Radiative Forcing

AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/spr2022
https://myelms.umd.edu/courses/137772

Goals:

- Understanding interaction between gases and IR radiation
- Radiative forcing of greenhouse gases
- Radiative forcing of aerosols

Wavenumber = 1 / Wavelength

1 μm (micron) = 10^{-6} m
1 nm (nanometer) = 10^{-9} m

Therefore, 1 μm = 1000 nm

Lecture 7

17 February 2022

Announcements

1) AOSC Weekly Seminar: Thursday, 3:30 pm

2) Problem Set #1 was due today on Tuesday

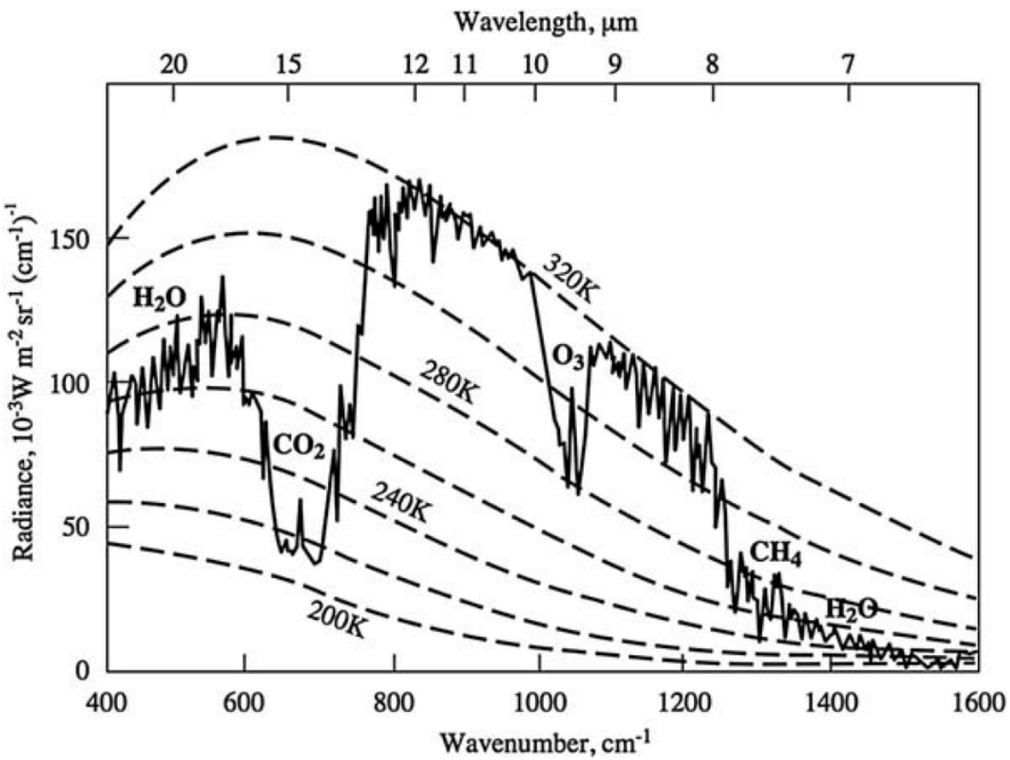
3) 10 points per day late, unless there is a legitimate medical or extra-curricular circumstance brought to our attention prior to the due date!

3) Will hold problem set review Wed, 23 Feb, 6:30 pm, ATL 2428 (this room)

4) Problem Set #2 due Thurs, 24 Feb has been posted

5) First exam is Thurs, 3 Mar:
- If held in class, will be closed book / no notes
- Will focus on concepts much more than calculations, although a very simple calculation-type question could appear
- New exams every year; will review prior exam on Tues 1 Mar to help you prepare

Overview

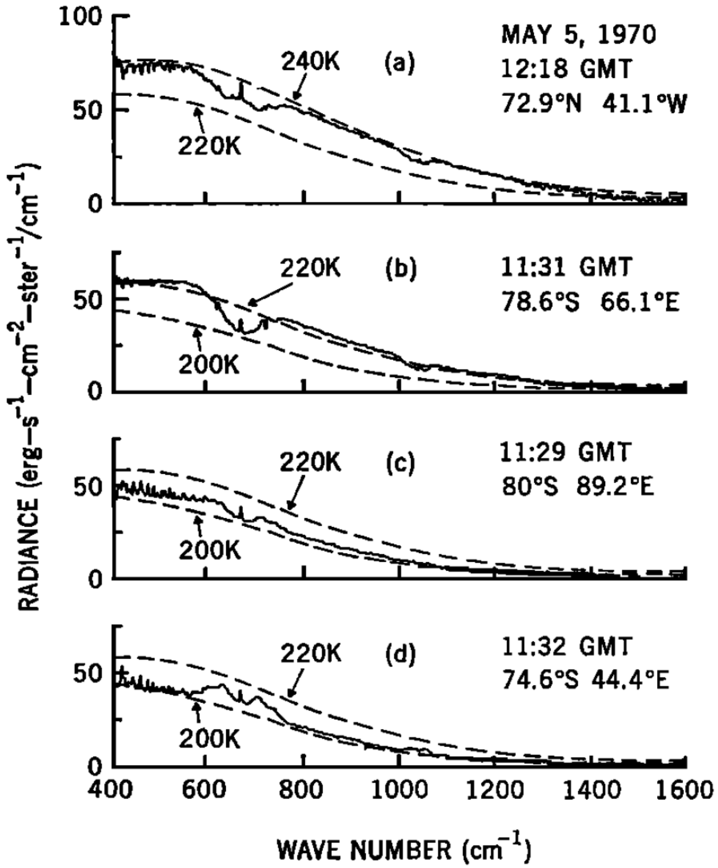


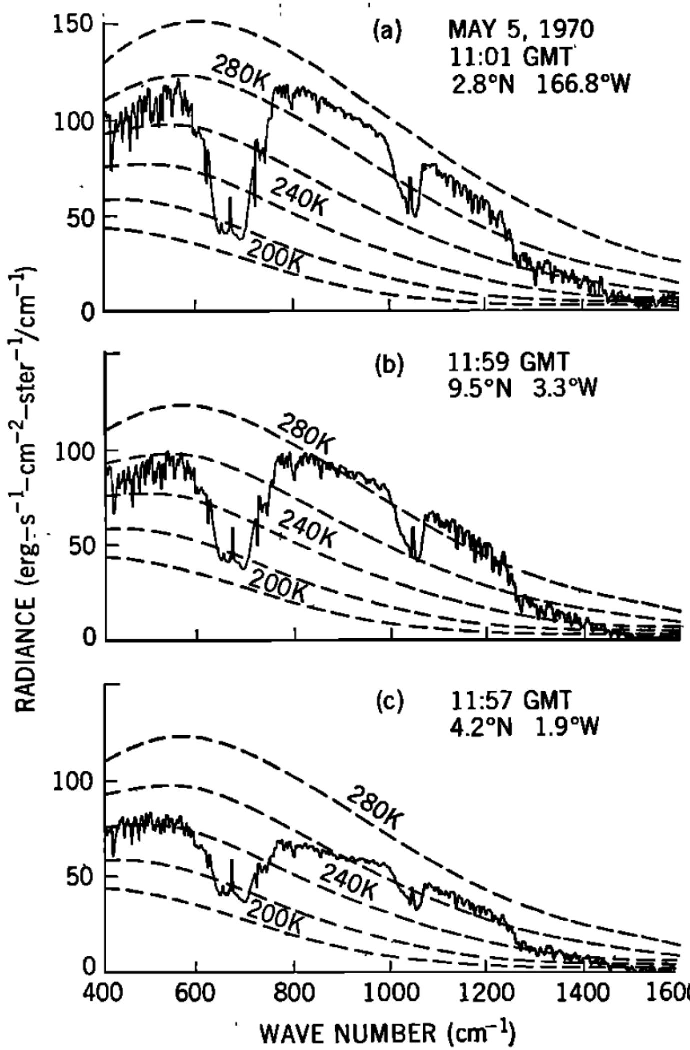
Hanel *et al*., JGR, 1972:
https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/JC077i015p02629

Viewed from space and averaged over space and time, Earth emits ~238 W/m^2 of thermal radiation between wavelengths of 5 and 50 μm.

The terrestrial emission spectrum matches that of a combination of blackbody spectra of temperatures between 220 and 320K.

The four most important gases that absorb terrestrial radiation (H_2O, CO_2,CH_4, O_3) are noted.





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Overview

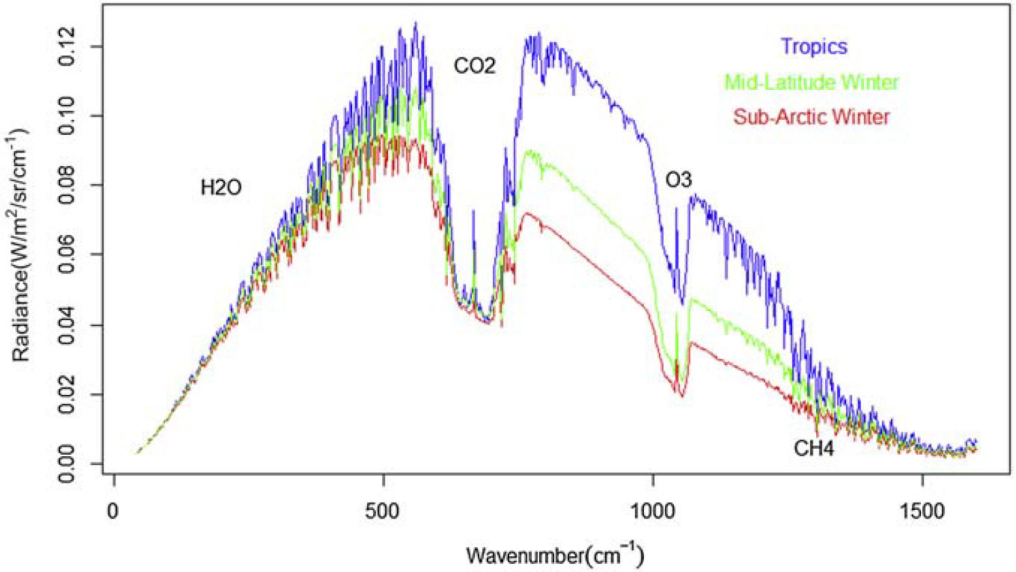


FIGURE 3.4.5 Overview of the earth's outgoing infrared radiation as a function of wave number (the inverse of wavelength) and latitude.[43] Radiances for this figure were calculated using Modtran and a web interface developed by David Archer available here: http://climatemodels.uchicago.edu/modtran/.

