

Energy Generation, Storage, and Transformation

Roderick M. Macrae



1. Chemical Fuels

ENERGY

“work within” - the capacity to do work

$$w = F d$$

kinetic (related to movement)

$$E_k = \frac{1}{2} m v^2$$

e.g. Mechanical energy (macroscopic object in motion)

Thermal energy (random microscopic agitation of atoms)

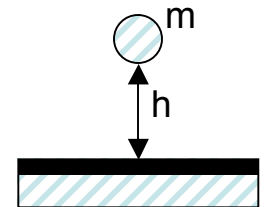
Electrical energy (motion of electrons through wire)

potential (related to **position** w.r.t. some external force)

e.g. Gravitational energy

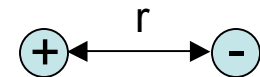
$$E = mgh$$

$$g = 9.8 \text{ m s}^{-2}$$



Electrostatic energy

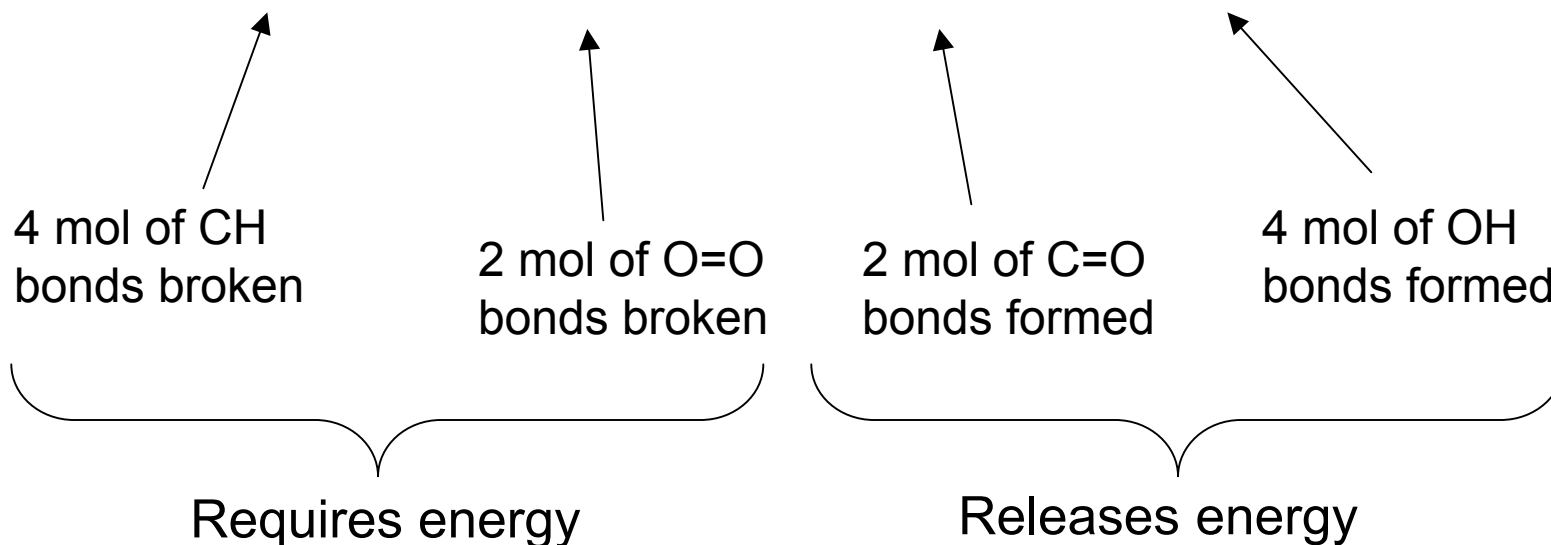
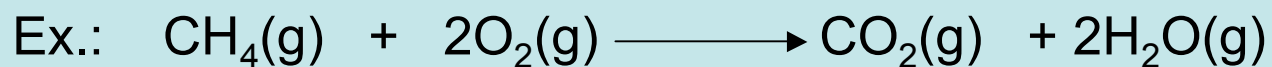
$$V \propto \frac{q_1 q_2}{r}$$



Coulomb's law

Thermochemistry

(combustion of methane)



In this case, (heat) energy released > (heat) energy absorbed - combustion of fuels is a useful heat source.

In general, reactions either absorb or release heat energy overall.

Energy changes come from redistribution of bonding pattern, changes of state, etc.

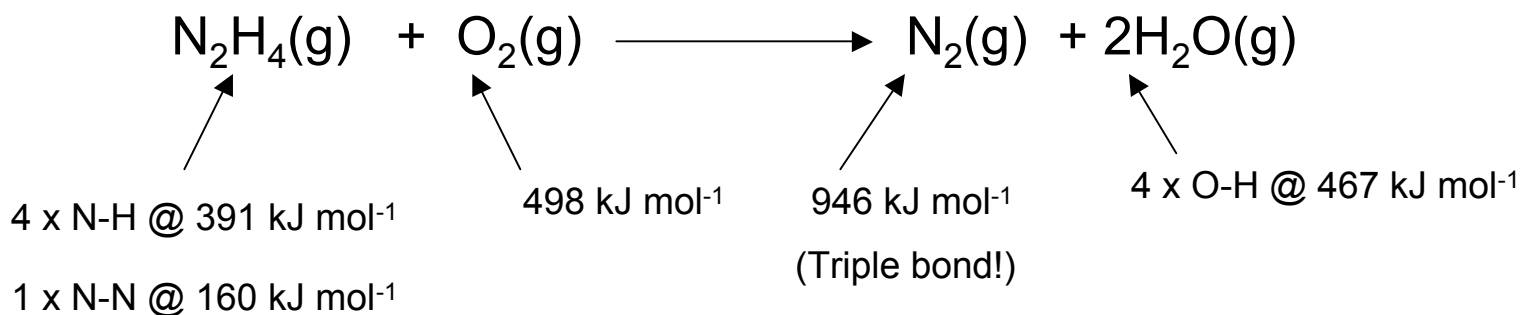
Chemical Fuels

React exothermically with O₂ from the air.
(Should be) available fairly readily and cheaply.

Naturally-occurring finite resources. (e.g. Fossil fuels)

“Renewable” fuel sources e.g. biodiesel, ethanol from corn

Example: Hydrazine (rocket fuel)



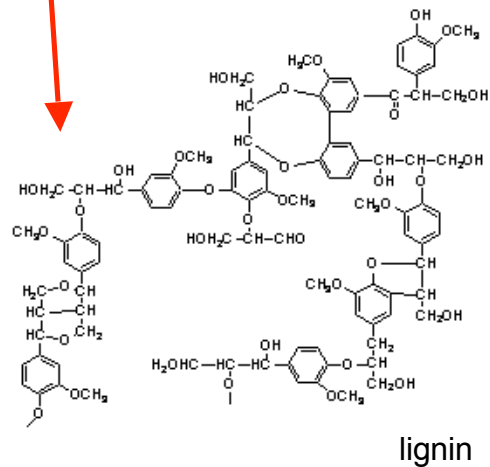
$$\Delta H = 4 \times 391 + 160 + 498 - 946 - 4 \times 467 = \underline{\underline{-592 \text{ kJ mol}^{-1}}}$$

Fossil fuels

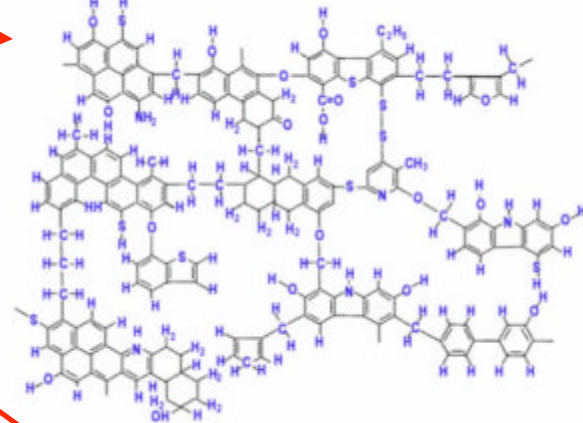
Residues of ancient plant and animal matter.

Mainly mixtures of hydrocarbons – e.g. oil, natural gas.

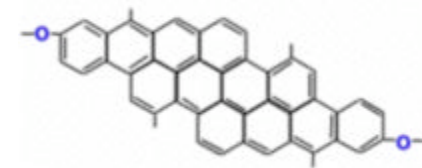
Coal consists mostly of complex C-containing molecules, with some sulfur (yields SO_2 on combustion).



Bituminous Coal Representation

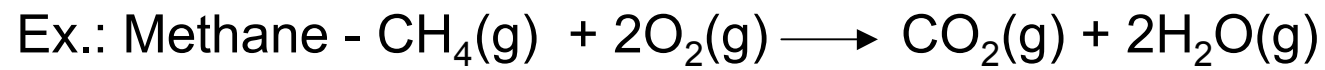


Representation of anthracite

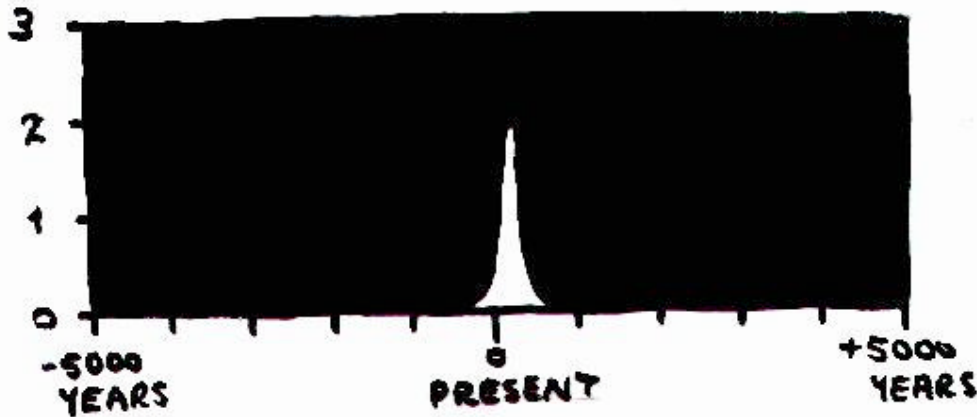


Similar combustion reactions:

- Complete → CO₂ + H₂O only
- Incomplete → CO, other products



Fossil fuel supply is limited.



Matter deposited over ca. 10^9 years used over ca. 10^2 years.

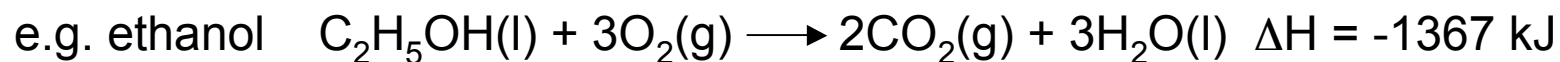
Alternative future **combustion-based** energy sources



Liquefaction difficult (b.p. 20.8 K) - H storage is an issue. (Ideas: In Td holes of ccp Ti as TiH, in nanotubes, MOFs, etc. Target: reversible, 6 wt.% H₂.)

Other problems: H₂ *production* **requires** energy (electrolysis of water, etc.)

“Biomass” (e.g. carbohydrates (C_x(H₂O)_y), ethanol, etc.)

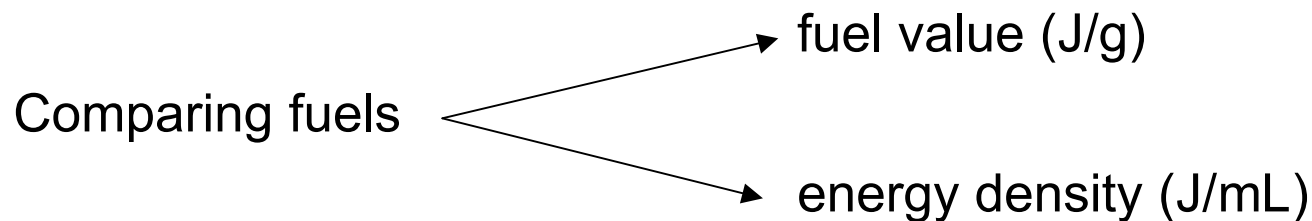


Disadvantages:

ΔH less than gasoline (EtOH already partly oxidized)

By-product is acetaldehyde (component of urban smog)

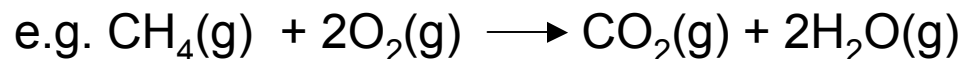
To meet 10% of current demand would need to convert 25% of farmland to fuel production.



| | | | |
|-------------------------------------|------------|------------|--------------------------|
| e.g. CH ₄ (g) | 0.656 g/L | 50.0 kJ/g | 32.8 kJ/L |
| C ₂ H ₅ OH(g) | 0.785 g/mL | 26.8 kJ/g | 2.1x10 ⁴ kJ/L |
| H ₂ (g) | 0.082 g/L | 120.0 kJ/g | 9.84 kJ/L |

Example calculation:

Balanced combustion (H₂ → H₂O, C → CO₂, N → N₂)



$$\Delta H^\circ = (-393.0 \text{ kJ} + 2 \times -241.818 \text{ kJ}) - (-74.81 \text{ kJ}) = -802.34 \text{ kJ}$$

$$\text{F.V.} = 802.34 \text{ kJ/mol} \times 1 \text{ mol}/16.0428 \text{ g} = 50.013 \text{ kJ/g}$$

$$\text{E.D.} = 50.013 \text{ kJ/g} \times 0.656 \text{ g/L} = 32.8 \text{ kJ/L}$$

Non-fossil-fuel energy sources based on combustion may be “renewable” but are not “sustainable”.

