

transition energies ~ 0.1 eV (infrared photon energies)

transition energies ~ 0.001 eV (microwave photon energies)

Back of the envelope calculation for molecular vibrations



← harmonic oscillator approximation

$$\approx U_0 + \tfrac{1}{2} k x^2$$

$$k = \left.\frac{d^2 U}{dr^2}\right|_{r_0}$$

Order of magnitude $k \sim \dfrac{1\,eV}{(0{,}1\,A)^2} = 10^4 \dfrac{eV}{nm^2}$

E_n (vibrational) $= -U_0 + \hbar\omega\left(n + \tfrac{1}{2}\right)$ where $\omega = \sqrt{\dfrac{k}{\mu}}$

reduced mass

$$\mu = \frac{M_1 M_2}{M_1 + M_2}$$

Transition energies

$E_{n+1} - E_n = \hbar\omega$

$E_{n+2} - E_n = 2\hbar\omega$ more rarely

For example, consider O_2.

$$\mu = 8\ u = 8 \times 931.5\ \text{MeV}/c^2$$

$$\Delta E = \hbar\omega = \hbar c\sqrt{\frac{k}{\mu c^2}} = 200\ \text{eV-nm}\sqrt{\frac{10^4\ \text{eV}/\text{nm}^2}{8 \times 931.5 \times 10^6\ \text{eV}}}$$

$$\Delta E = 0.23\ \text{eV} \qquad \boxed{\begin{array}{l}\text{transition energies}\\ \sim 0.1\ \text{eV}\end{array}}$$

The wavelength of a photon emitted or absorbed in this transition is

$$\lambda = \frac{c}{\nu} = \frac{hc}{E_\gamma} = \frac{2\pi\hbar c}{\Delta E} = \frac{2\pi \times 200\ \text{eV-nm}}{0.2\ \text{eV}}$$

$$\lambda = 6 \times 10^3\ \text{nm} = 6000\ \text{nm} \rightsquigarrow \boxed{6\ \text{microns}}$$

$$\boxed{\text{These transitions are in the infrared.}}$$

- Transitions between vibrational states are in the infrared part of the e.m. spectrum.

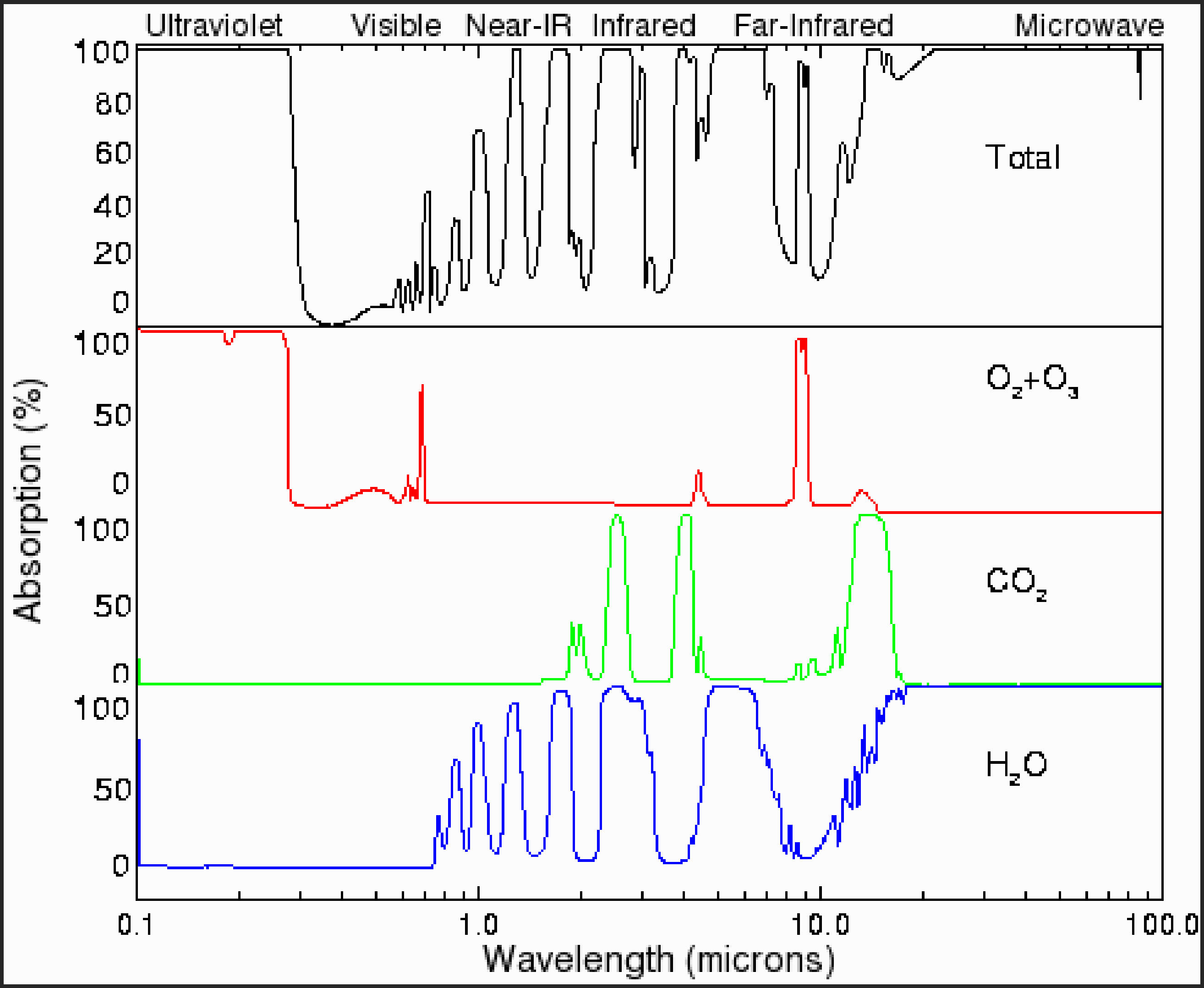
$$\Delta E \sim 0.1\ \text{eV} \quad \text{and} \quad \lambda \sim 10^3\ \text{nm} - 10^4\ \text{nm}$$