Kirk-Davidoff, Chapter 3.4, *Green Chemistry: An Inclusive Approach*, 2018

- GHGs prevent outgoing energy emitted from the surface from being released back into space, thereby trapping this energy and releasing it in the form of heat.
- Averaged over space and time, the Earth radiates to space an amount of energy consistent with that of a black body at 255 K.
- Some spectral regions are nearly filled (i.e., 667 cm^{-1}) whereas many others exhibit negligible attenuation of outgoing radiation.
- A newly discovered "miracle compound" with a long atmospheric lifetime will be much more damaging to Earth's climate system if it absorbs in a region that is _____, rather than a region that is _____.

Global Warming Potential

Table 3.2 Examples of Greenhouse Gases

Name and Chemical Formula	Preindustrial Concentration (1750)	Concentration in 2008	Atmospheric Lifetime (years)	Anthropogenic Sources	Global Warming Potential
carbon dioxide CO_2	270 ppm	388 ppm	50-200*	Fossil fuel combustion, deforestation, cement production	1
methane CH_4	700 ppb	1760 ppb	12	Rice paddies, waste dumps, livestock	21
nitrous oxide N_2O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310
CFC-12 CCl_2F_2	0	0.56 ppb	102	Liquid coolants, foams	8100

*A single value for the atmospheric lifetime of CO_2 is not possible. Removal mechanisms take place at different rates. The range given is an estimate based on several removal mechanisms.

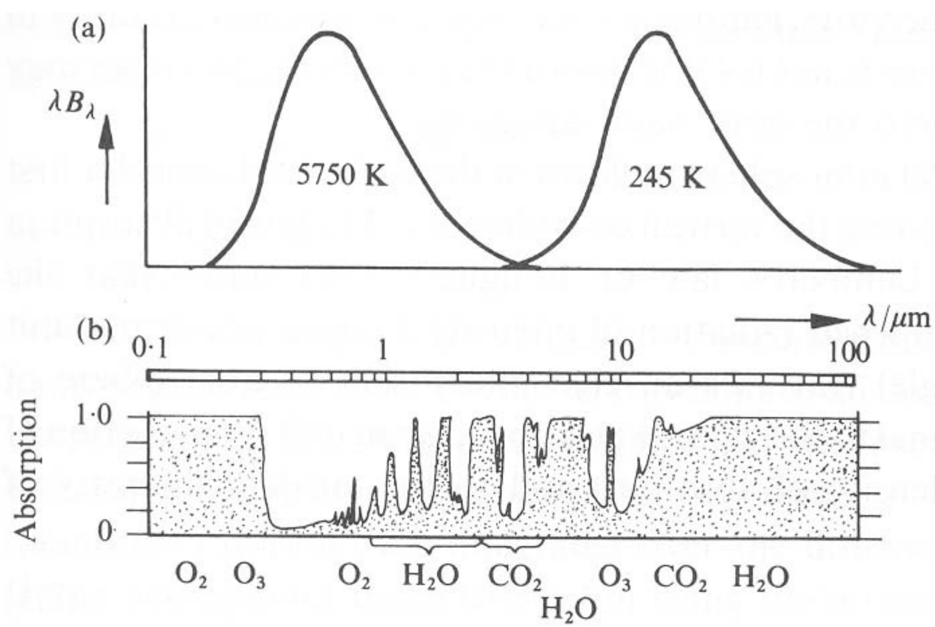
Chapter 3, *Chemistry in Context*

100 year time horizon

Some GHGs are much more effective than others, in terms of GWP (i.e., perturbation of RF per mass)

Atmospheric Radiation

- Solar irradiance (downwelling) at top of atmosphere occurs at wavelengths between ~200 and 2000 nm (~5750 K "black body" temperature)
- Thermal irradiance (upwelling) at top of the atmosphere occurs at wavelengths between ~5 and 50 μm (~245 K "black body" temperature for Earth's atmosphere)



Panel (a): Curves of black-body energy versus wavelength for 5750 K (Sun's approximate temperature) and for 245 K (Earth's mean temperature). The curves are drawn with equal area since, integrated over the entire Earth at the top of the atmosphere, the solar (downwelling) and terrestrial (upwelling) fluxes must be equal.

Panel (b): absorption by atmospheric gases for a clear vertical column of the atmosphere (1.0 represents complete absorption).

From Houghton, *Physics of Atmospheres*, 1991

- Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration of electrons) of molecules
- Absorption and re-emission in the IR occurs due to changes in vibrational and rotational states of molecules with electric dipole moments

Radiation & Molecules

Radiation can induce photo-dissociation (Mar 10 lecture), vibration, and rotation of molecules.

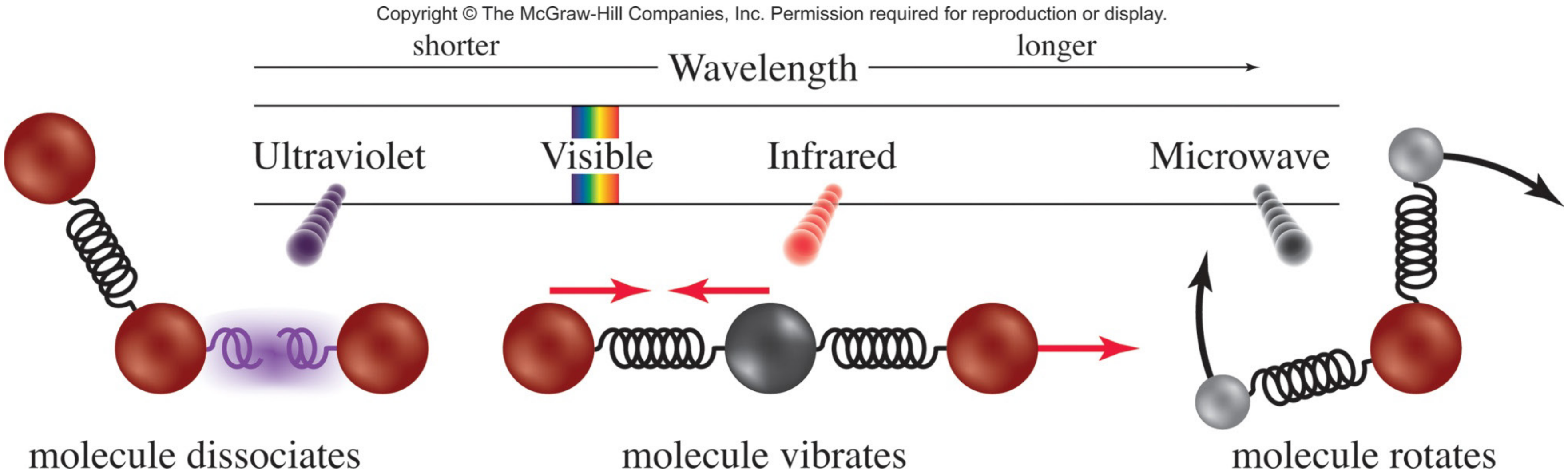


Fig 3.19, Chemistry in Context

Radiation & Molecules

Radiation can induce photo-dissociation (Mar 10 lecture), **vibration**, and rotation of molecules.

Thermal IR radiation is not energetic enough to break molecular bonds (i.e., photo-dissociate). Upon absorption, thermal IR will increase the vibrational energy of a molecule

CO_2 (linear molecule) has 4 vibrational modes (see below): for molecules vibrational frequencies are quantized. That is, only certain energies for the system are allowed. Most importantly, only photons with certain wavelengths (energies) will excite molecular vibrations.

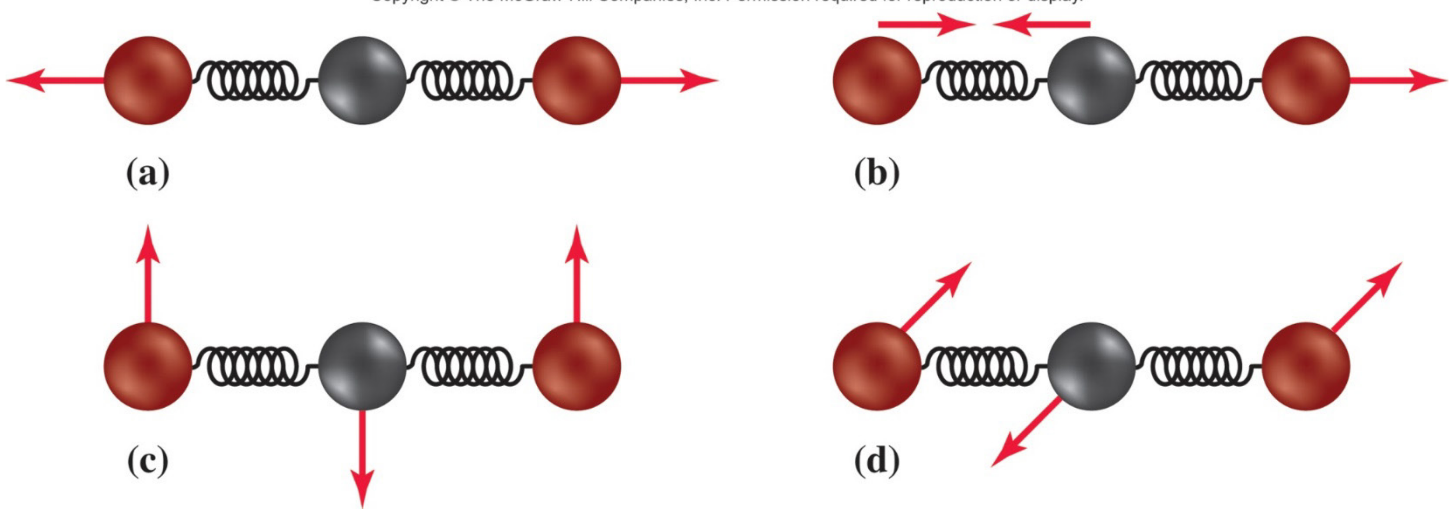


Fig 3.16, Chemistry in Context

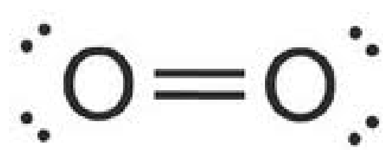
Excitation of Molecules

A greenhouse gas must have either

- naturally occurring **dipole moment**
- exhibit a **dipole moment** during vibration