Why not?

CO₂ production, climate change and the Greenhouse Effect.

2. The Greenhouse Effect

Molecular Vibrations and the Greenhouse Effect

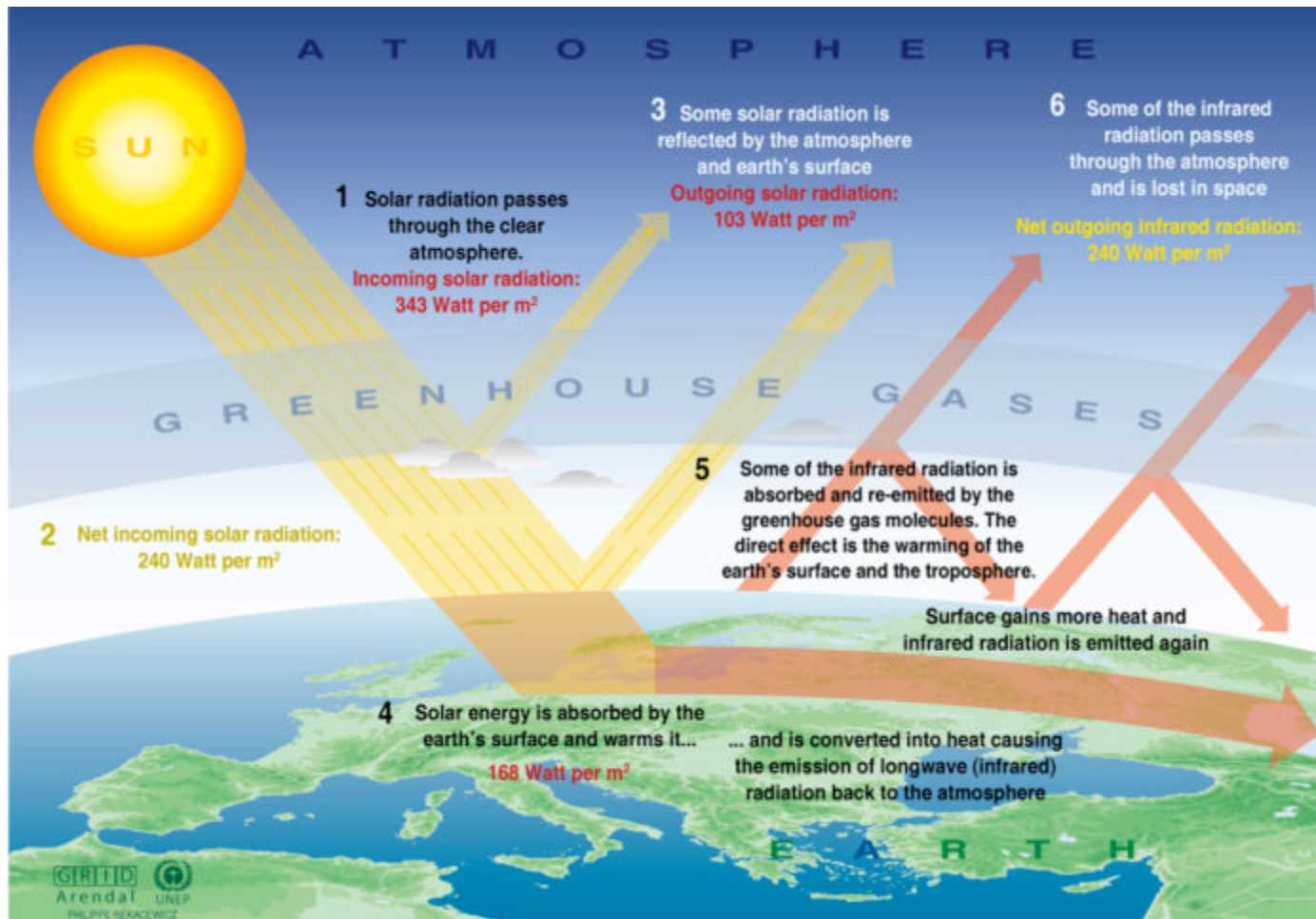
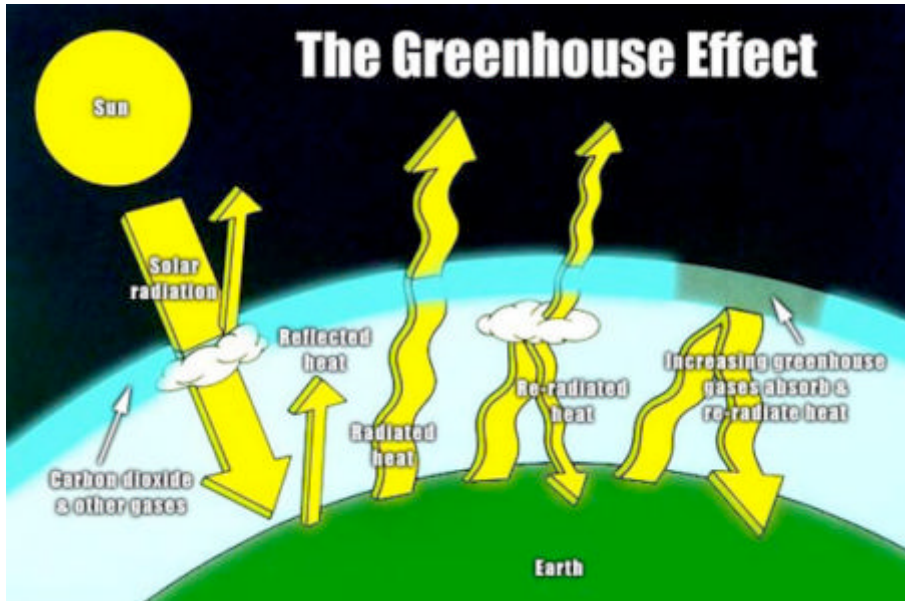


Image source: <http://maps.grida.no/go/graphic/greenhouse-effect>

Energy balance - greenhouse effect



Viewed from space, the Earth has an “average radiating temperature” (blackbody spectrum) of -18°C .

However, actual average **surface** temperature is $+15^{\circ}\text{C}$.

Difference is due to the **greenhouse effect**.

Solar radiation can be:

Reflected by atmosphere

Absorbed by Earth

Reradiated as infrared (300 K BBR) and

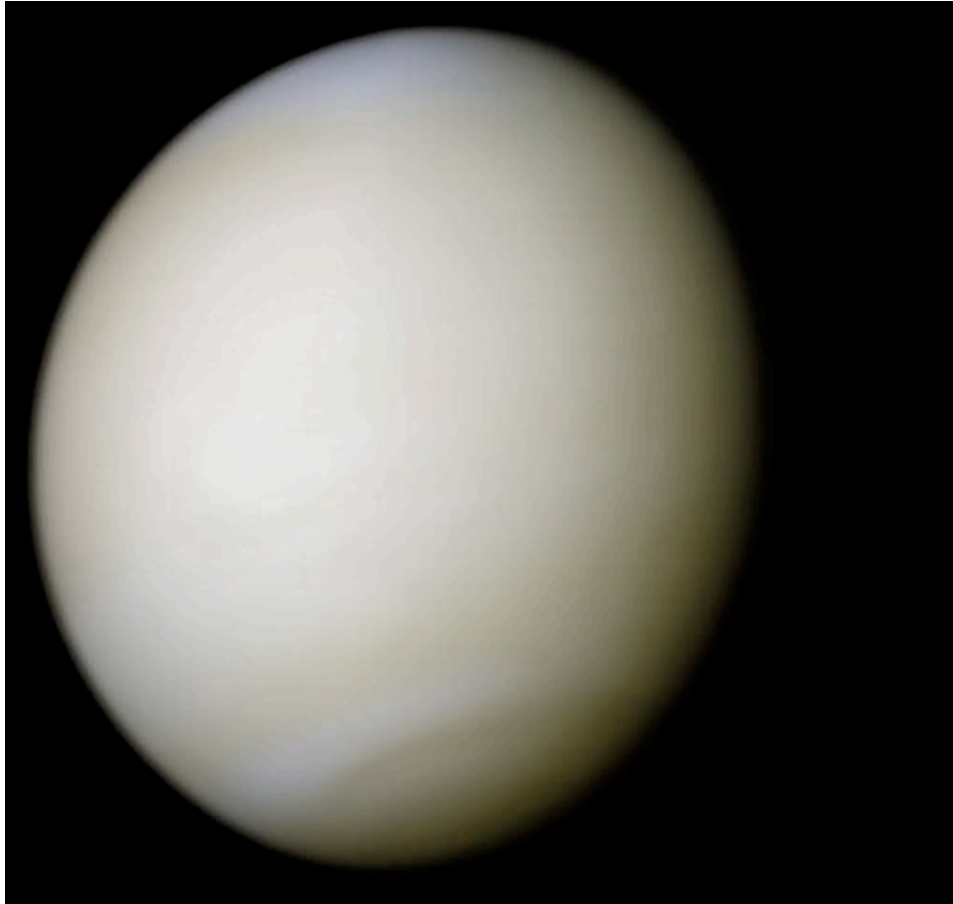
Lost from atmosphere OR

Reabsorbed by atmospheric gases -
origin of greenhouse effect

Of the 390 W m^{-2} emitted by the Earth's surface, only 240 W m^{-2} escapes to space - this is the **global greenhouse effect**.

An increase in this difference corresponds to an **enhanced greenhouse effect**.

Example of “runaway greenhouse effect”



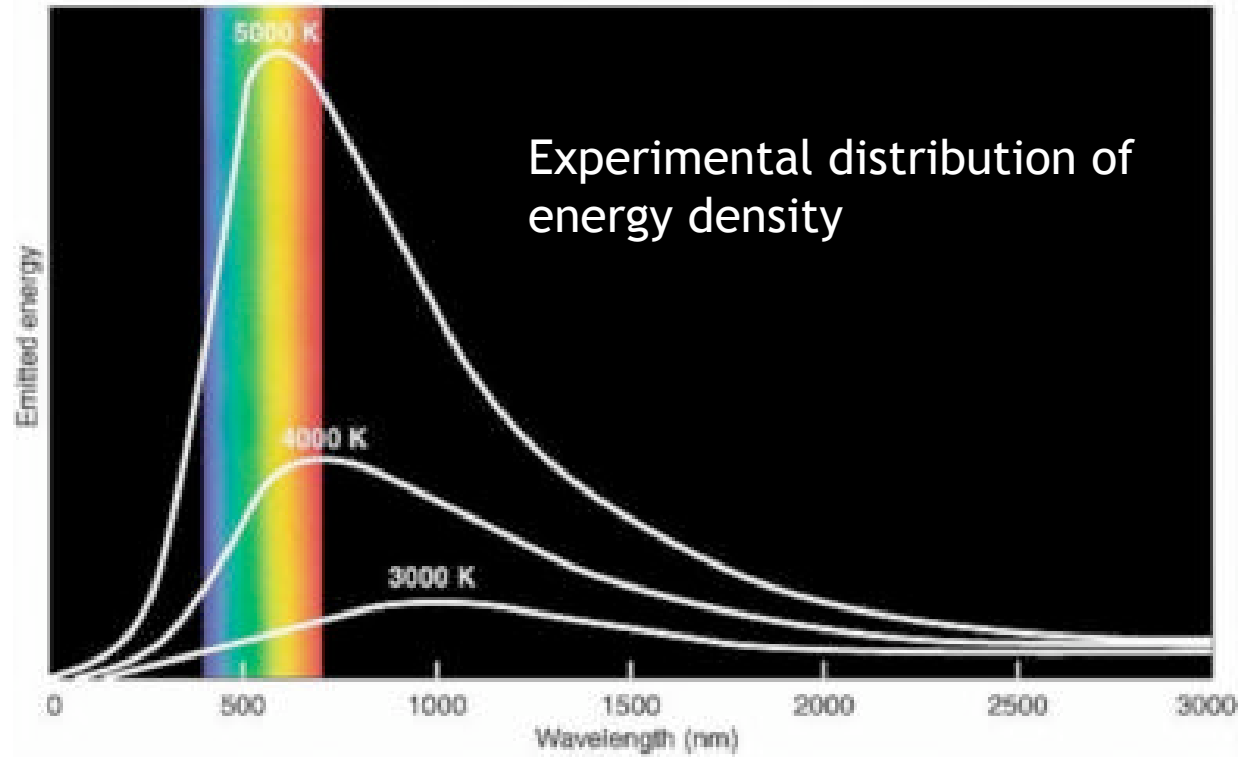
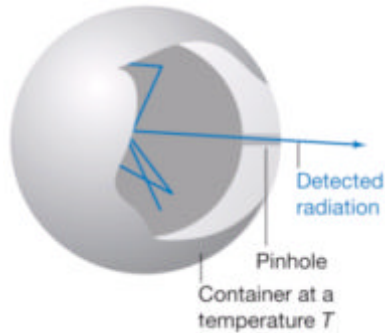
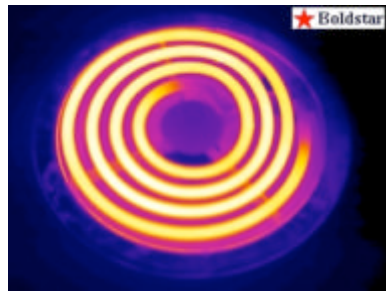
Venus:

Surface T predicted using
distance from Sun: 100°C

Measured surface T: 450°C

Atmosphere: 96% CO_2 , 4%
 H_2SO_4 ; $P = 90 \text{ atm}$

Blackbody Radiation (aka “Hohlraumstrahlung”)



“White hot” is hotter than “red hot” - i.e. spectrum of emitted radiation shifts to higher *frequencies* at higher temperature.

