

# Radiative Forcing

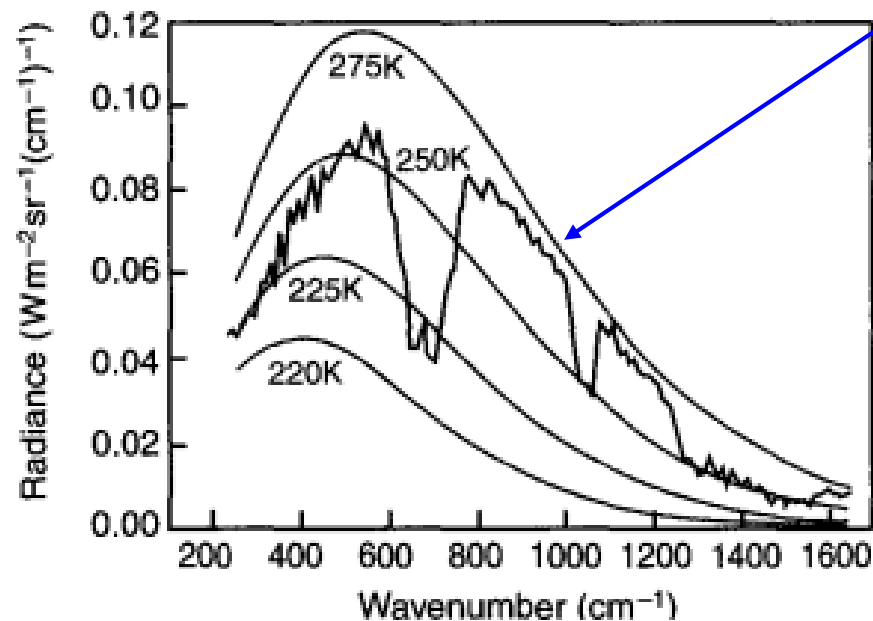
## AOSC 433/633 & CHEM 433

Pam Wales

### Goals:

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

Earth's radiance as viewed from space



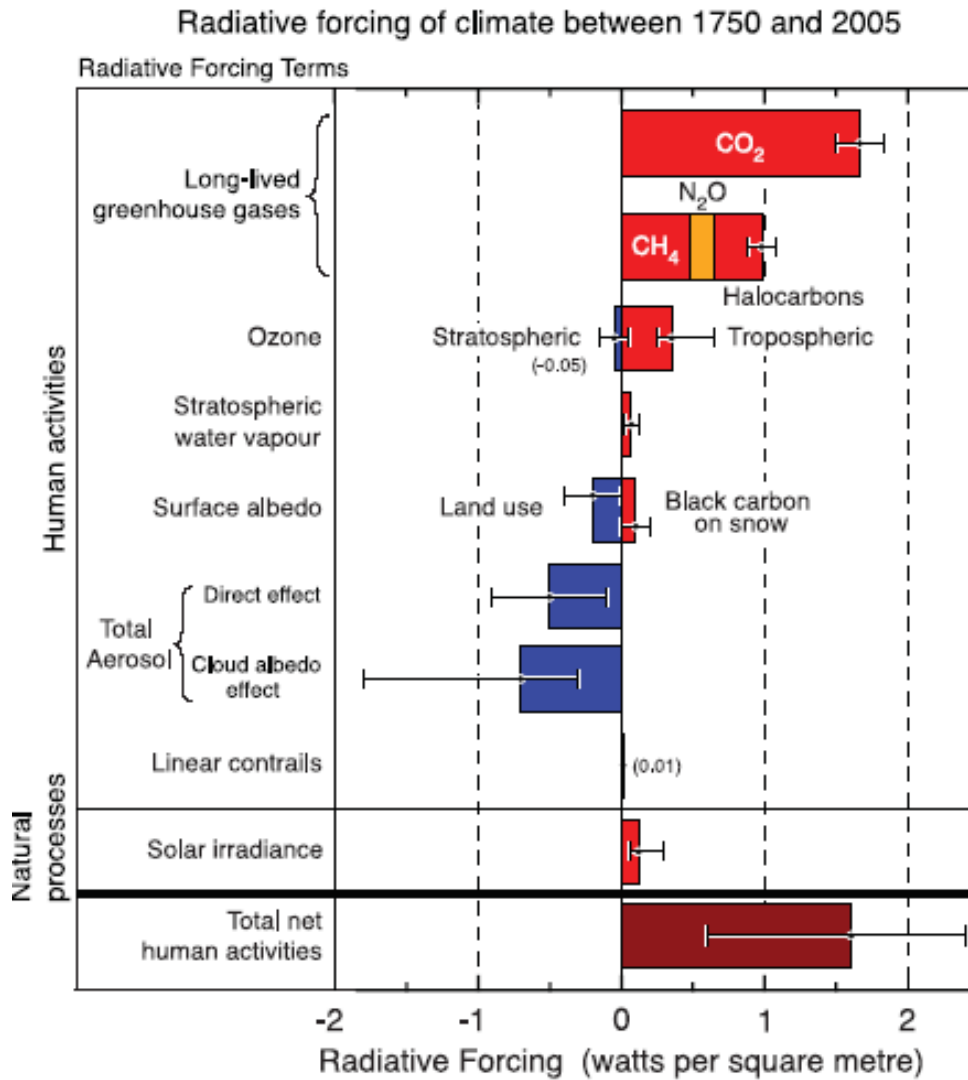
<https://scienceofdoom.files.wordpress.com/2010/03/radiation-earth-from-space-taylor-499px.png>