Dipole moment ⇨ product of magnitude of charges & distance of separation between charges:
i.e., a molecule is said to have a dipole moment if it has a non-zero spatial distribution of charge

No dipole moment, either naturally or during vibration:



Excitation of Molecules

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Dipole moment ⇨ product of magnitude of charges & distance of separation between charges:
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spatial distribution of charge

CO_2 has ho natural dipole moment

$O^- — C^+ — O^-$

DP = 0

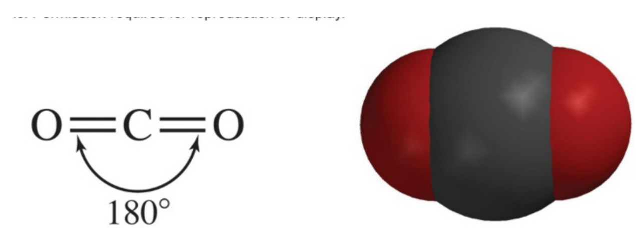

Fig 3.14, Chemistry in Context

Excitation of Molecules

A greenhouse gas must have either

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- exhibit a **dipole moment** during vibration

Dipole moment ⇨ product of magnitude of charges & distance of separation between charges: i.e., a molecule is said to have a dipole moment if it has a non-zero spatial distribution of charge

Symmetric Stretch: no dipole moment

Symmetric stretch

$O^- — C^+ — O^-$

$O^- —— C^+ —— O^-$

DP = 0

Excitation of Molecules

A greenhouse gas must have either

- naturally occurring **dipole moment**
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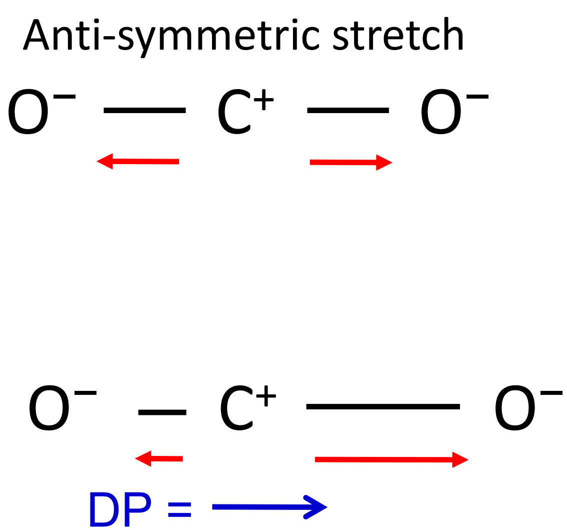
Anti-symmetric Stretch: *dipole moment*



Excitation of Molecules

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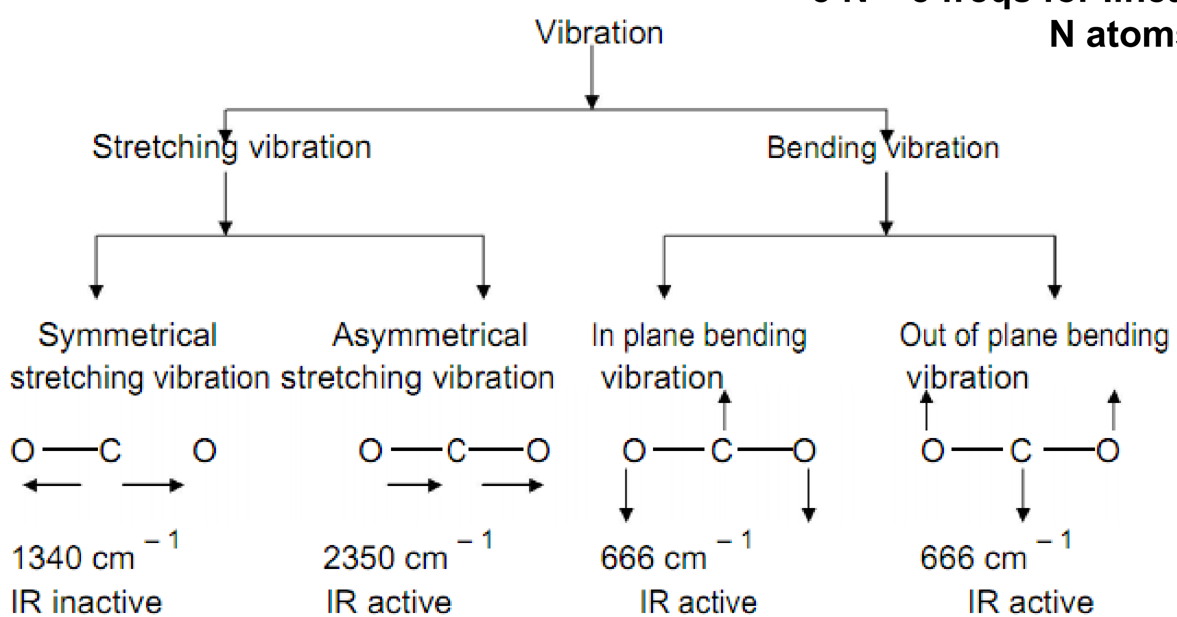
Dipole moment ⇨ product of magnitude of charges & distance of separation between charges: i.e., a molecule is said to have a dipole moment if it has a non-zero spatial distribution of charge

3 N – 5 freqs for linear molecules, N atoms: 4 freqs for CO_2



http://www.vidyarthiplus.in/2013/12/cy6151-engineering-chemistry-1.html#.VOUqai4RXIY

Excitation of Molecules

Wavenumber = 1 / Wavelength

1 / 2350 cm^{-1} = 4.25×10^{-4} cm = 4.25×10^{-6} m = 4.25 μm
1 / 666 cm^{-1} = 1.50×10^{-3} cm = 15.0×10^{-6} m = 15.0 μm