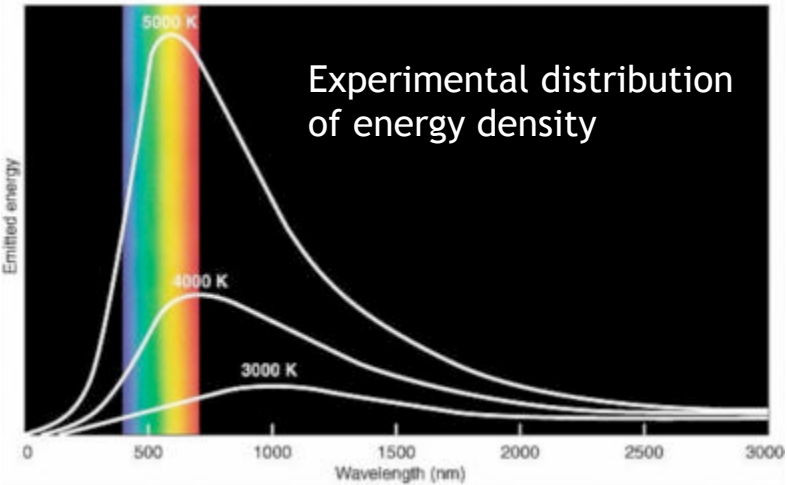
BBR (theoretical concept) is ideally efficient emitter/absorber of radiation at all wavelengths.

Frequency distribution depends on T , not on material - sun is (approximately) a BBR at ca. 5500 K, Earth is a BBR at ca. 300 K.

Blackbody Radiation (aka “Hohlraumstrahlung”)

Empirical relationships:

| | |
|-----------------------------|-----------------------|
| $\lambda T = \text{const.}$ | Wien displacement law |
| $I = \sigma T^4$ | Stefan-Boltzmann law |



Explained by Max Planck (1900) - explanation requires *quantization* of radiation into “packets” with energy hc/λ

| | | |
|---|---|---|
| $\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{\beta h\nu} - 1}$ <p>Planck formula for energy density</p> | → | $\lambda_{\max} = \frac{hc}{4.965kT}$ |
| | → | $\sigma = \frac{2\pi^5 k^4}{15c^2 h^3}$ |

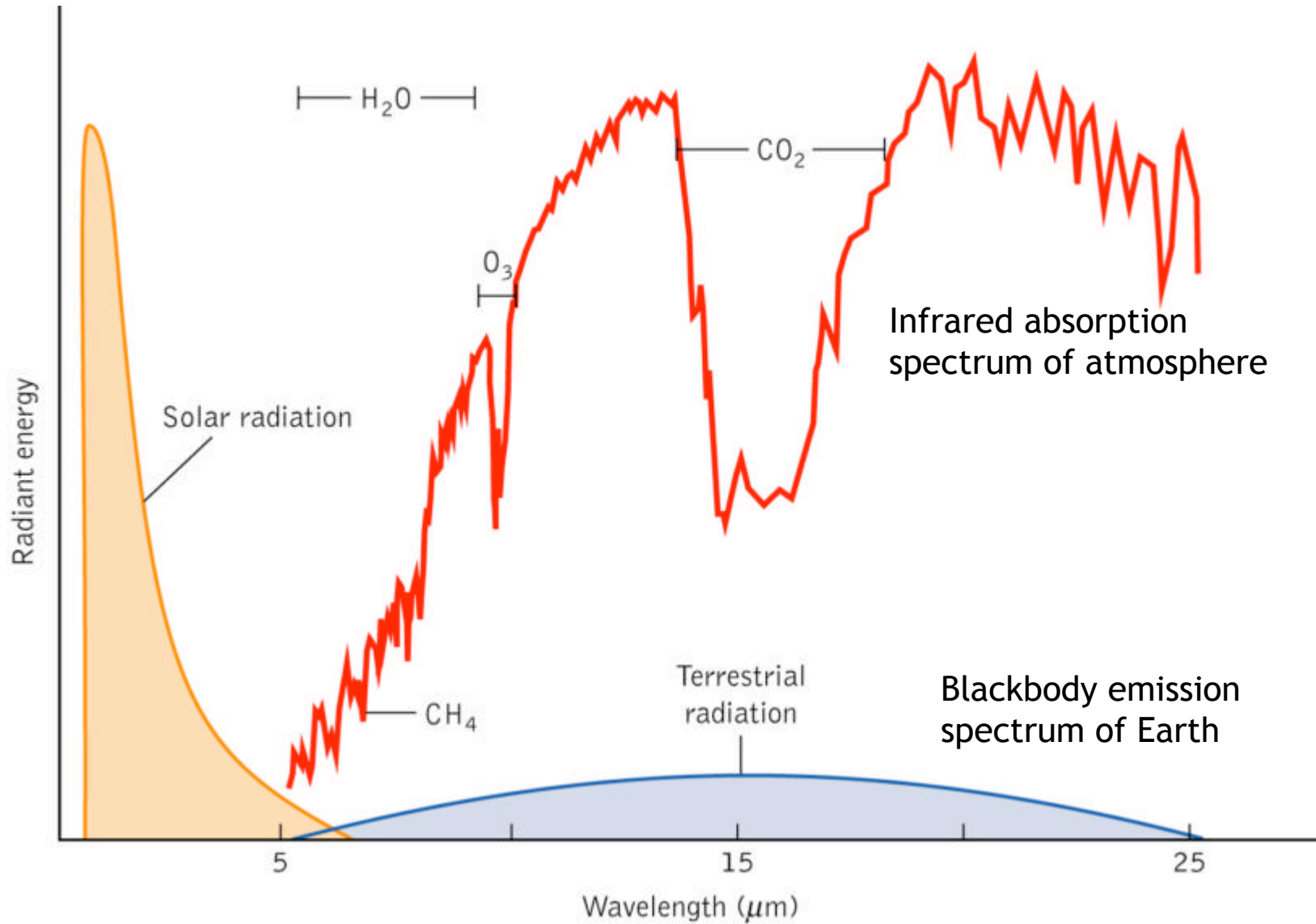


$h = 6.626 \times 10^{-34} \text{ Js}$ Planck constant

$\sigma = 56.7 \text{ nWm}^{-2} \text{ K}^{-4}$ Stefan’s constant

Spectra of the Sun and Earth

The infrared radiation emitted by the Earth's surface is absorbed by atmospheric gases such as H₂O, O₃, CO₂, CH₄ (but not N₂ or O₂).



Spectra of the Sun and Earth

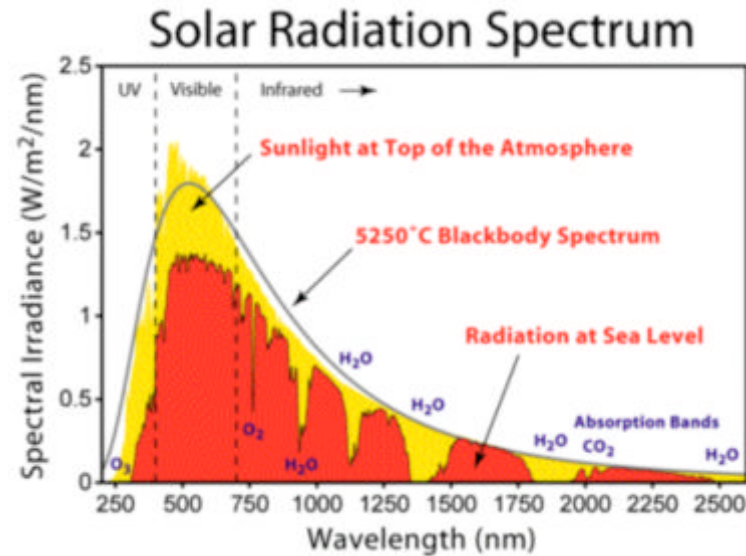
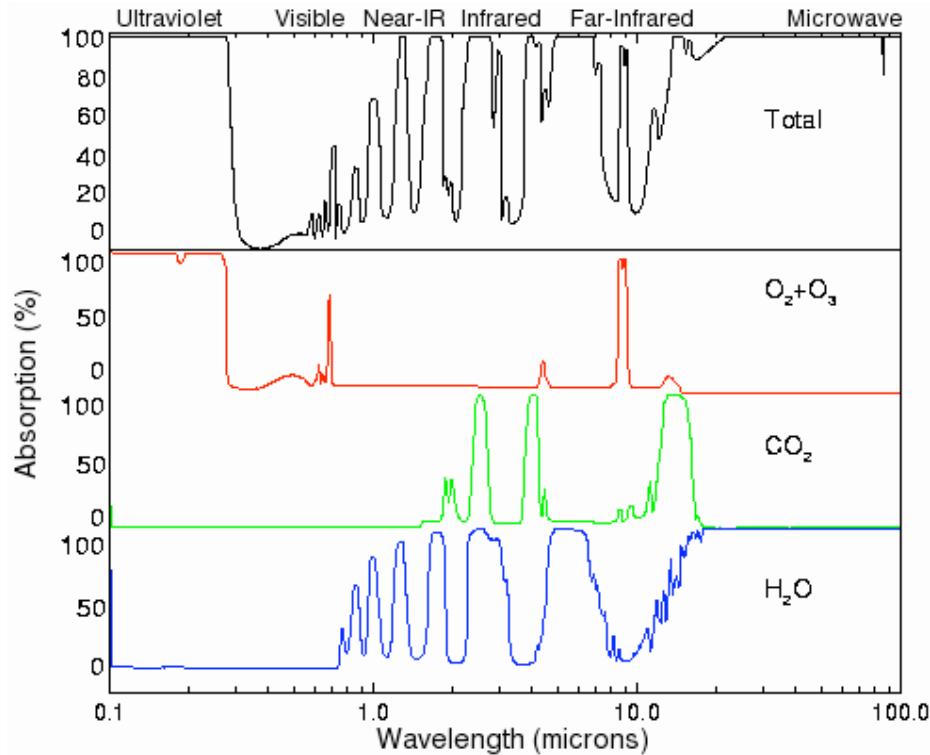
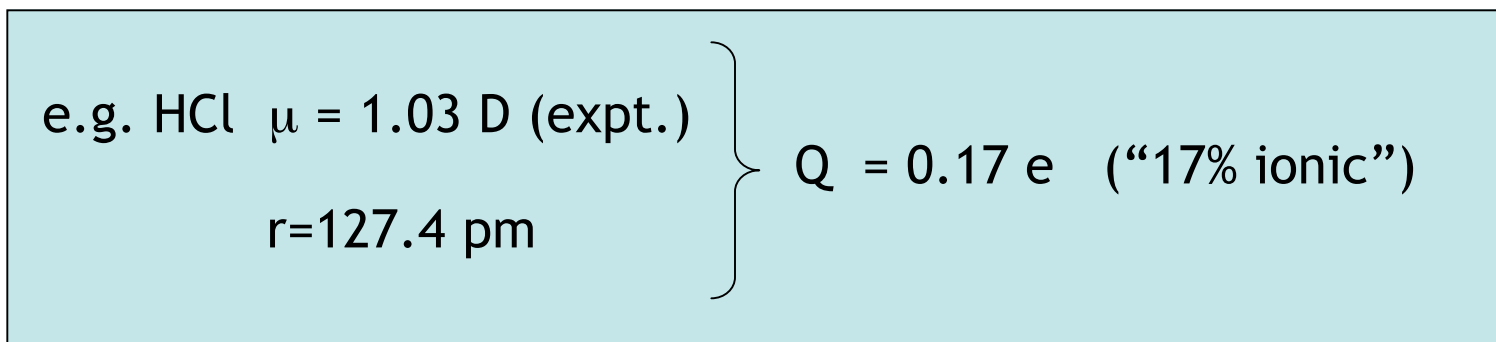
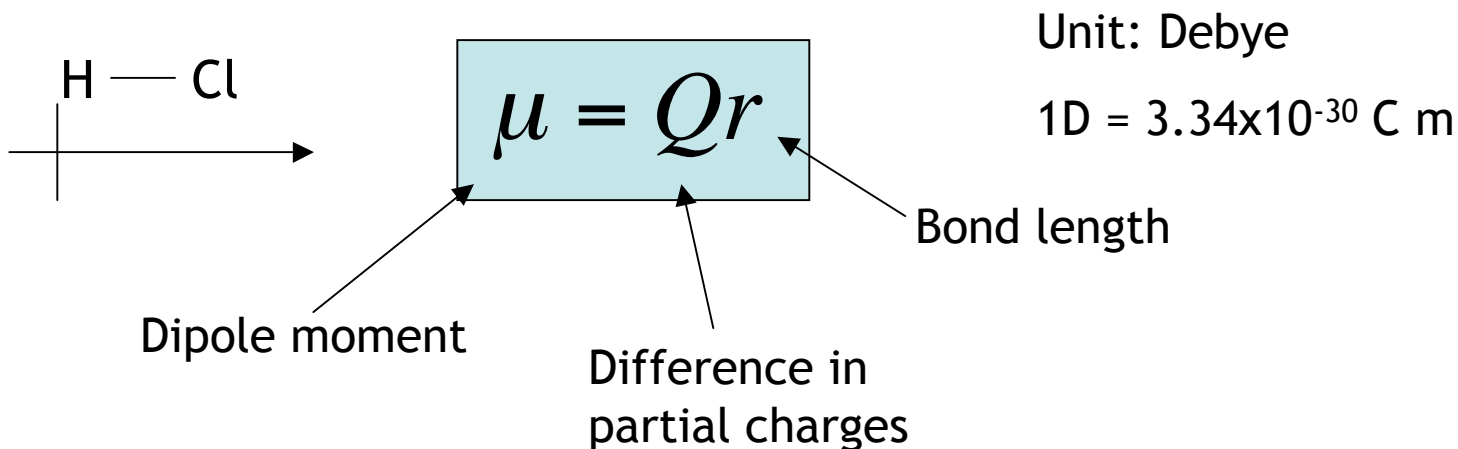