### Lecture 7, 16 February 2017

# Announcements

- Problem Set #1 review will be Monday, 20 Feb, at 6 pm
  - We will hand out solutions at the review ... hence no credit for P Set #1 if we do not have by start of this review
- Problem Set #2 due Thurs, 23 Feb; will review Mon, 27 Feb
- First exam is Tues, 28 Feb, in class:
  - Closed book, no calculator or e-device
  - Will focus on concepts rather than calculations
  - New exams every year; we will review prior exam in class on Thurs, 23 Feb to help you prepare

# Radiative Forcing of Climate, 1750 to 2005



How does radiative forcing relate to the abundance of GHGs?

Lecture 2

FAQ 2.1, Figure 2. Summary of the principal components of the radiative forcing of climate change. All these

# Global Warming Potential

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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 <sub>2</sub>	270 ppm	388 ppm	50-200*	Fossil fuel combustion, deforestation, cement production	1
methane CH <sub>4</sub>	700 ppb	1760 ppb	12	Rice paddies, waste dumps, livestock	21
nitrous oxide N <sub>2</sub> O	275 ppb	322 ppb	120	Fertilizers, industrial production, combustion	310
CFC-12 CCl <sub>2</sub> F <sub>2</sub>	0	0.56 ppb	102	Liquid coolants, foams	8100

\*A single value for the atmospheric lifetime of CO<sub>2</sub> 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*