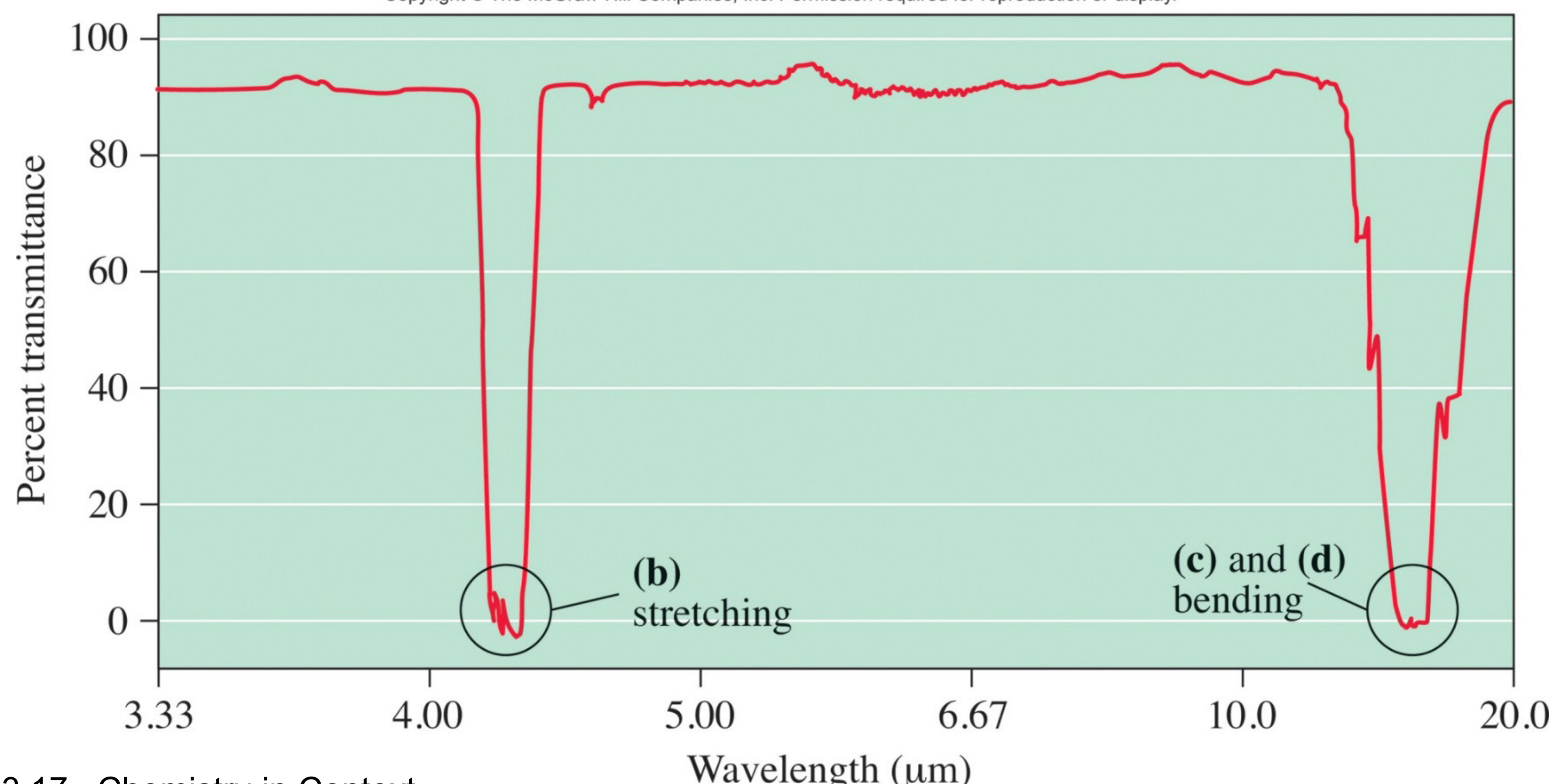


Fig 3.17, Chemistry in Context

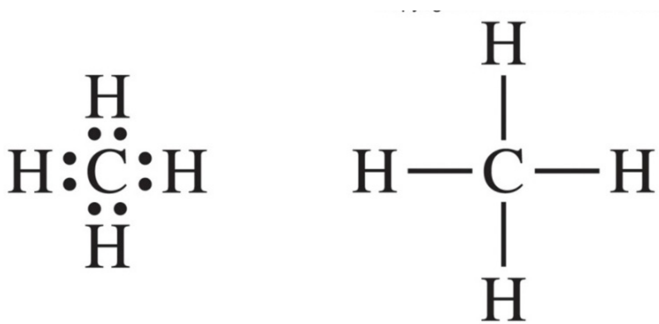
Excitation of Molecules

A greenhouse gas must have either

- naturally occurring **dipole moment**
- exhibit a **dipole moment** during vibration

Dipole moment ⇨ product of magnitude of charges & distance of separation between charges:
i.e., a molecule is said to have a dipole moment if it has a non-zero spatial distribution of charge

CH_4 also has no natural dipole moment: charge is uniformly distributed



Figs 3.10 & 3.11, Chemistry in Context

Excitation of Molecules

A greenhouse gas must have either

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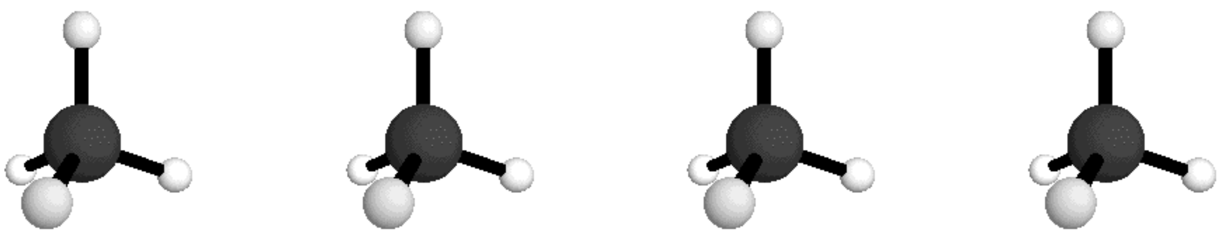
Dipole moment ⇨ product of magnitude of charges & distance of separation between charges: i.e., a molecule is said to have a dipole moment if it has a non-zero spatial distribution of charge

CH_4 has 4 unique vibrational modes, 2 of which interact with the IR field



#1	#2	#3	#4
3.3 μm	6.3 μm	3.2 μm	7.6 μm

http://www2.ess.ucla.edu/~schauble/MoleculeHTML/CH4_html/CH4_page.html

Excitation of Molecules

A greenhouse gas must have either

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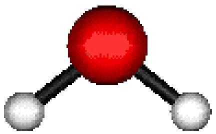
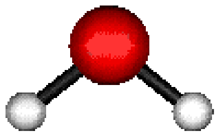
Dipole moment ⇨ product of magnitude of charges & distance of separation between charges: i.e., a molecule is said to have a dipole moment if it has a non-zero spatial distribution of charge

H_2O has a natural dipole moment (bent molecule) and absorbs in three spectral regions:



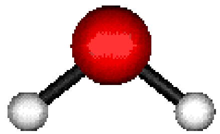
2.5 μm

Asymmetric Stretch



2.6 μm

Symmetric Stretch



6.1 μm

Bending Mode

http://www2.ess.ucla.edu/~schauble/MoleculeHTML/H2O_html/H2O_page.html

Excitation of Molecules

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Dipole moment ⇨ product of magnitude of charges & distance of separation between charges: i.e., a molecule is said to have a dipole moment if it has a non-zero spatial distribution of charge

N_2O also has a natural dipole moment (since it is an asymmetric molecule) and also absorbs in three spectral regions:

4.5 μm

7.8 μm

17.0 μm

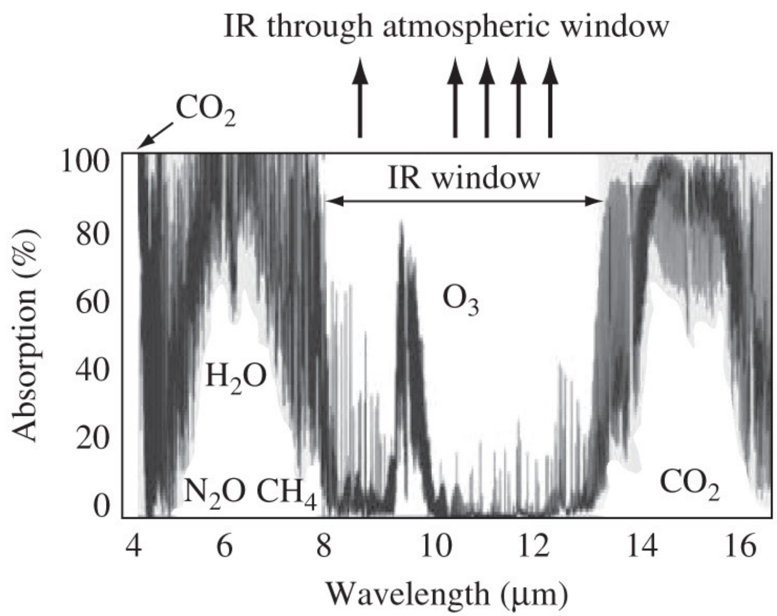
http://www2.ess.ucla.edu/~schauble/MoleculeHTML/N2O_html/N2O_page.html

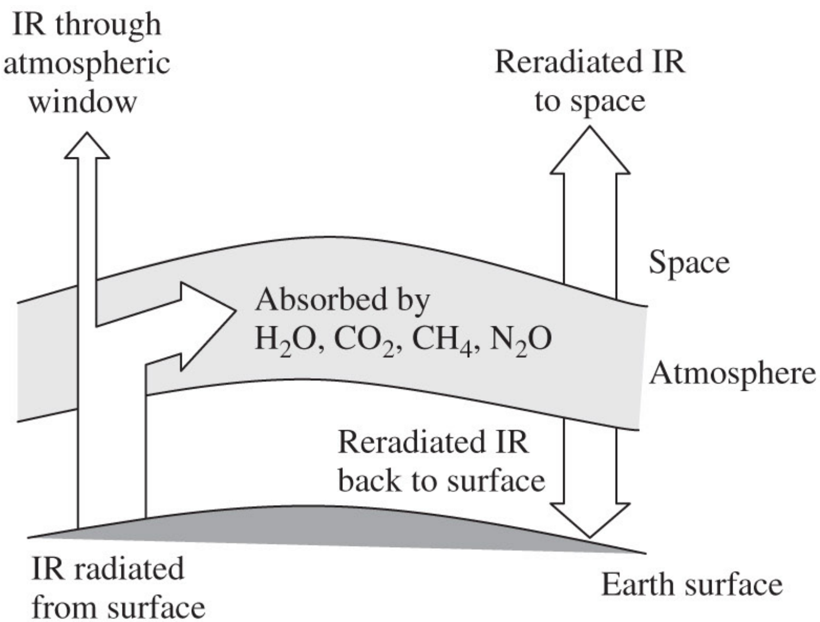
The Greenhouse Effect

Molecules of that absorb specific wavelengths of IR energy experience different fates:

- **Some hold that extra energy for a brief time, then re-emit it in all directions as heat.**
- **Others collide with atmospheric molecules such as N_2 and O_2 and transfer the absorbed energy to those molecules, as heat**

Both processes "trap" radiation emitted by the Earth; this trapping of energy heats the lower atmosphere and surface

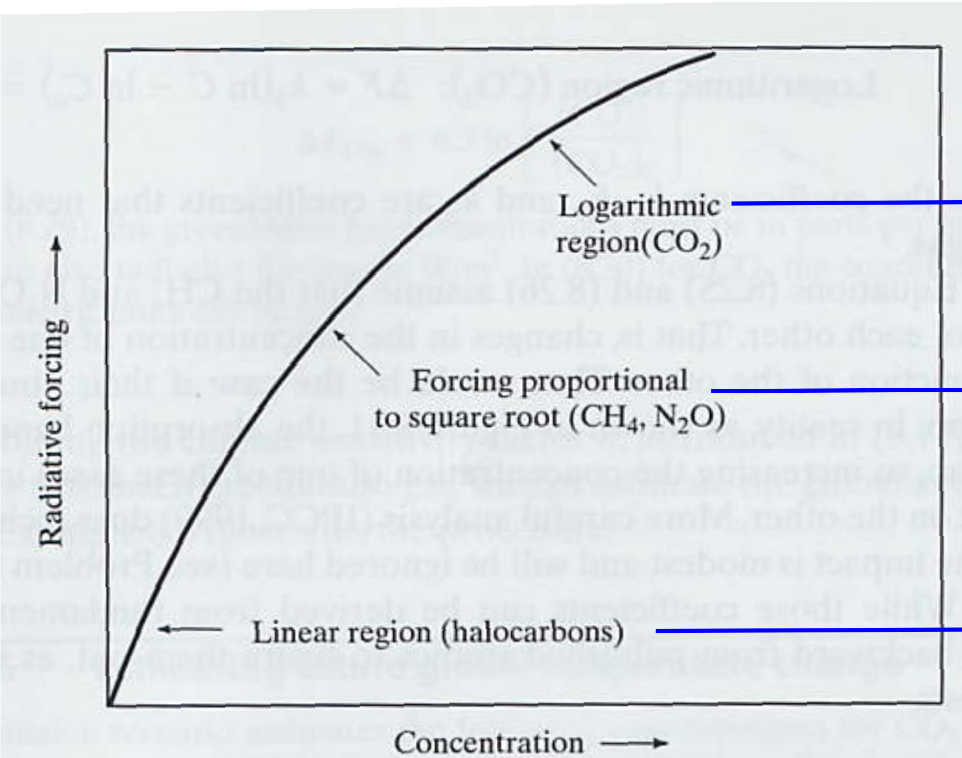




Masters, Intro. to Environmental Engineering and Science, 3d ed.