Image source: http://ockhams-axe.com/global_warming

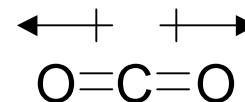
Potential greenhouse gases are: any that have an infrared absorption spectrum.

Molecular Vibrations and Infrared Spectra

Polar bonds: unequal electron-sharing leads to a **dipole moment**



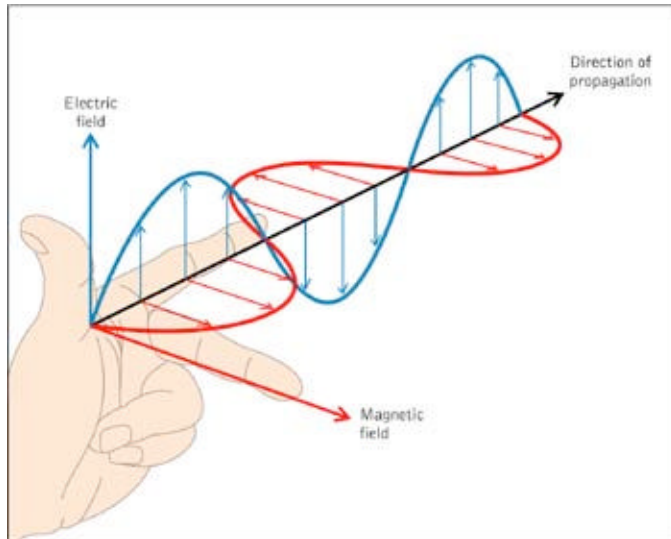
Larger molecules: individual bond dipoles may or may not cancel (vector sum to zero).



Molecular Vibrations and Infrared Spectra

Electromagnetic radiation (classical view): Oscillating electric and magnetic fields propagating through space at the speed of light.

Absorption of electromagnetic radiation requires an oscillatory rearrangement of charge - a change in molecular dipole moment:



Can be:

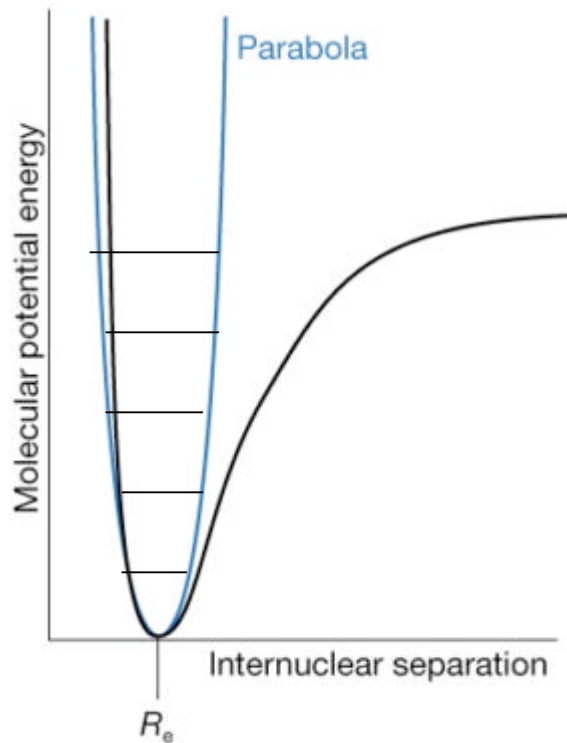
Electronic - excitation leads to redistribution of electrons (UV)

Vibrational - bond stretches distort molecular symmetry (IR)

Rotational - EM wave “sees” oscillating dipole (microwave)

Vibrations and absorption of EM Radiation

Diatomic molecules: the harmonic approximation



Let $x = r - r_e$. Then (Taylor series)

$$V(x) = V_0 + \left(\frac{dV}{dx}\right)_0 x + \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_0 x^2 + \dots$$

Can be set
arbitrarily to
zero.

Zero for a
minimum.

i.e. $V(x) \approx \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_0 x^2 \equiv \frac{1}{2}kx^2$ with $k = \left(\frac{d^2V}{dx^2}\right)_0$

force constant

QM: $E_v = \left(v + \frac{1}{2}\right)h\omega$; $\omega = \left(\frac{k}{\mu}\right)^{1/2}$; $v = 0, 1, 2, \dots$

Vibrations and absorption of EM Radiation

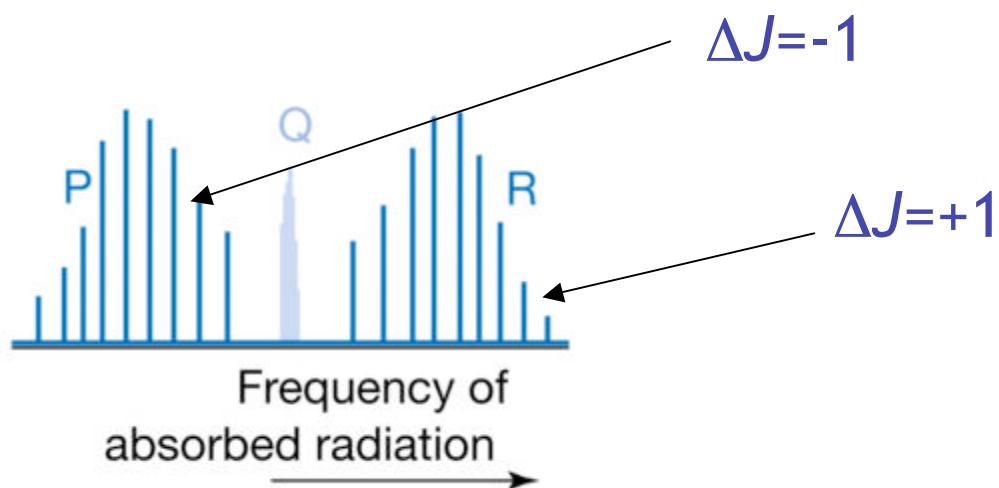
Selection rules

Dipole moment must be changed by transition

$$\mu_{v',v} = \mu_0 \langle v' | v \rangle + \left(\frac{d\mu_\epsilon}{dx} \right)_0 \langle v' | x | v \rangle + \dots$$

leading to $\Delta v = \pm 1$ $\Delta J = \pm 1$

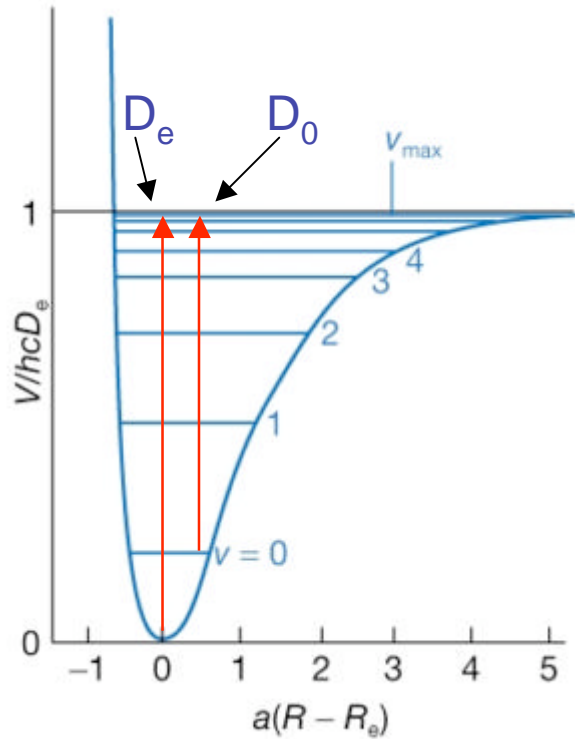
Rotational fine structure



Q branch allowed when molecule has nonzero orbital angular momentum in ground state (e.g. NO)

Vibrations and absorption of EM Radiation

Diatomic molecules: anharmonicity



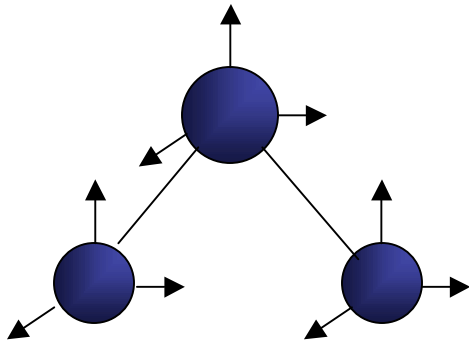
Relaxes selection rules.

$\Delta v = \pm 2$ now weakly allowed.

$\Delta v = \pm 1$ transitions no longer degenerate.

Vibrations and absorption of EM Radiation

Polyatomic molecules: normal modes



$$V = V_0 + \sum_i \left(\frac{\partial V}{\partial X_i} \right)_0 X_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V}{\partial X_i \partial X_j} \right)_0 X_i X_j + \dots$$
$$\equiv \frac{1}{2} \sum_{i,j} k_{ij} X_i X_j \quad w/ \quad k_{ij} = \left(\frac{\partial^2 V}{\partial X_i \partial X_j} \right)_0$$

N atoms => 3N displacements

Remove 3 translations and 3 rotations (2 for linear).

Coordinate transformation removes cross terms.

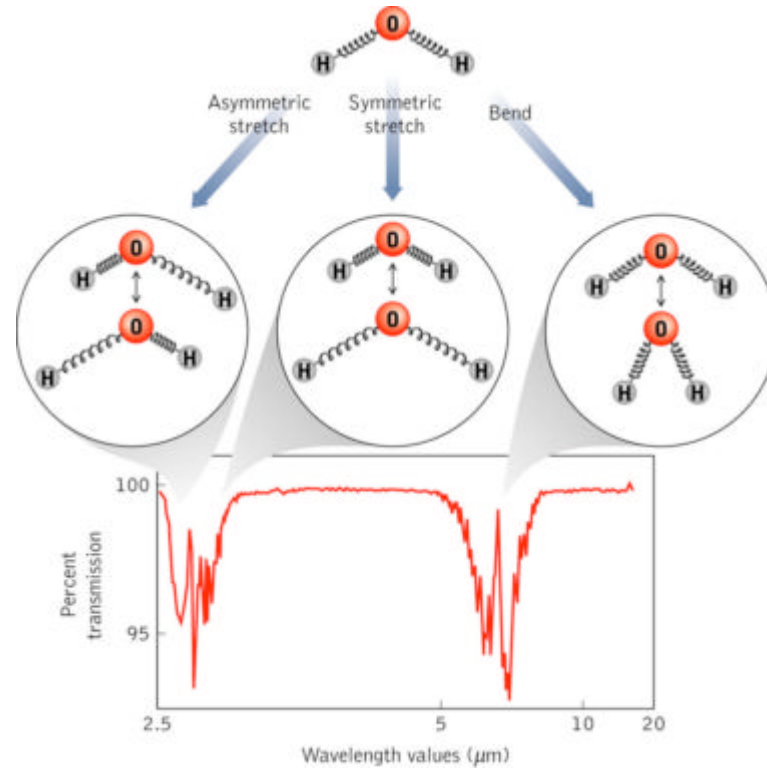
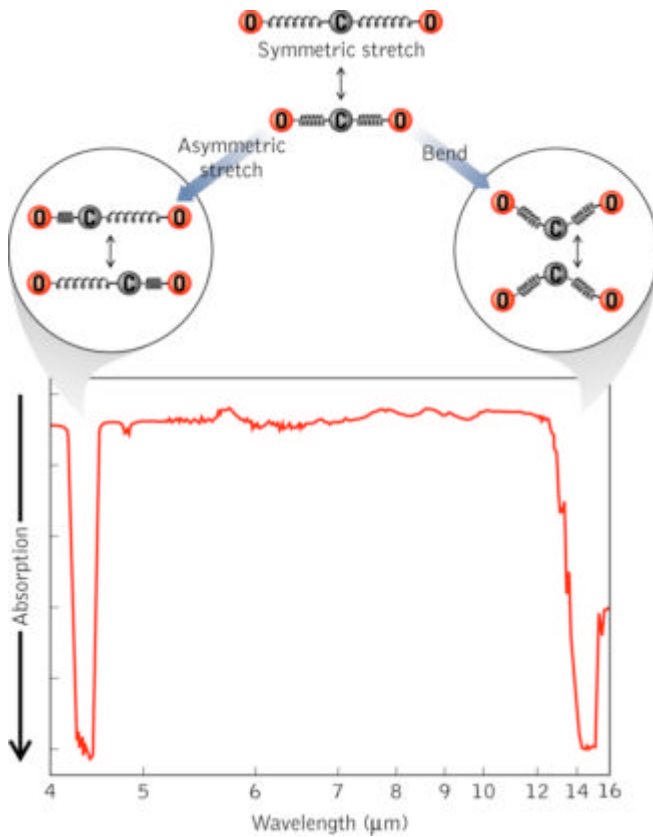
$$E = \frac{1}{2} \sum_i \dot{Q}_i^2 + \frac{1}{2} \sum_i \kappa_i Q_i^2$$