## Lecture 6

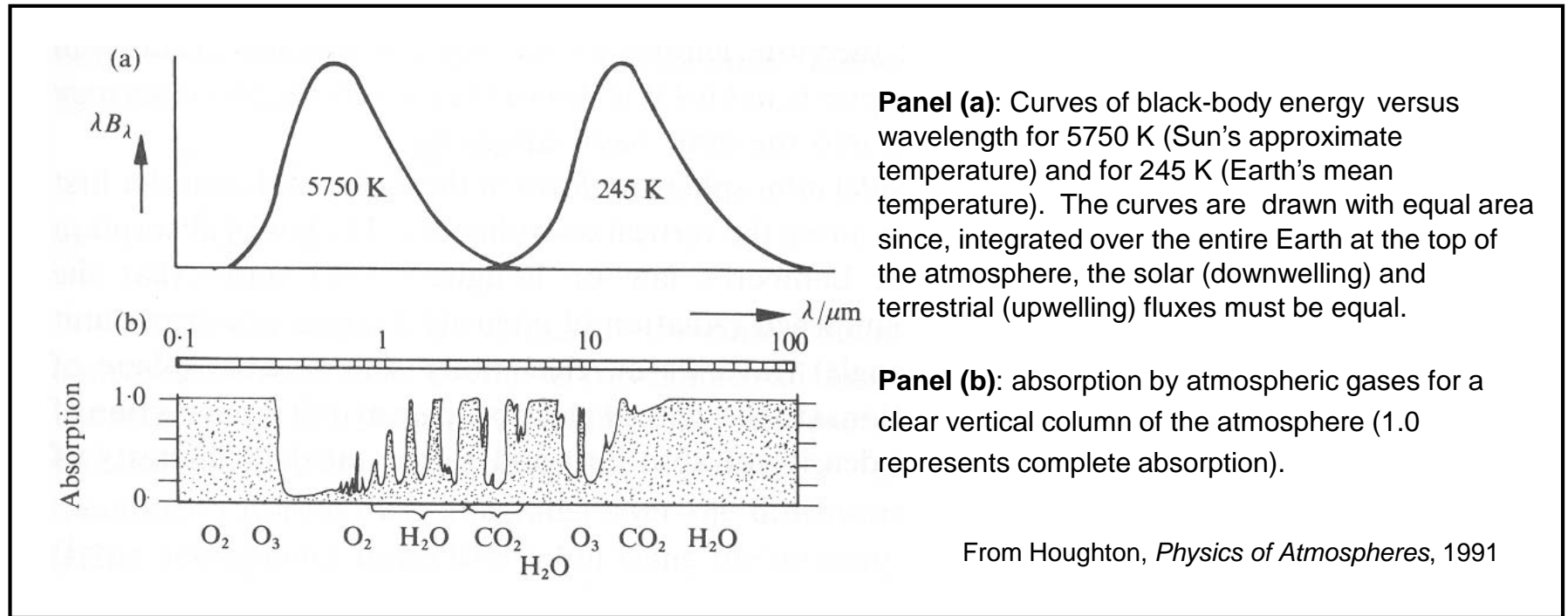
\_\_\_\_\_ year time horizon

**Why are some GHGs so much more effective than others, in terms of GWP (i.e., perturbation of RF per mass)?**

## Lecture 3

# 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  $\mu\text{m}$  (~245 K “black body” temperature)



- Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration) 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 (March 7 lecture), vibration, and rotation of molecules.

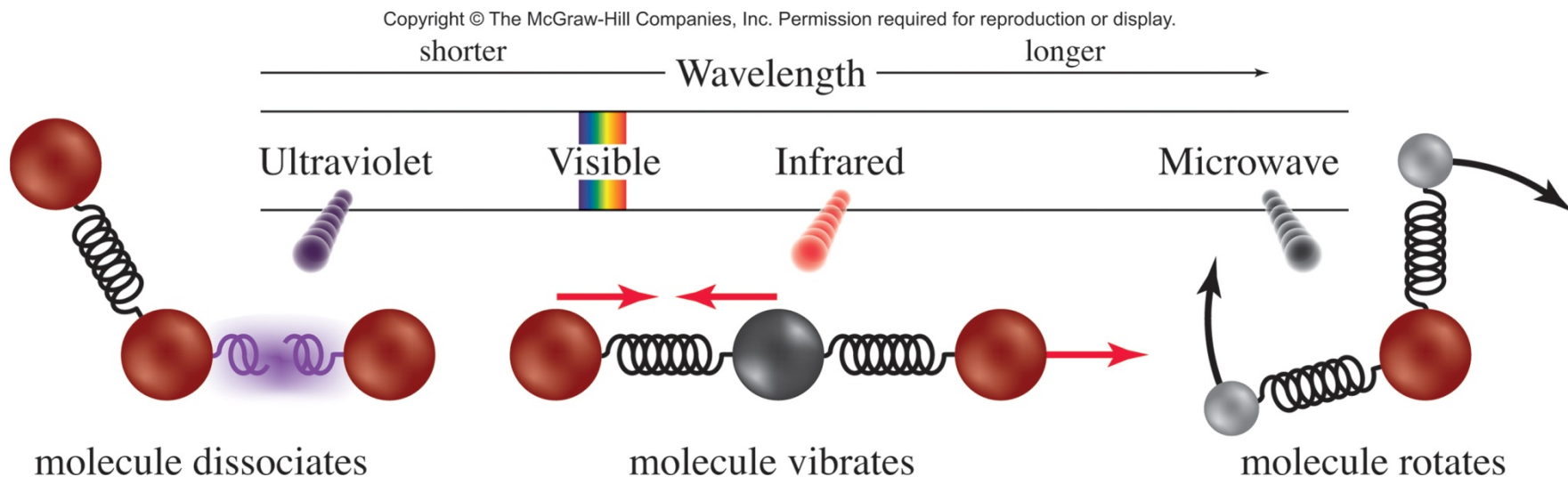


Fig 3.19, Chemistry in Context

# Radiation & Molecules

Radiation can induce photo-dissociation (March 7 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<sub>2</sub> (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.