See Chapter 3.4 by Dan Kirk-Davidoff,
in *Green Chemistry: An Inclusive Approach*, 2018
in Additional Readings for a simple, differential equation description of the GHG effect based on a so-called two layer model.

How does RF change with concentration?



Masters, Introduction to Environmental Engineering and Science, 1998

Wigley (1987)

$$\Delta RF = \alpha \ln\left(\frac{C}{C_o}\right)$$

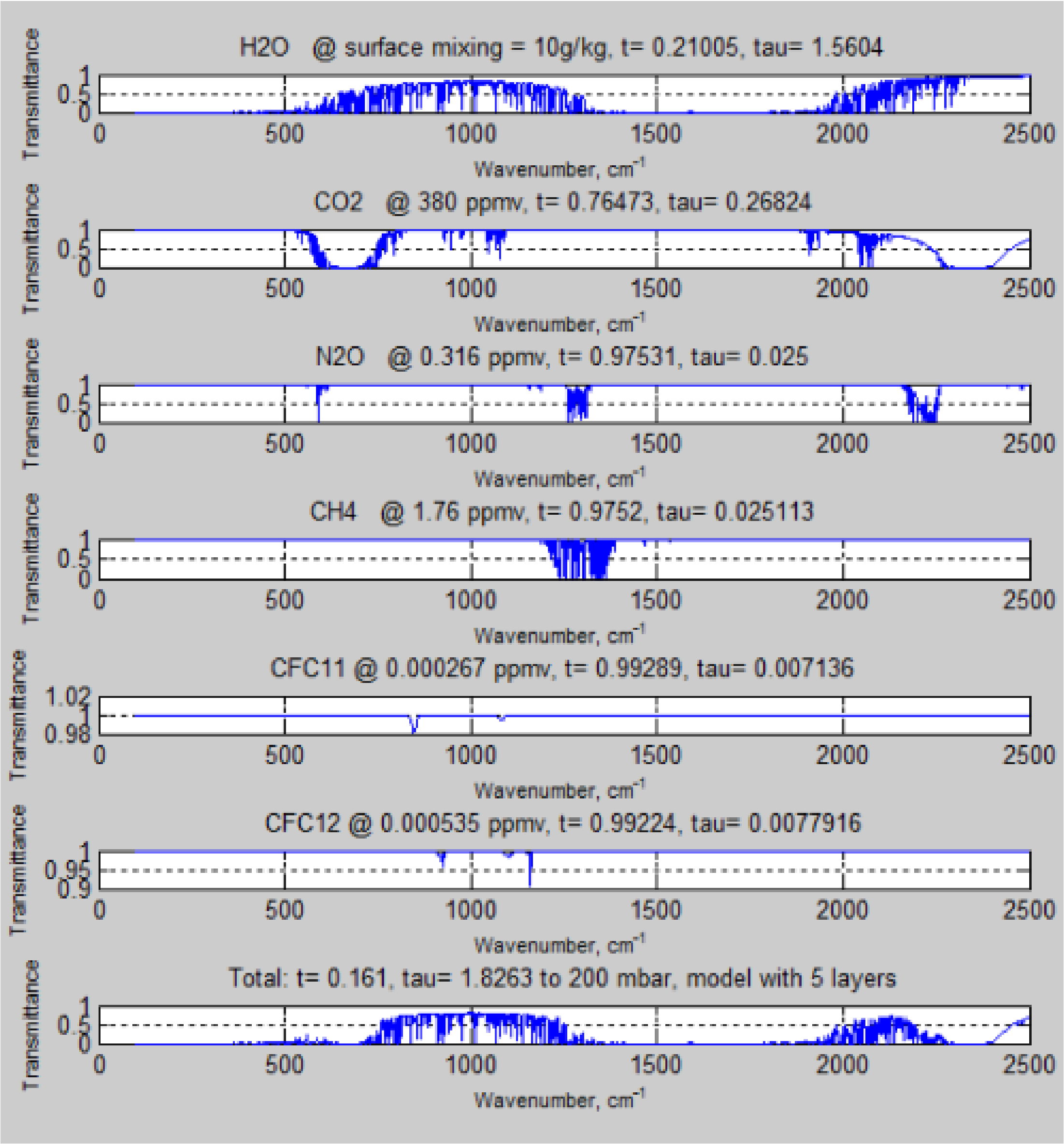
$$\Delta RF = \alpha\left(\sqrt{C} - \sqrt{C_o}\right)$$

$$\Delta RF = \alpha\left(C - C_o\right)$$

Effectiveness of a GHG depends on “saturation” of absorption band.

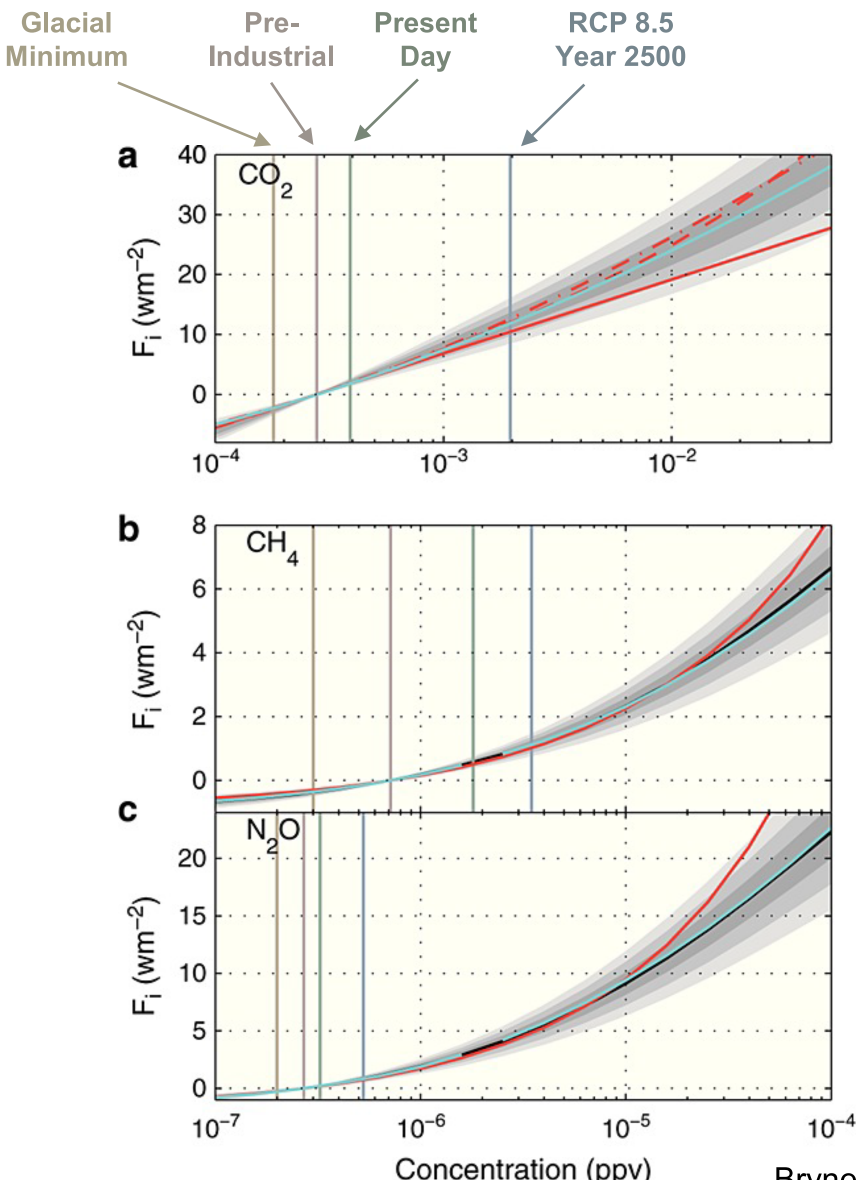
Highly saturated (most of the outgoing radiation is already absorbed) bands are less sensitive to increases in GHG concentration than partially or non saturated bands.