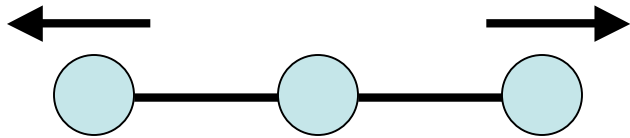
O₂, N₂ - homonuclear diatomics - $\mu = 0$ for all possible internuclear distances r - no IR absorption.



3 “normal modes”, some of which can absorb IR

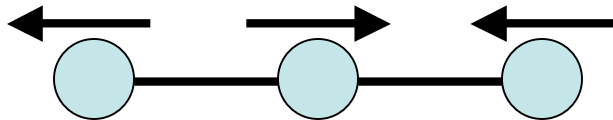


A closer look at the normal modes of CO₂



symmetric stretch

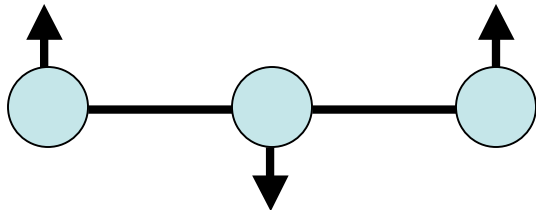
$\omega = 1288 \text{ cm}^{-1}$ IR-inactive



antisymmetric stretch

$\omega = 2349 \text{ cm}^{-1}$

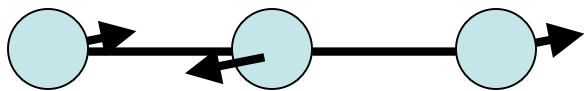
IR-active



Bend (doubly degenerate)

$\omega = 667 \text{ cm}^{-1}$

IR-active

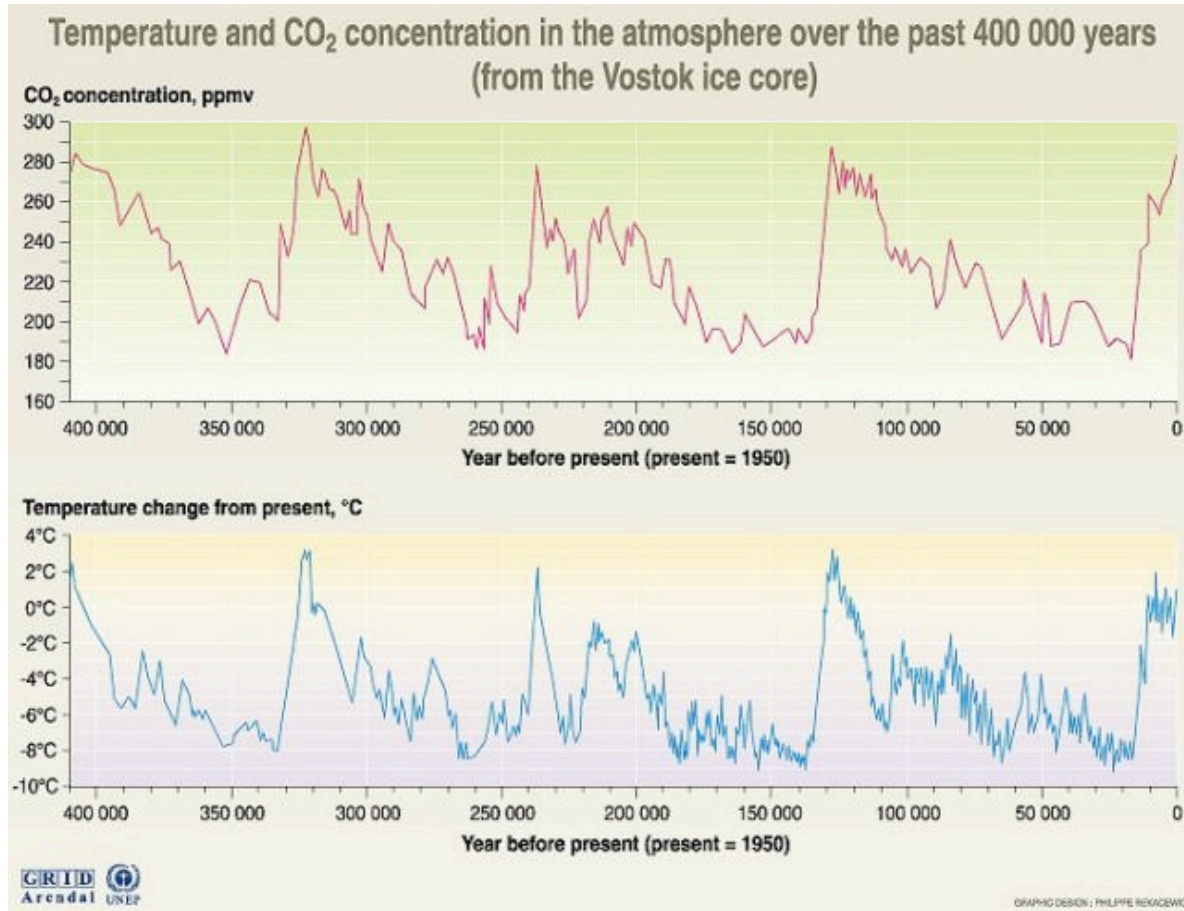


Other atmospheric IR absorbers include
H₂O, NH₃, CH₄, CH₂Cl₂,...

concentration large but relatively
constant due to equilibrium with oceans

CO₂ is most significant overall.

Correlation between global average temperature and atmospheric [CO₂]



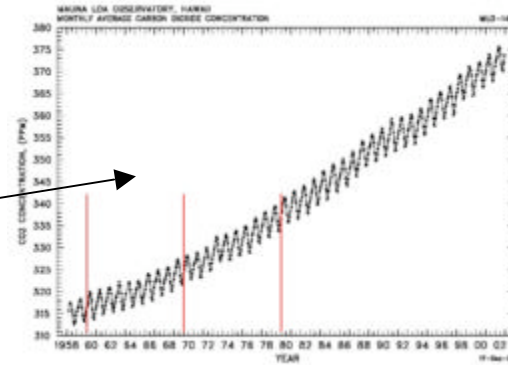
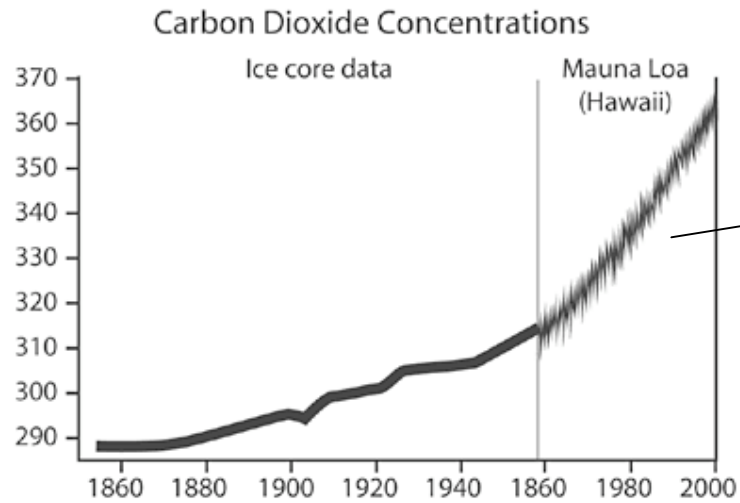
Source: J.R. Petit, J. Jouzel, et al. Climate and atmospheric history of the past 420 000 years from the Vostok ice core in Antarctica, *Nature* 399 (3 June), pp 429-436, 1999.

Ice core data :

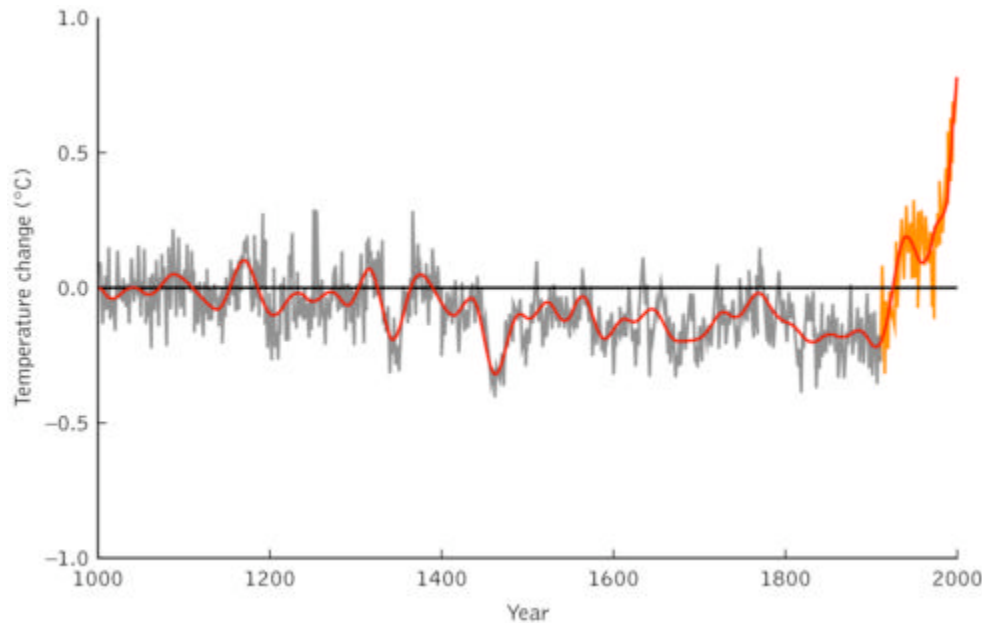
CO₂ (direct measurement from trapped air)

temperature (from hydrogen/deuterium isotope ratio)

Recently (industrial era) CO₂ release into atmosphere has accelerated.