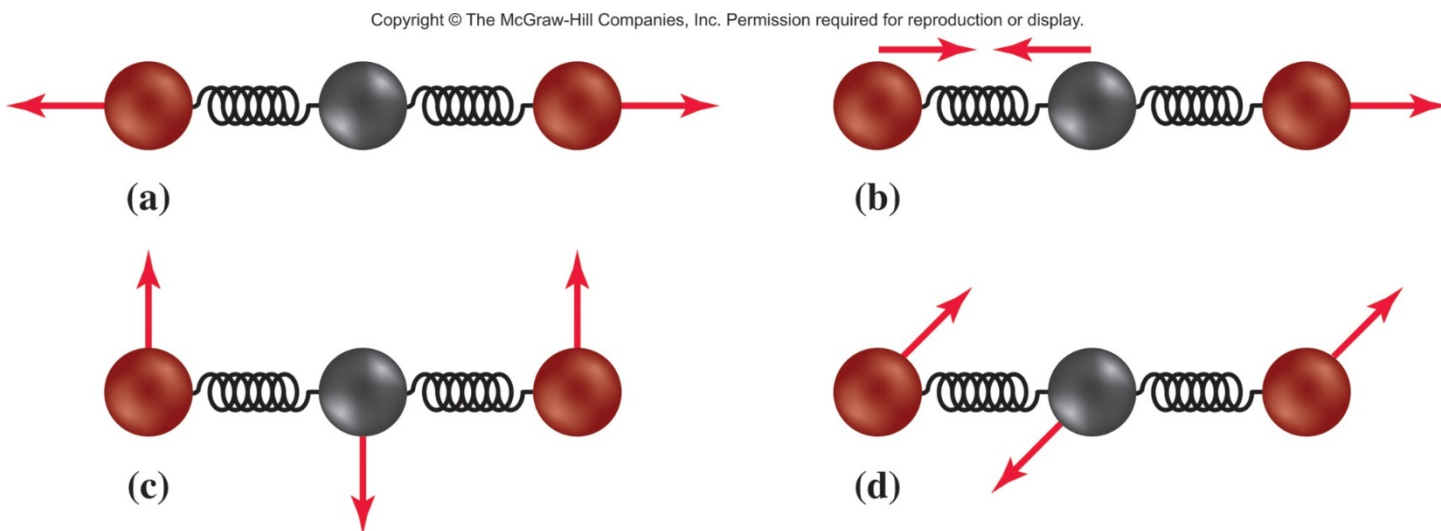


Fig 3.16, Chemistry in Context

# Excitation of Molecules

A greenhouse gas must have either

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

**Dipole moment**  $\Rightarrow$  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

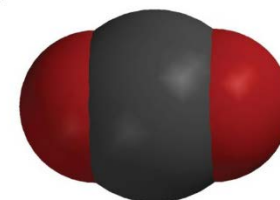
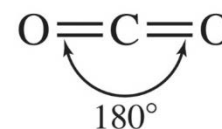
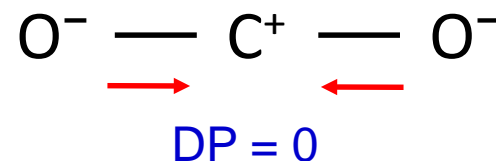
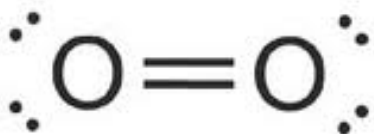


Fig 3.14, Chemistry in Context



# Excitation of Molecules

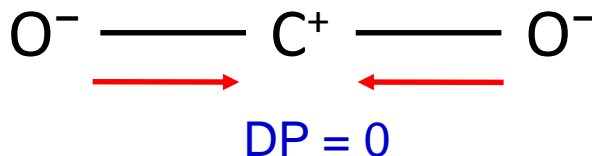
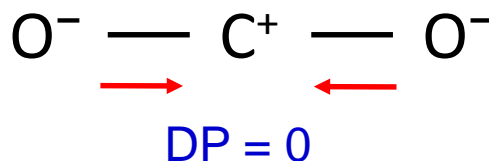
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## Symmetric Stretch: no dipole moment