How does RF change with concentration?



https://scienceofdoom.com/2011/05/28/the-mystery-of-tau-–-miskolczi-part-six-minor-ghgs

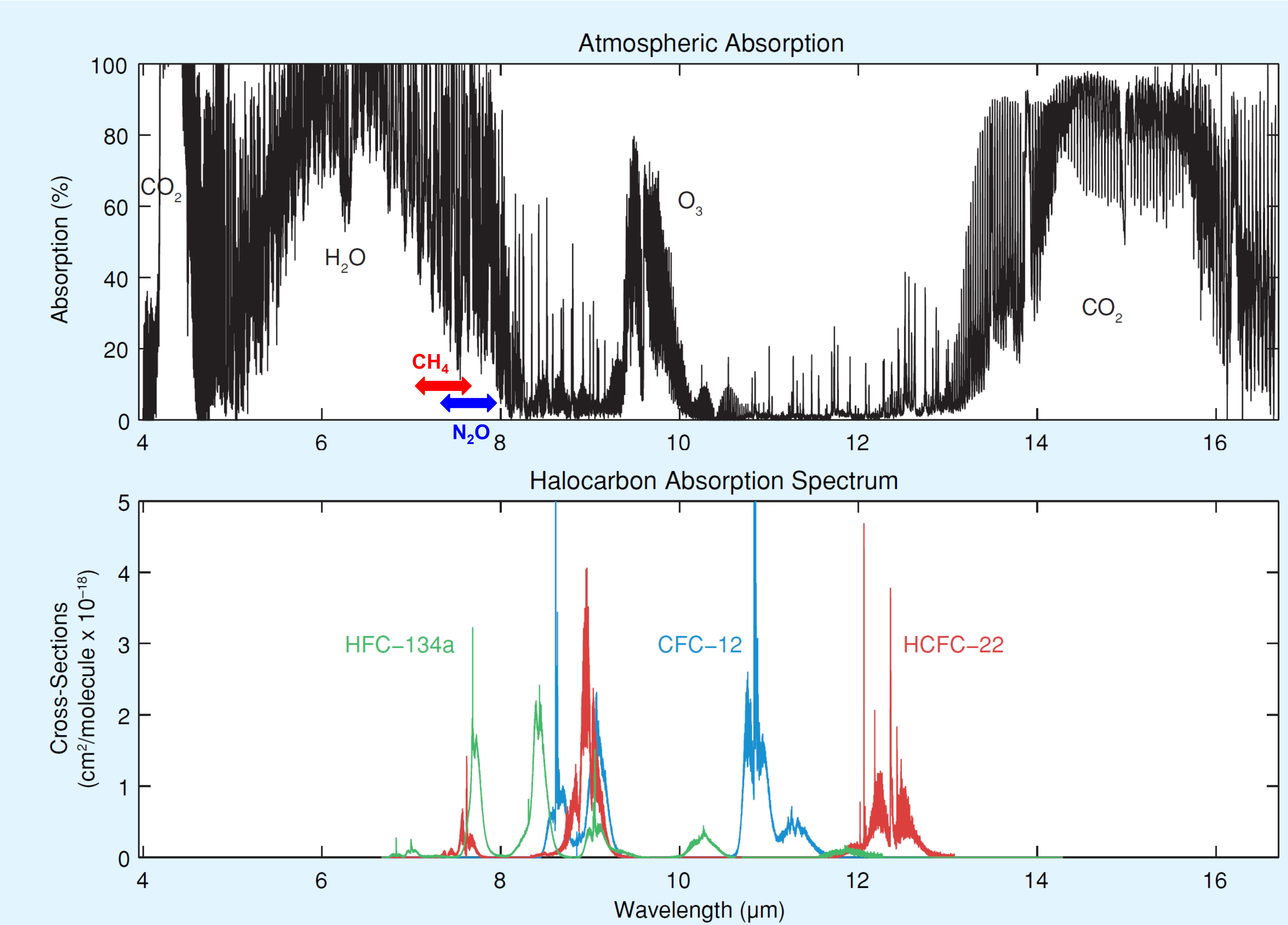
How does RF change with concentration?



- Black line is calculated RF using the Spectral Mapping for Atmospheric Radiative Transfer (SMART) radiative transfer code
- Light and dark grey show 1σ & 2σ uncertainties
- Cyan line is "fit" to the results
- Red lines are older fits from various IPCC and WMO/UNEP Ozone Depletion Reports

Bryne and Goldblatt, JGR, 2013
https://agupubs.onlinelibrary.wiley.com/doi/full/10.1002/2013GL058456

Absorption vs. Wavelength



How does RF change with concentration?

These formulae have been used for AR3 (IPCC, 2001), AR4 (IPCC, 2007) and AR5 (IPCC, 2013). AR6 (IPCC, 2021) uses slightly different, um more complicated formulae to compute values of ΔRF shown in the next slide. In Problem Set 2 (boo dat) we'll compute ΔRF using these formulae (for CO_2 and CH_4), and compare to the values shown in the AR6 figure that appears on the next slide.

$$\Delta\text{RF CO}_2 = 5.35 \ln\left(\frac{\text{C}}{\text{C}_\text{o}}\right) \text{ W m}^{-2}$$

$$\Delta\text{RF CH}_4 = 0.036 \left(\sqrt{\text{M}} - \sqrt{\text{M}_\text{o}}\right) - \left(f(\text{M, N}) - f(\text{M}_\text{o}, \text{N})\right) \text{W m}^{-2}$$

$$\Delta\text{RF N}_2\text{O} = 0.120 \left(\sqrt{\text{N}} - \sqrt{\text{N}_\text{o}}\right) - \left(f(\text{M, N}) - f(\text{M}, \text{N}_\text{o})\right) \text{W m}^{-2}$$

$$\Delta\text{RF CFC-11} = 0.25 \times \text{CFC-11 W m}^{-2} \quad \& \quad \Delta\text{RF CFC-12} = 0.32 \times \text{CFC-12 W m}^{-2}$$

where

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

C is mixing ratio of CO_2 in ppm

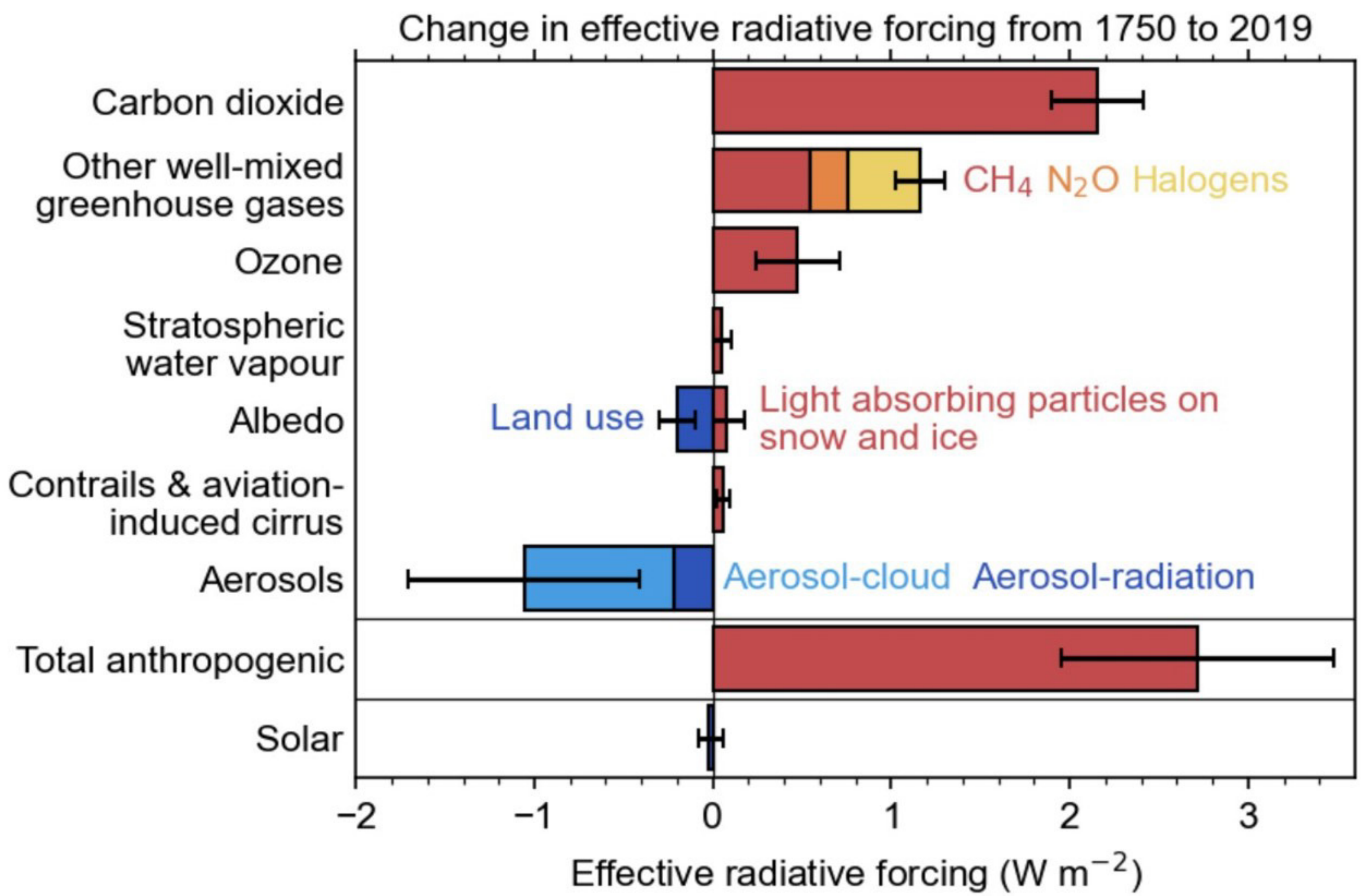
M is mixing ratio of CH_4 in ppb

N is mixing ratio of N_2O in ppb

CFC-11 and CFC-12 are mixing ratios of these species in ppb

& the subscript "o" refers to pre-industrial values of the respective mixing ratios

ΔRF of Climate



RF Due to Tropospheric Aerosols: Indirect Effect

Indirect Effects of Aerosols on Clouds

Anthropogenic aerosols lead to more cloud condensation nuclei (CCN)

Resulting cloud particles consist of smaller droplets, promoted by more sites (CCN) for cloud nucleation