(1 – 10 microns)

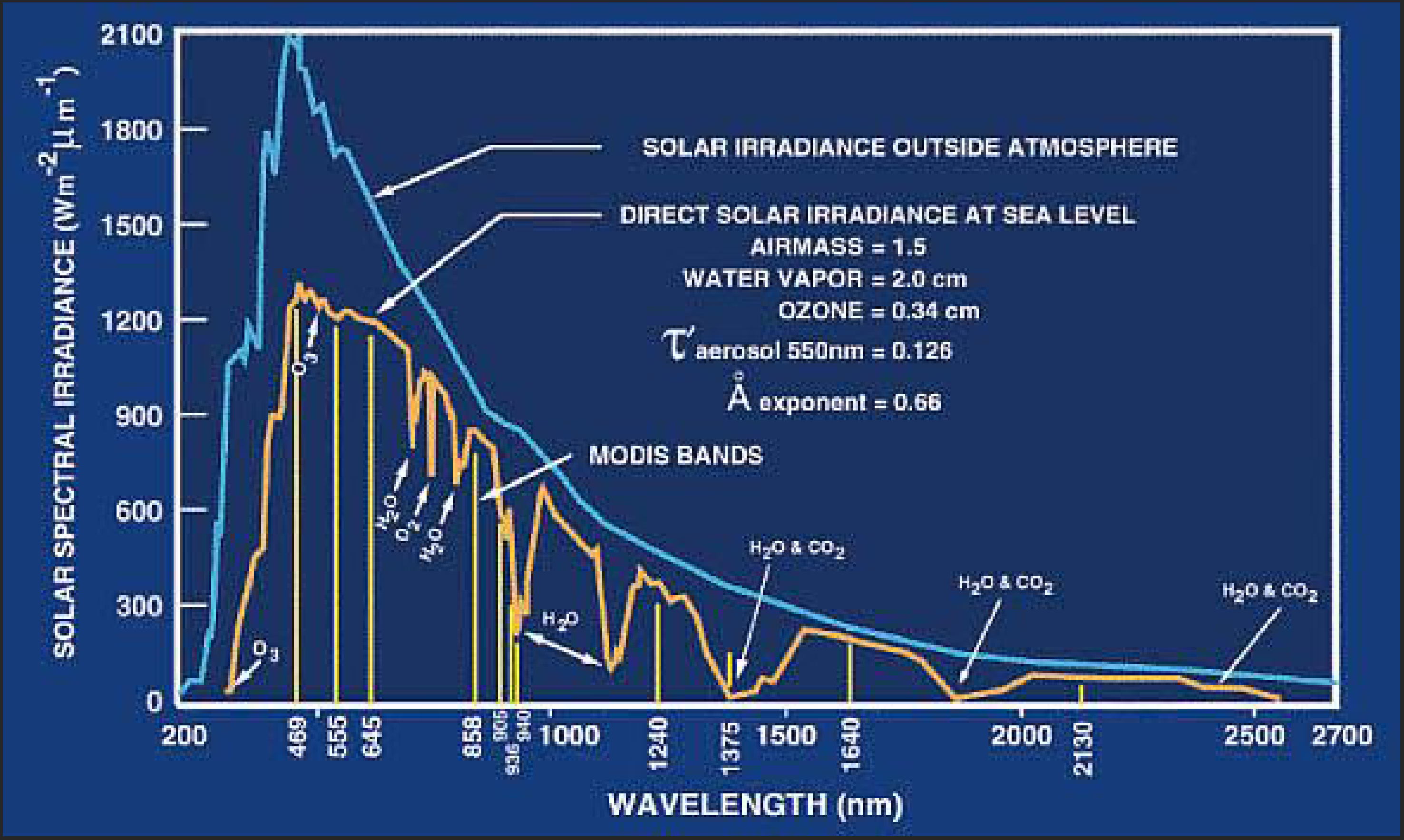
- Transitions between rotational states are in the microwave part of the e.m. spectrum