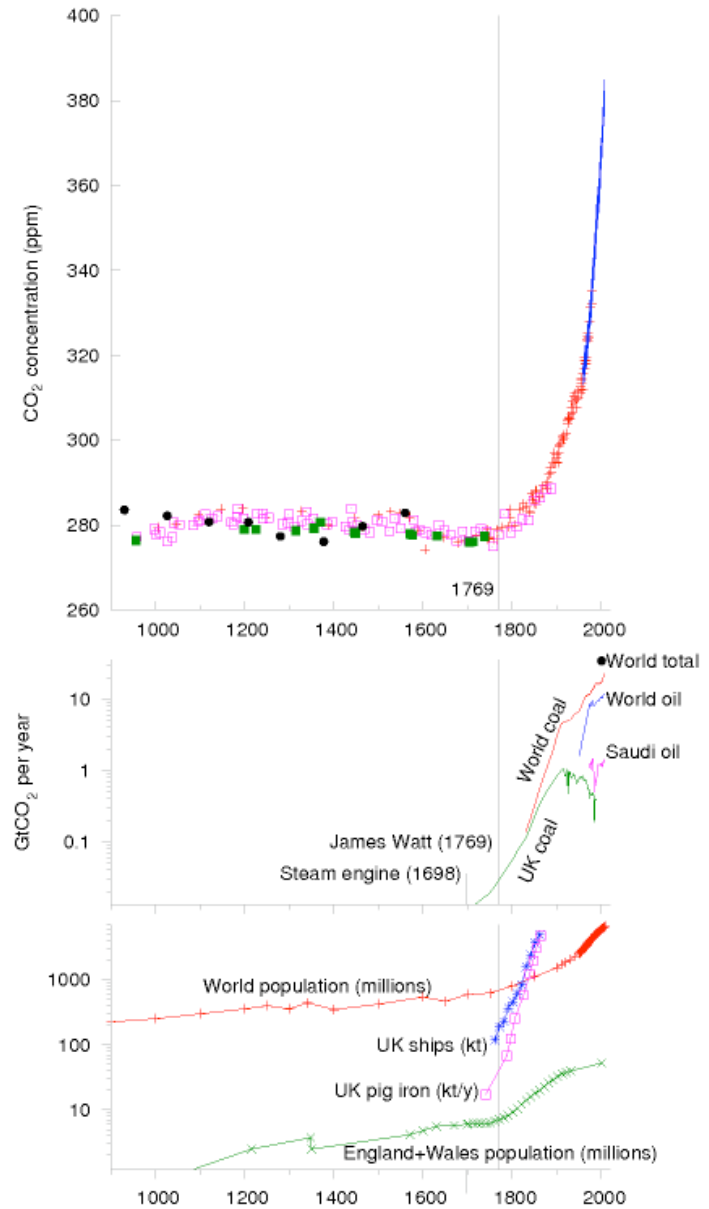


(seasonal oscillations - transfer of carbon between biosphere and atmosphere)



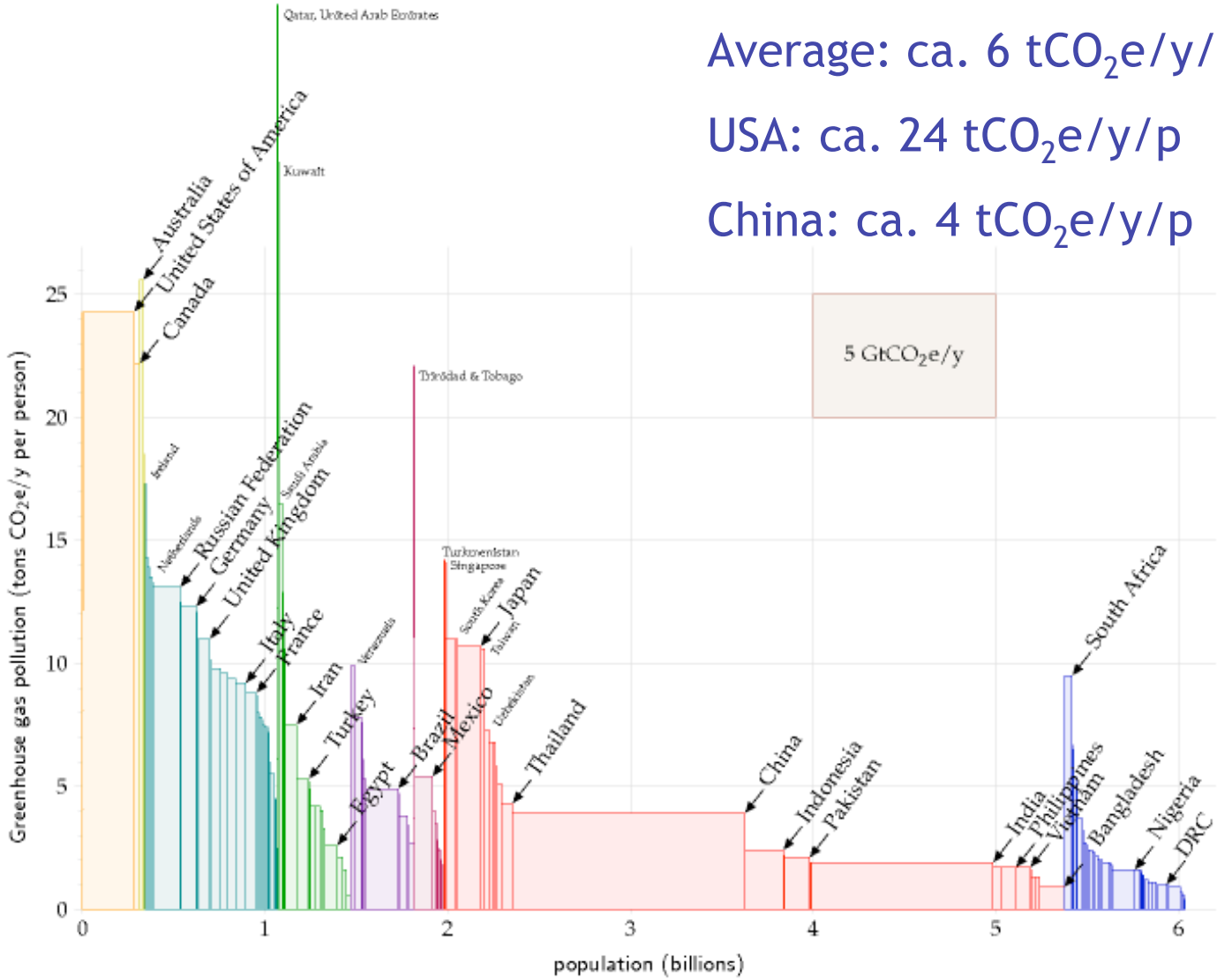
Appears to be correlated with accelerated global temperature rise - "global warming"

Atmospheric [CO₂] tracks global fossil fuel use.



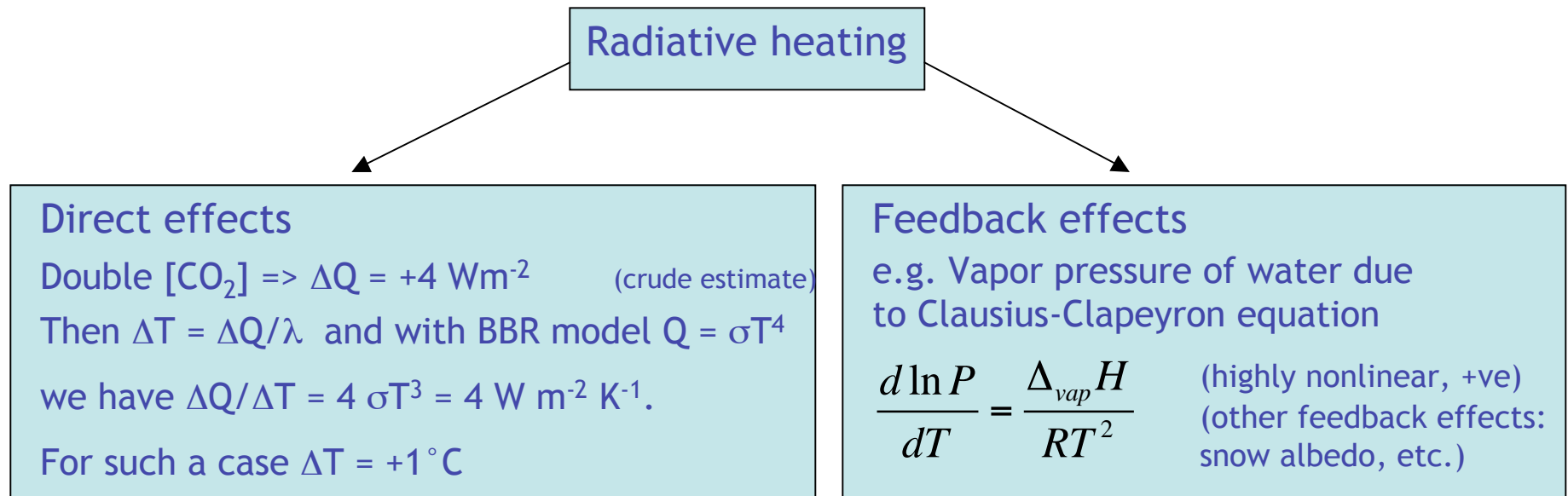
The biggest CO₂ producers

Global total: 34 GtCO₂e/y
 Population: 6 x 10⁹ people
 Average: ca. 6 tCO₂e/y/p
 USA: ca. 24 tCO₂e/y/p
 China: ca. 4 tCO₂e/y/p



Modeling Climate Change

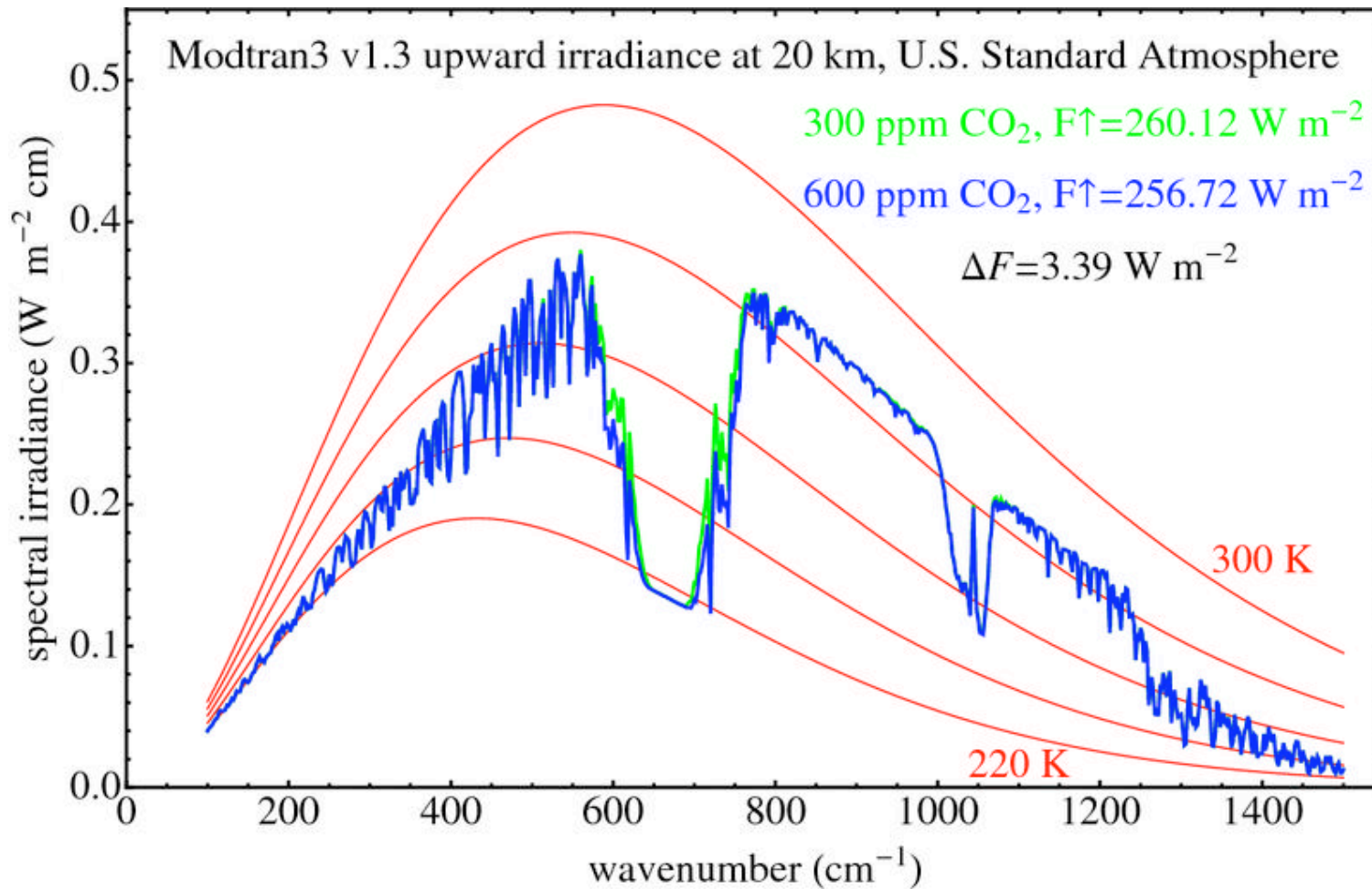
IPCC: “The radiative forcing of the surface-troposphere system (due to a change, for example, in greenhouse gas concentration) is the change in net (solar plus longwave) irradiance in W/m^2 at the tropopause AFTER allowing the stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperature and state held fixed at the unperturbed values.”