The cloud that is formed is therefore brighter (reflects more sunlight) ⇨

Twomey effect, aka 1st Indirect Effect

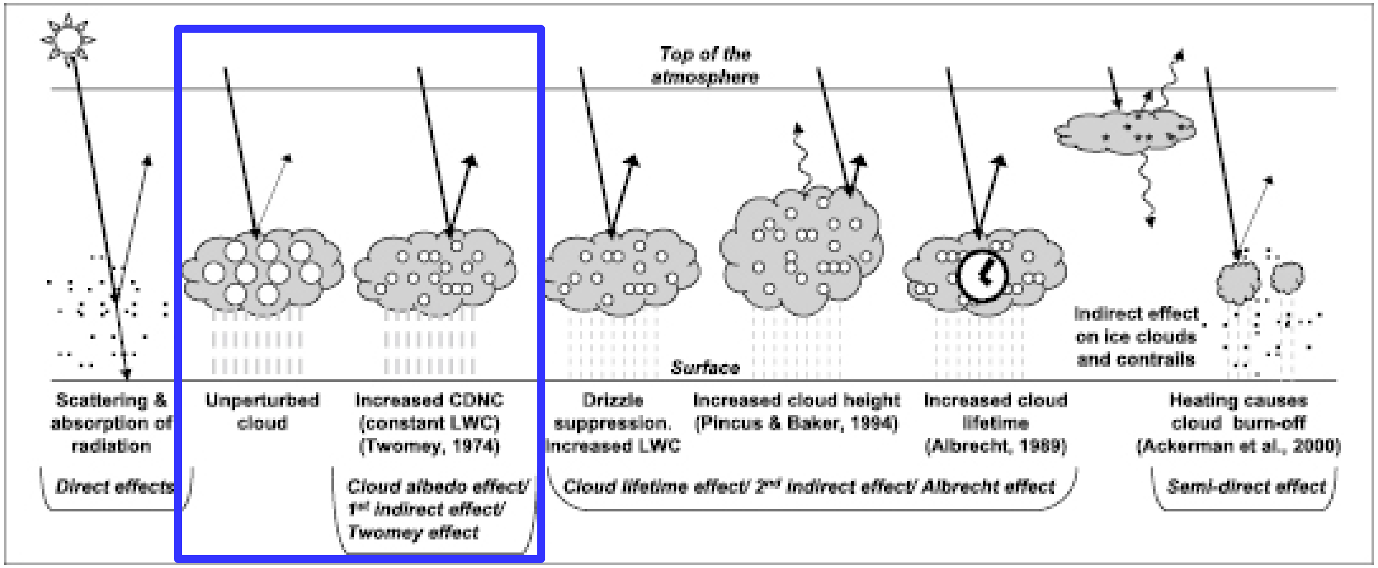


Fig 2-10, IPCC 2007

Large uncertainty in aerosol RF

- scatter and absorb radiation (**direct radiative forcing**)
- affect cloud formation (**indirect radiative forcing**)

RF Due to Tropospheric Aerosols: Indirect Effect

Indirect Effects of Aerosols on Clouds

Anthropogenic aerosols lead to more cloud condensation nuclei (CCN)

Resulting cloud particles consist of smaller droplets, promoted by more sites (CCN) for cloud nucleation

The cloud that is formed is therefore brighter (reflects more sunlight) ***and*** has less efficient precipitation, i.e. is longer lived) ⇨

Albrecht effect, aka 2nd Indirect Effect

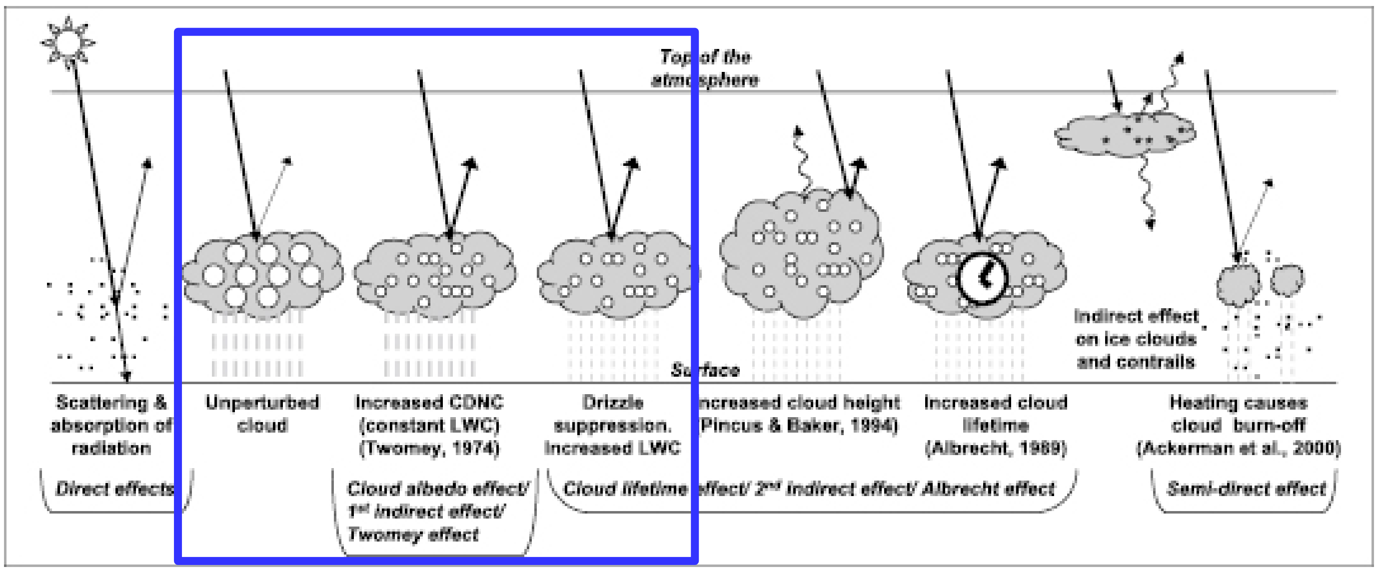
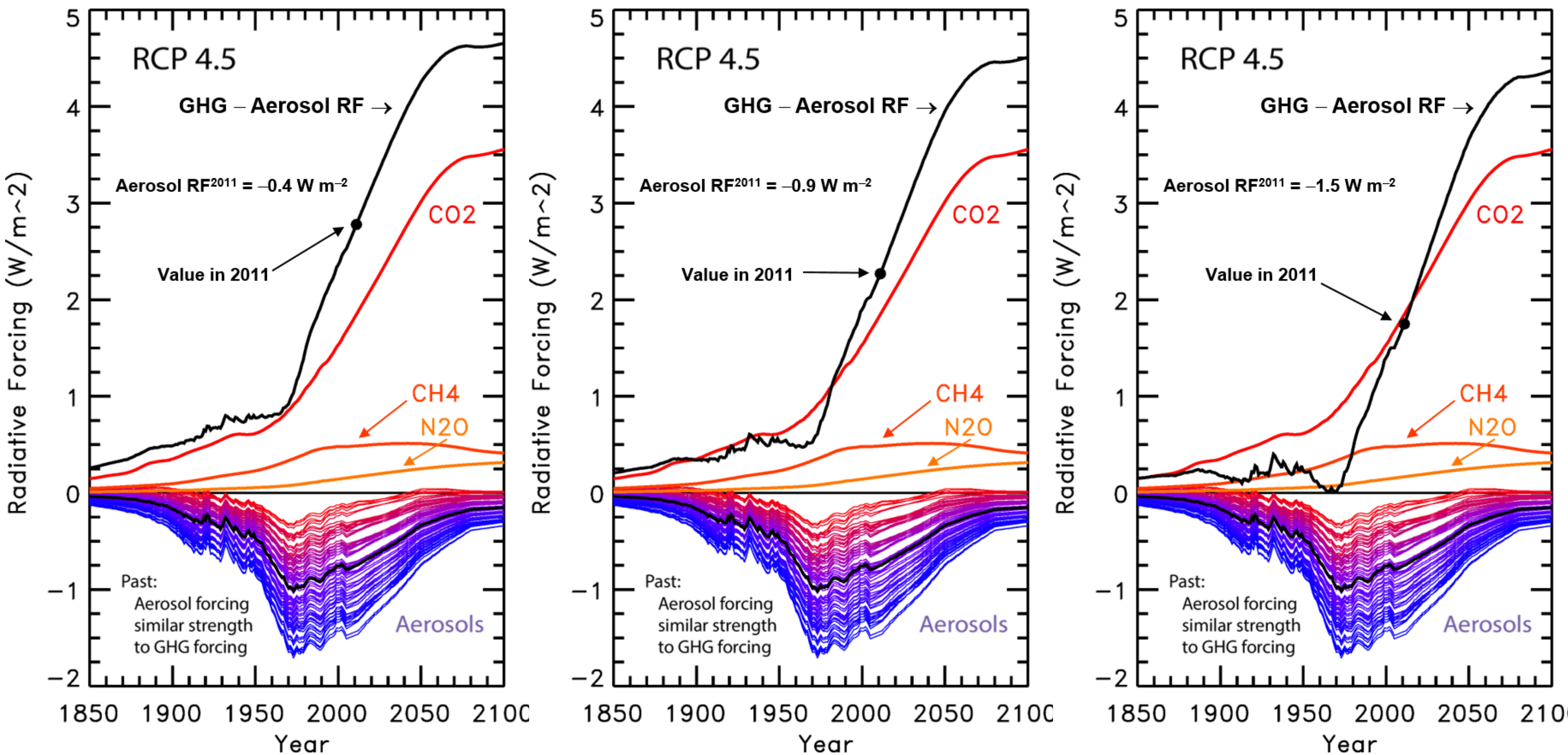


Fig 2-10, IPCC 2007

Large uncertainty in aerosol RF

- scatter and absorb radiation (**direct radiative forcing**)
- affect cloud formation (**indirect radiative forcing**)