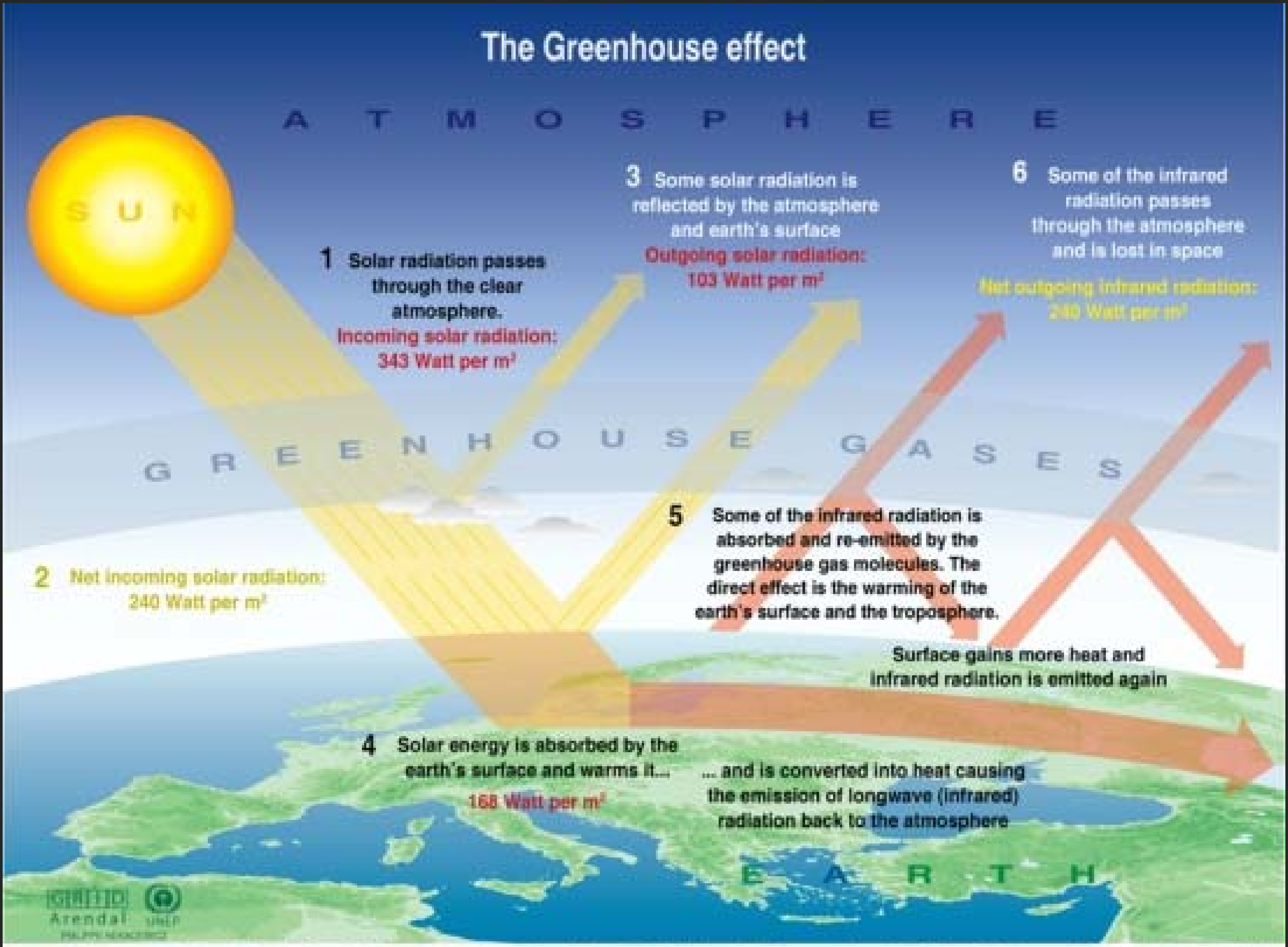
$$\Delta E \sim 0.001\ \text{eV} \quad \text{and} \quad \lambda \sim 0.1 \text{ to } 1\ \text{mm}$$

See also Boeker&Grondelle, Figure 2.3



See also Boeker&Grondelle, Figure 2.2





Sources: Okanagan university college in Canada, Department of geography, University of Oxford, school of geography; United States Environmental Protection Agency (EPA), Washington; Climate change 1995, The science of climate change, contribution of working group 1 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge university press, 1996.