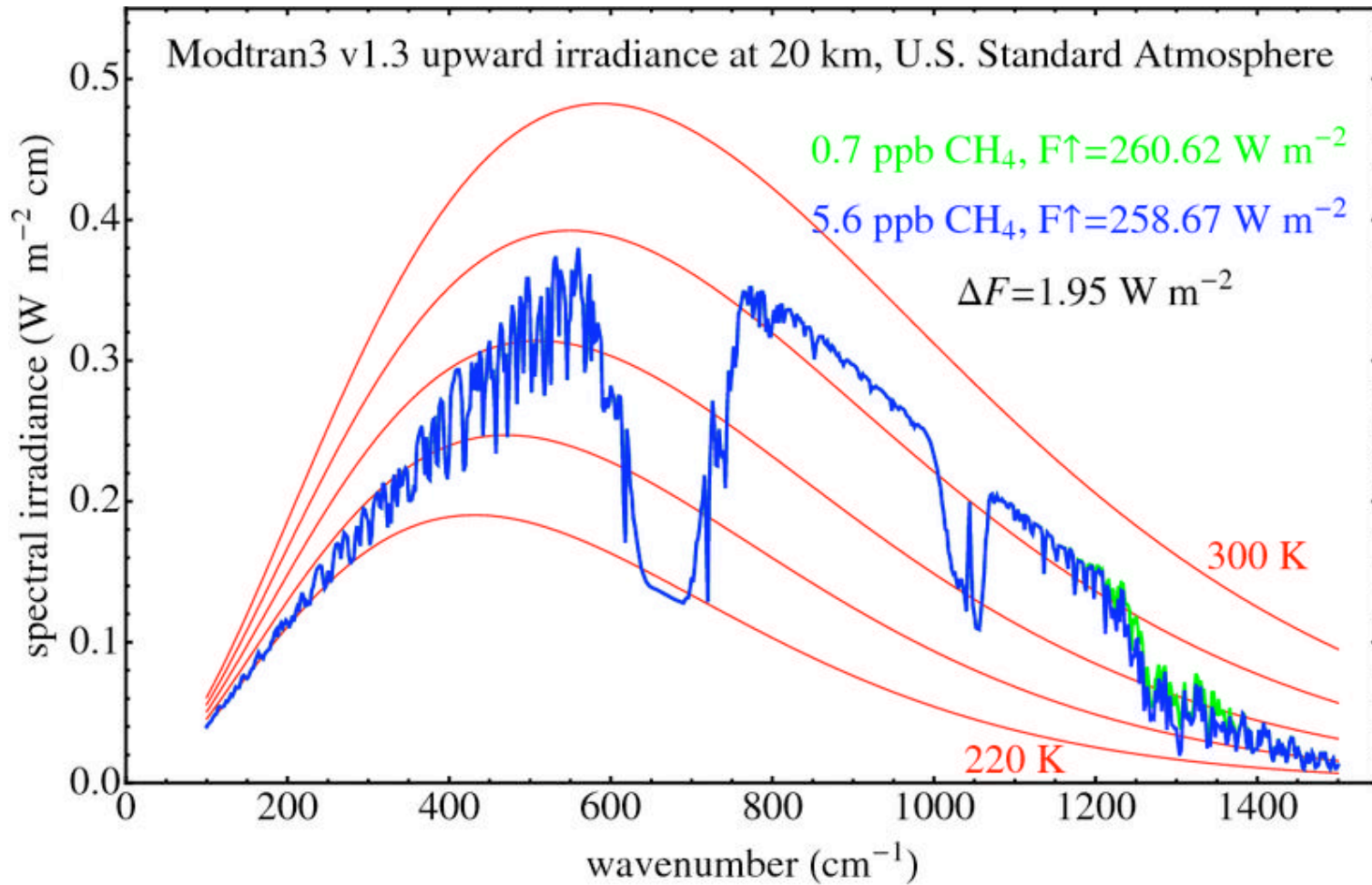
Other contributions: Clouds, oceans, aerosol effects on albedo, ...

cf. “Carbon dioxide and climate: a scientific assessment”, Woods Hole report, 1979

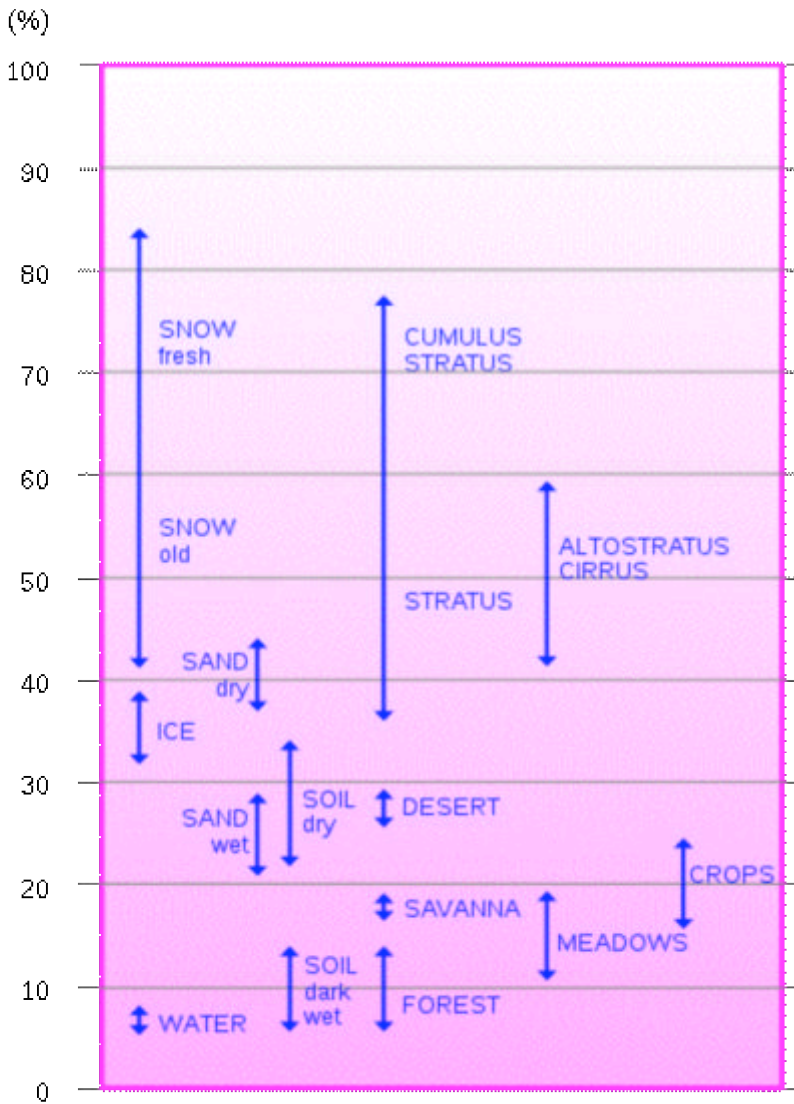
Modeling Climate Change



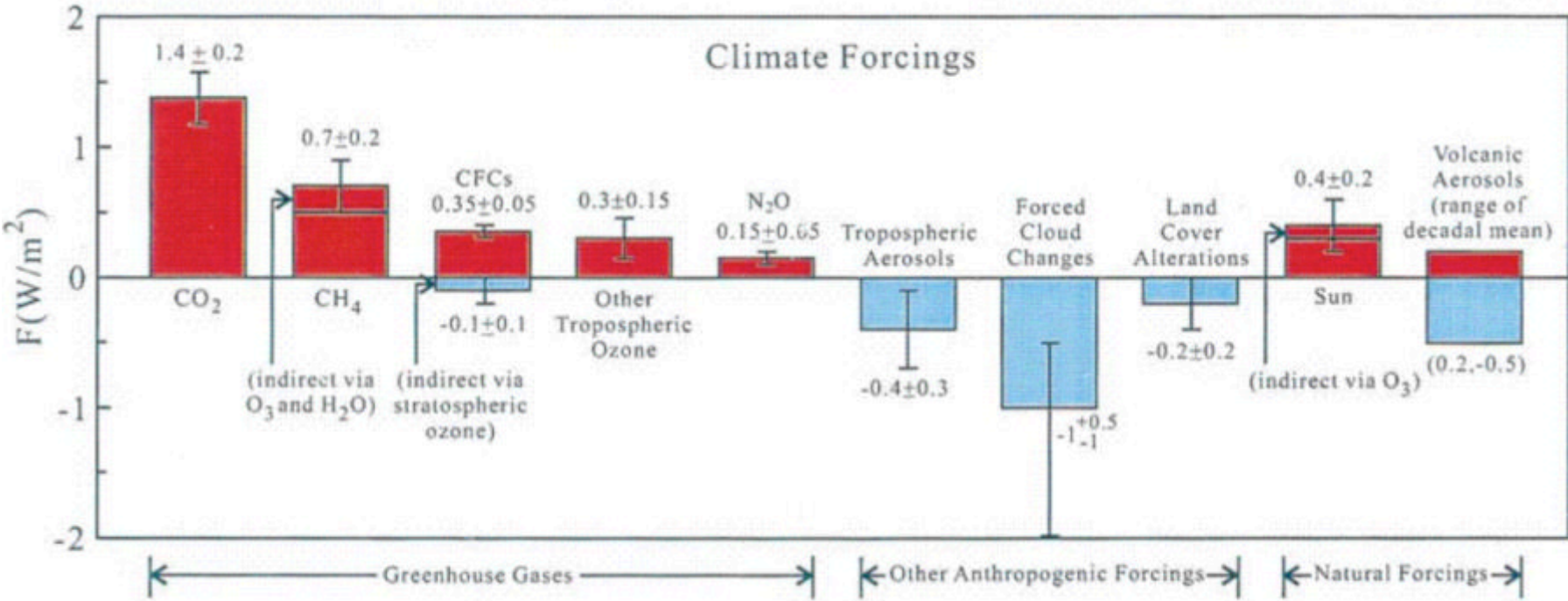
Modeling Climate Change



Albedo effects



Sources of “climate forcing”



Source: James Hansen (NASA)

Table 6.2: Simplified expressions for calculation of radiative forcing due to CO₂, CH₄, N₂O, and halocarbons. The first row for CO₂ lists an expression with a form similar to IPCC (1990) but with newer values of the constants. The second row for CO₂ is a more complete and updated expression similar in form to that of Shi (1992). The third row expression for CO₂ is from WMO (1999), based in turn on Hansen et al. (1988).

| Trace gas | Simplified expression Radiative forcing, ΔF (Wm ⁻²) | Constants |
|------------------|---|----------------------------------|
| CO ₂ | $\Delta F = \alpha \ln(C/C_0)$ | $\alpha = 5.35$ |
| | $\Delta F = \alpha \ln(C/C_0) + \beta (\sqrt{C} - \sqrt{C_0})$ | $\alpha = 4.841, \beta = 0.0906$ |
| | $\Delta F = \alpha(g(C) - g(C_0))$ where $g(C) = \ln(1 + 1.2C + 0.005C^2 + 1.4 \times 10^{-6}C^3)$ | $\alpha = 3.35$ |
| CH ₄ | $\Delta F = \alpha(\sqrt{M} - \sqrt{M_0}) - (f(M, N_0) - f(M_0, N_0))$ | $\alpha = 0.036$ |
| N ₂ O | $\Delta F = \alpha(\sqrt{N} - \sqrt{N_0}) - (f(M_0, N) - f(M_0, N_0))$ | $\alpha = 0.12$ |
| CFC-11a | $\Delta F = \alpha(X - X_0)$ | $\alpha = 0.25$ |
| CFC-12 | $\Delta F = \alpha(X - X_0)$ | $\alpha = 0.32$ |

$$f(M, N) = 0.47 \ln[1 + 2.01 \times 10^{-5} (MN)^{0.75} + 5.31 \times 10^{-15} M(MN)^{1.52}]$$

C is CO₂ in ppm

M is CH₄ in ppb

N is N₂O in ppb

X is CFC in ppb

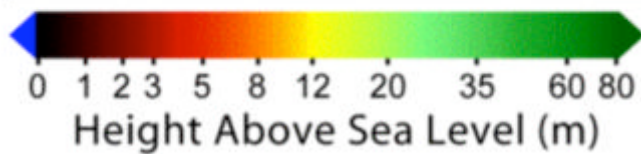
The constant in the simplified expression for CO₂ for the first row is based on radiative transfer calculations with three-dimensional climatological meteorological input data (Myhre et al., 1998b). For the second and third rows, constants are derived with radiative transfer calculations using one-dimensional global average meteorological input data from Shi (1992) and Hansen et al. (1988), respectively.

The subscript 0 denotes the unperturbed concentration.

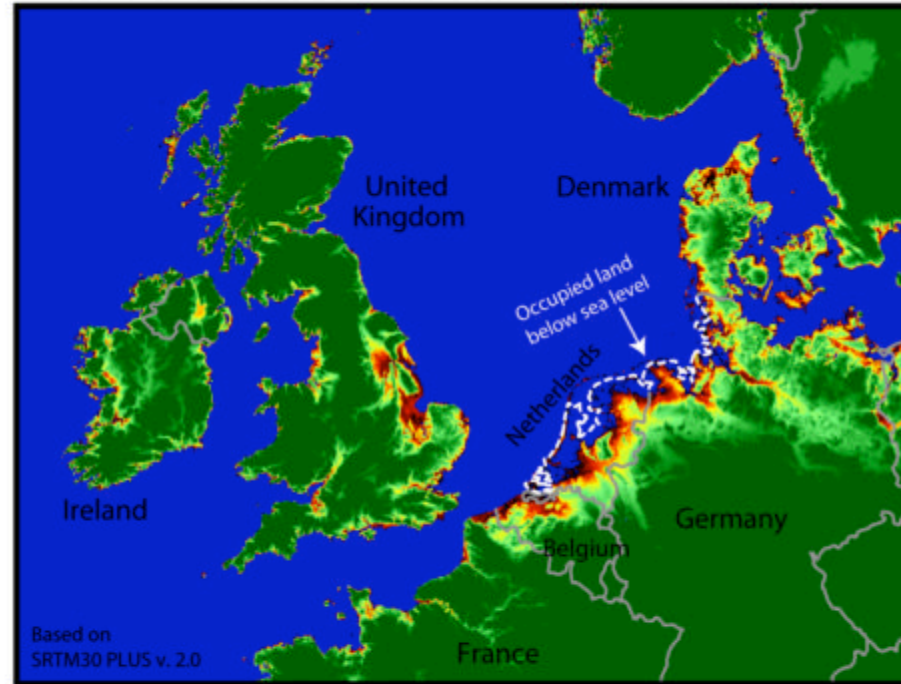
^a The same expression is used for all CFCs and CFC replacements, but with different values for α (i.e., the radiative efficiencies in Table 6.7).