Combining RF GHGs & Aerosols



Based upon Fig 1.10, *Paris, Beacon of Hope*

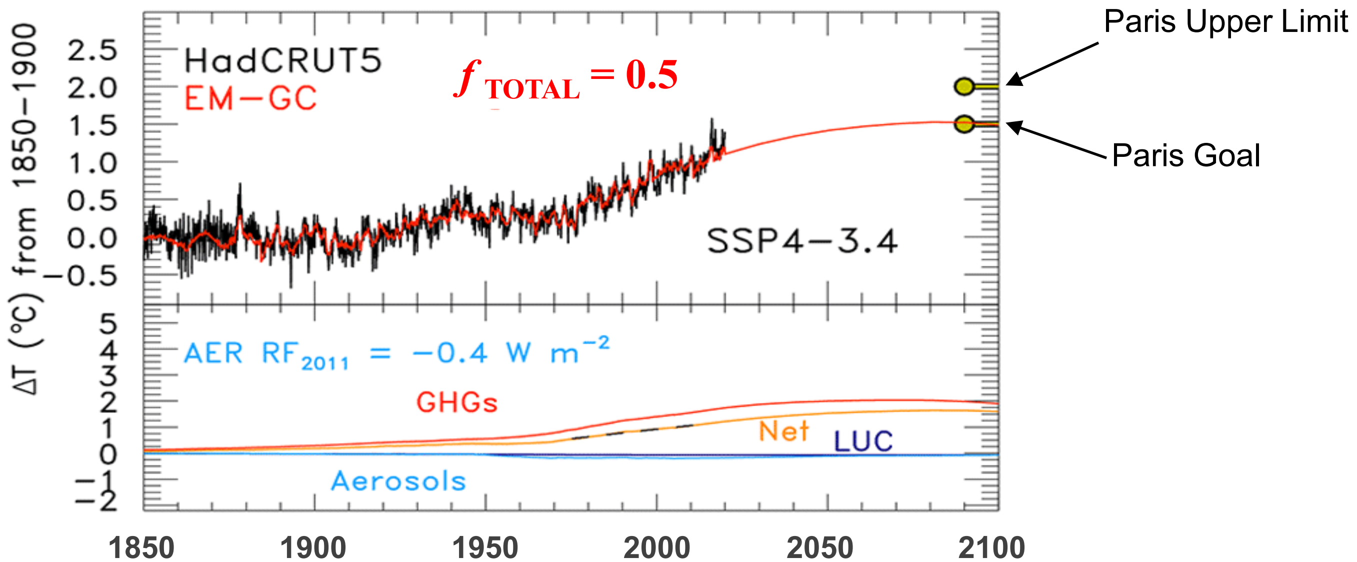
Uncertainty in RF of climate due to tropospheric aerosols is huge complication leading to fundamental uncertainty on forecasts of future global warming

$$\Delta T = \lambda_{Planck} \times (1 + f_{TOTAL}) \times \Delta RF - OHE$$

where:

f_{TOTAL} = feedbacks due to water vapor, clouds, lapse rate, etc

OHE = ocean heat export



McBride *et al.*, 2021
https://esd.copernicus.org/articles/12/545/2021

We assume that whatever value of climate feedback is inferred from the climate record will persist into the future. For Aerosol RF in 2011 of **–0.4 W m^{-2}** & assuming best estimate for H_2O and Lapse Rate feedback is correct, this simulation implies sum of other feedbacks (clouds, surface albedo) must be ***close to zero.***

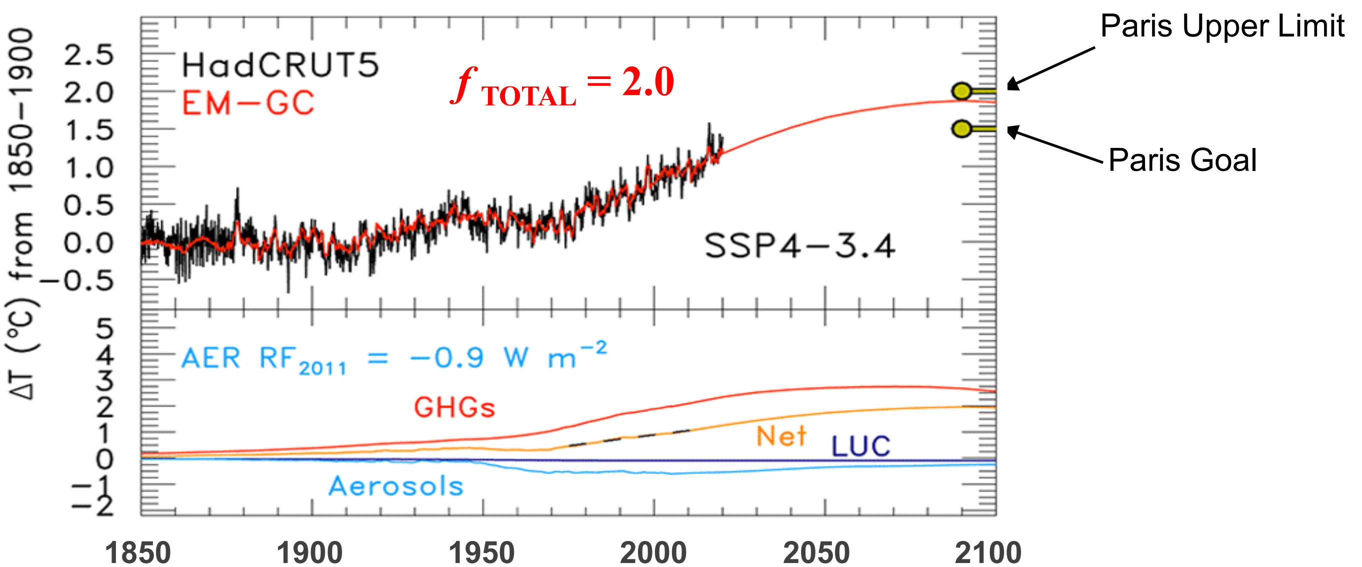
Uncertainty in RF of climate due to tropospheric aerosols is huge complication leading to fundamental uncertainty on forecasts of future global warming

$$\Delta T = \lambda_{\text{Planck}} \times (1 + f_{\text{TOTAL}}) \times \Delta RF - OHE$$

where:

f_{TOTAL} = feedbacks due to water vapor, clouds, lapse rate, etc

OHE = ocean heat export



McBride *et al.*, 2021

https://esd.copernicus.org/articles/12/545/2021

We assume that whatever value of climate feedback is inferred from the climate record will persist into the future. For Aerosol RF in 2011 of **−0.9 W m^{-2}** & assuming best estimate for H_2O and Lapse Rate feedback is correct, this simulation implies sum of other feedbacks (clouds, surface albedo) must be ***strongly positive***.

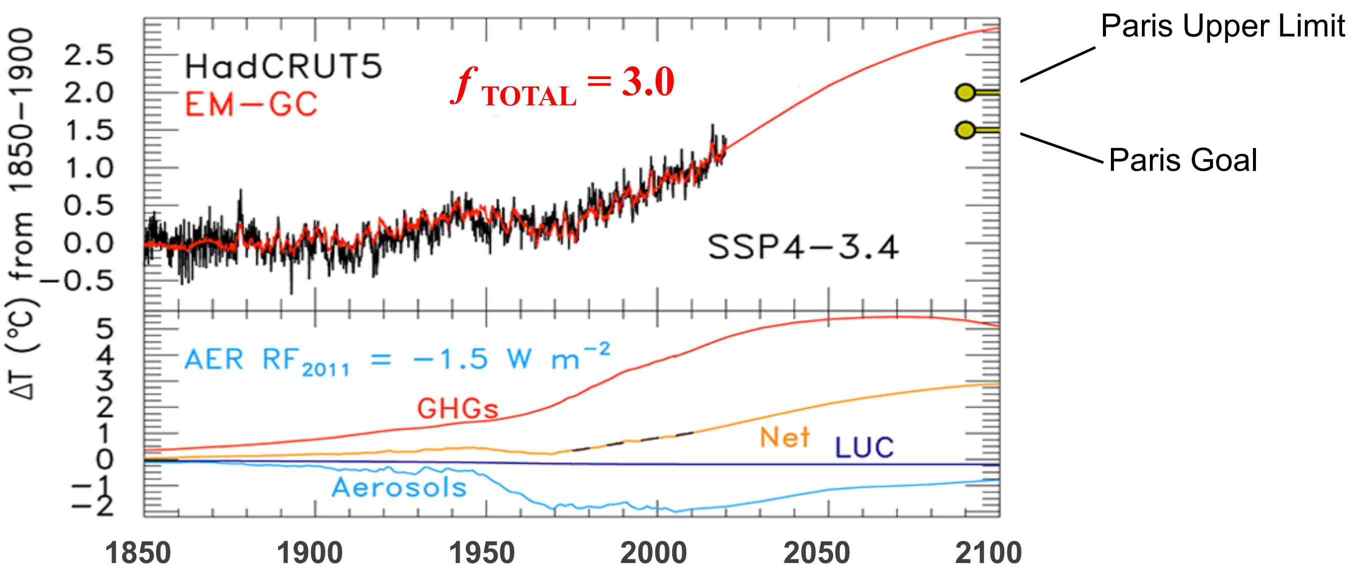
Uncertainty in RF of climate due to tropospheric aerosols is huge complication leading to fundamental uncertainty on forecasts of future global warming

$$\Delta T = \lambda_{Planck} \times (1 + f_{TOTAL}) \times \Delta RF - OHE$$

where:

f_{TOTAL} = feedbacks due to water vapor, clouds, lapse rate, etc

OHE = ocean heat export



McBride *et al.*, 2021
https://esd.copernicus.org/articles/12/545/2021

We assume that whatever value of climate feedback is inferred from the climate record will persist into the future. For Aerosol RF in 2011 of **−1.5 W m^{-2}** & assuming best estimate for H_2O and Lapse Rate feedback is correct, this simulation implies sum of other feedbacks (clouds, surface albedo) must be ***very strongly positive***.