Impact of Climate Change - sea level rise

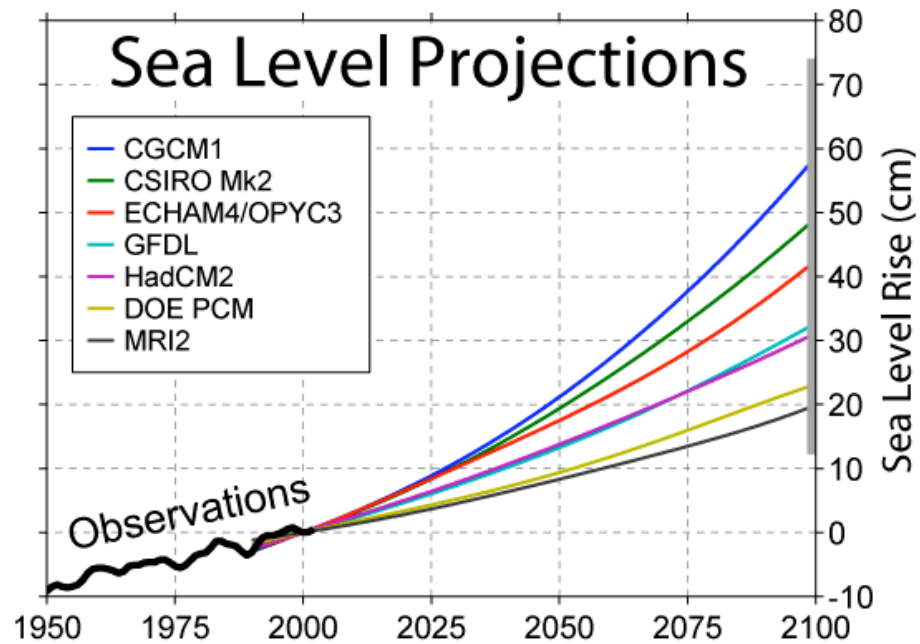
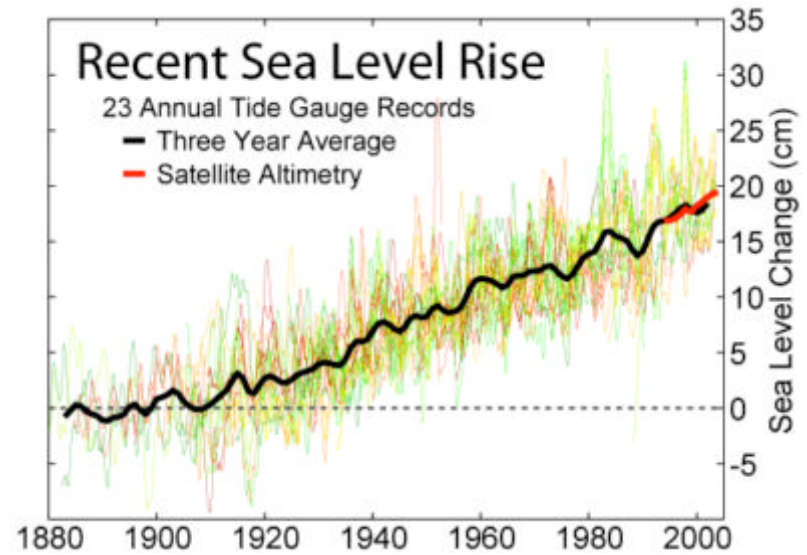
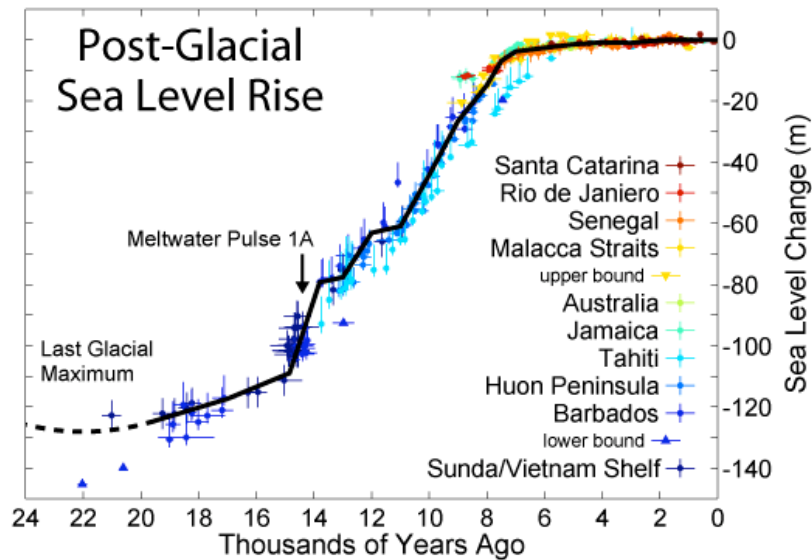
Sea Level Risks - Florida

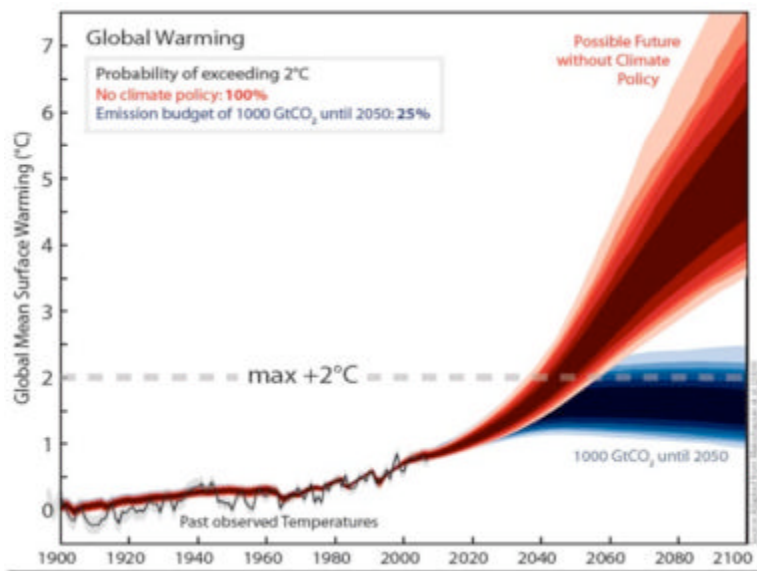
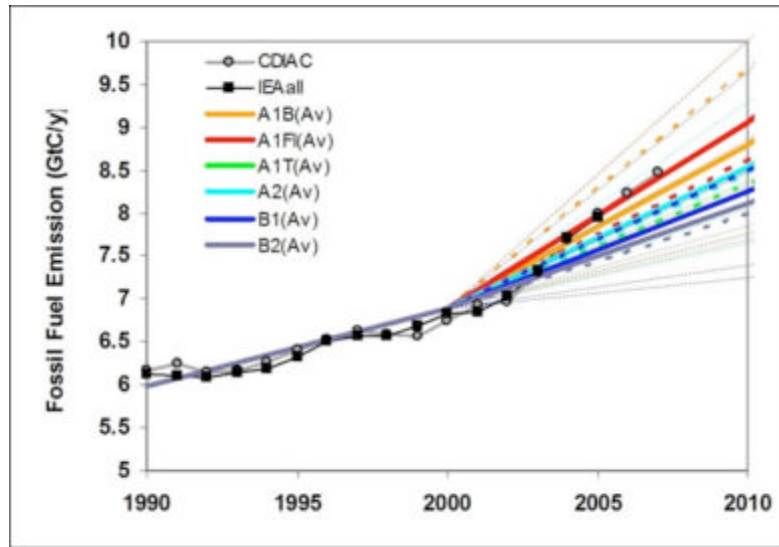


Sea Level Risks - North Sea

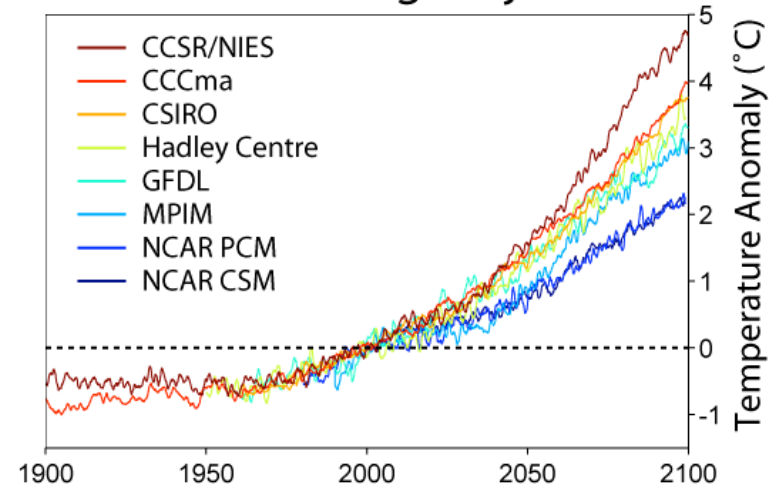


Source: <http://www.globalwarmingart.com/>





Global Warming Projections



Measures required to limit global T rise

Modeling => Doubling atmospheric $[CO_2]$ leads to surface heating power increased by ca. 4 W m^{-2} .

Average absorbed power around 238 W m^{-2} (ca. 1.7% increase).

$+2^\circ\text{C} < \Delta T < +3.5^\circ\text{C}$, with larger increases at high latitudes.

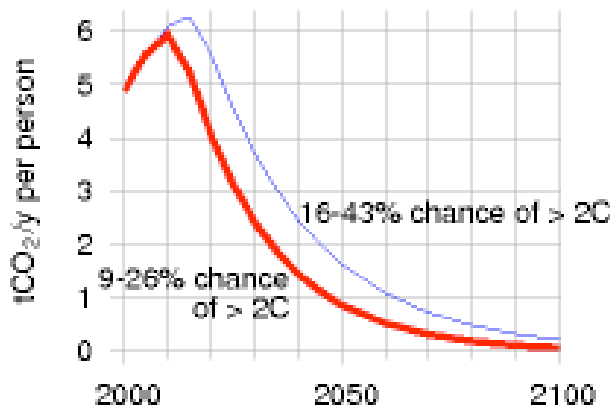


Figure: Baer and Mastrandrea (2006)

T rise of $>2^\circ\text{C}$ considered “catastrophic” - large-scale changes in coastline; habitat destruction; migration of human populations.

To achieve T rise $<2^\circ\text{C}$ requires approximately 85% reduction in CO_2 production by 2050 - much more drastic than Kyoto recommendations.

G8 Climate Scorecards



EMISSION TRENDS



Past emission trend from 1990 to 2007 **+16.8%**

Current (2007) distance to the Kyoto target **+23.8%-points**

Increase of the share of renewable energy sources **-0.2%-points**

Emissions per capita **25 tCO₂eq./cap**

Emissions per GDP **567 tCO₂eq./M\$**

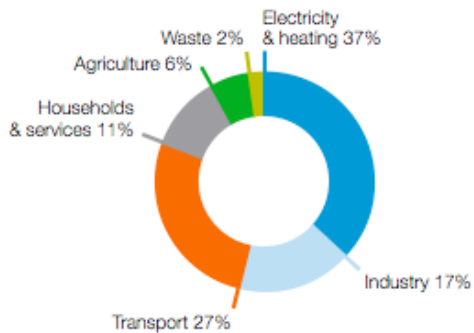
CO₂ per kWh electricity **625 gCO₂/kWh**

Energy efficiency in industry **1.6**

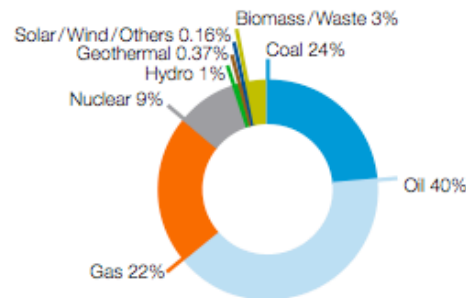
Emissions in transport per capita **6.3 tCO₂eq./cap**

Emissions in households and services per capita **2.6 tCO₂eq./cap**

EMISSIONS BY SECTOR



ENERGY SOURCES



Summary

Planet's surface temperature of 15°C attributed to a “greenhouse effect” of about 33°C.

Greenhouse effect is associated with atmospheric gases which trap infrared radiation, especially CO₂.

Recent average temperatures highest for past 1 k yrs, and increasing.

Great potential for climate change - e.g. complete melting of ice caps would lead to sea level rise of 110 m.

Policy efforts - IPCC, Kyoto Protocol (1997) - limitations on emissions.

Climate modeling - without restrictions, [CO₂] predicted to rise above 1000 ppm. Even with restrictions in place, [CO₂] expected to rise above 400 ppm (highest level since Eocene, when there were no polar ice caps).

Significant impact requires a reduction in CO₂ production far in excess of Kyoto recommendations.