Symmetric stretch



# Excitation of Molecules

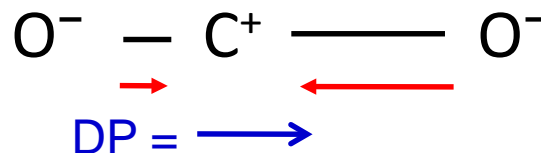
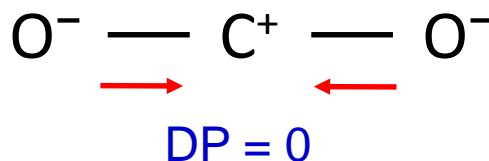
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## Anti-symmetric Stretch: dipole moment

Anti-symmetric stretch

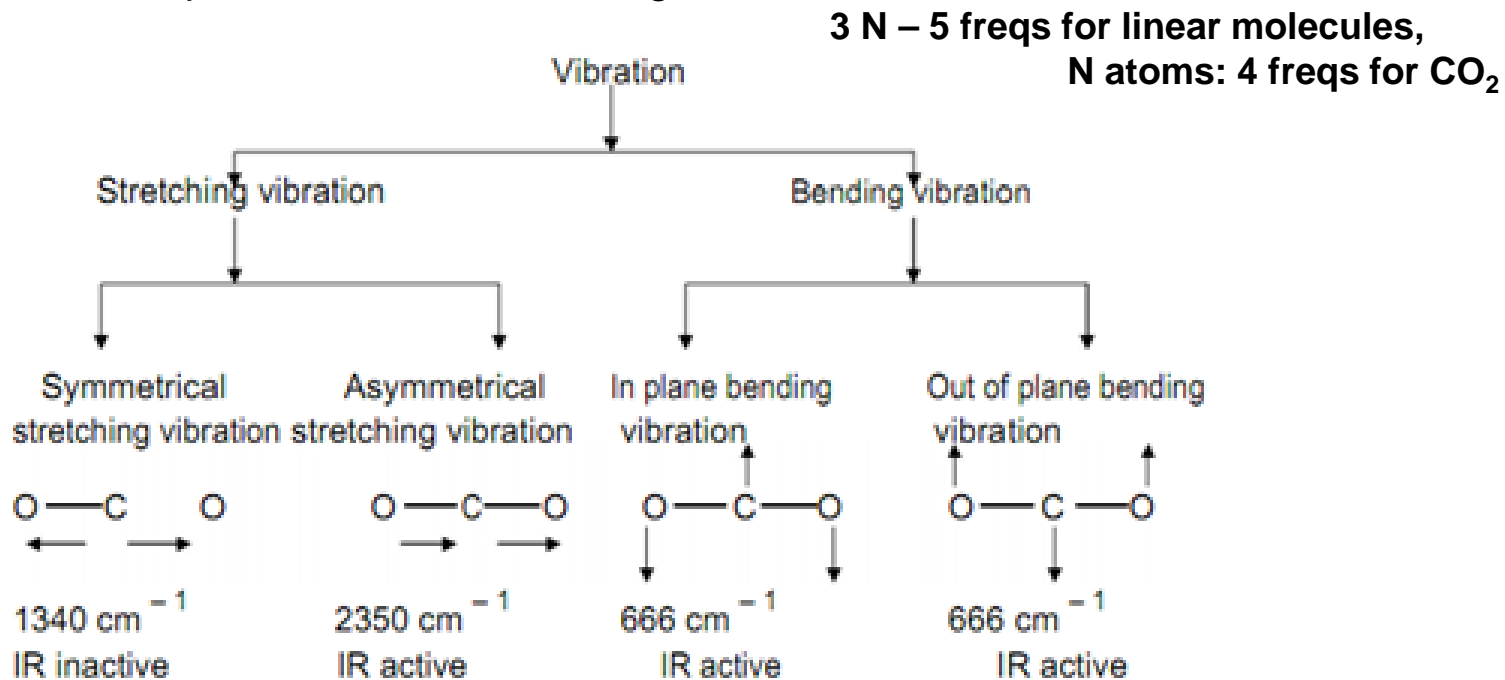


# Excitation of Molecules

A greenhouse gas must have either

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

# Excitation of Molecules

Wavenumber = 1 / Wavelength

$$1 / 2350 \text{ cm}^{-1} = 4.25 \times 10^{-4} \text{ cm} = 4.25 \times 10^{-6} \text{ m} = 4.25 \text{ } \mu\text{m}$$

$$1 / 666 \text{ cm}^{-1} = 1.50 \times 10^{-3} \text{ cm} = 15.0 \times 10^{-6} \text{ m} = 15.0 \text{ } \mu\text{m}$$

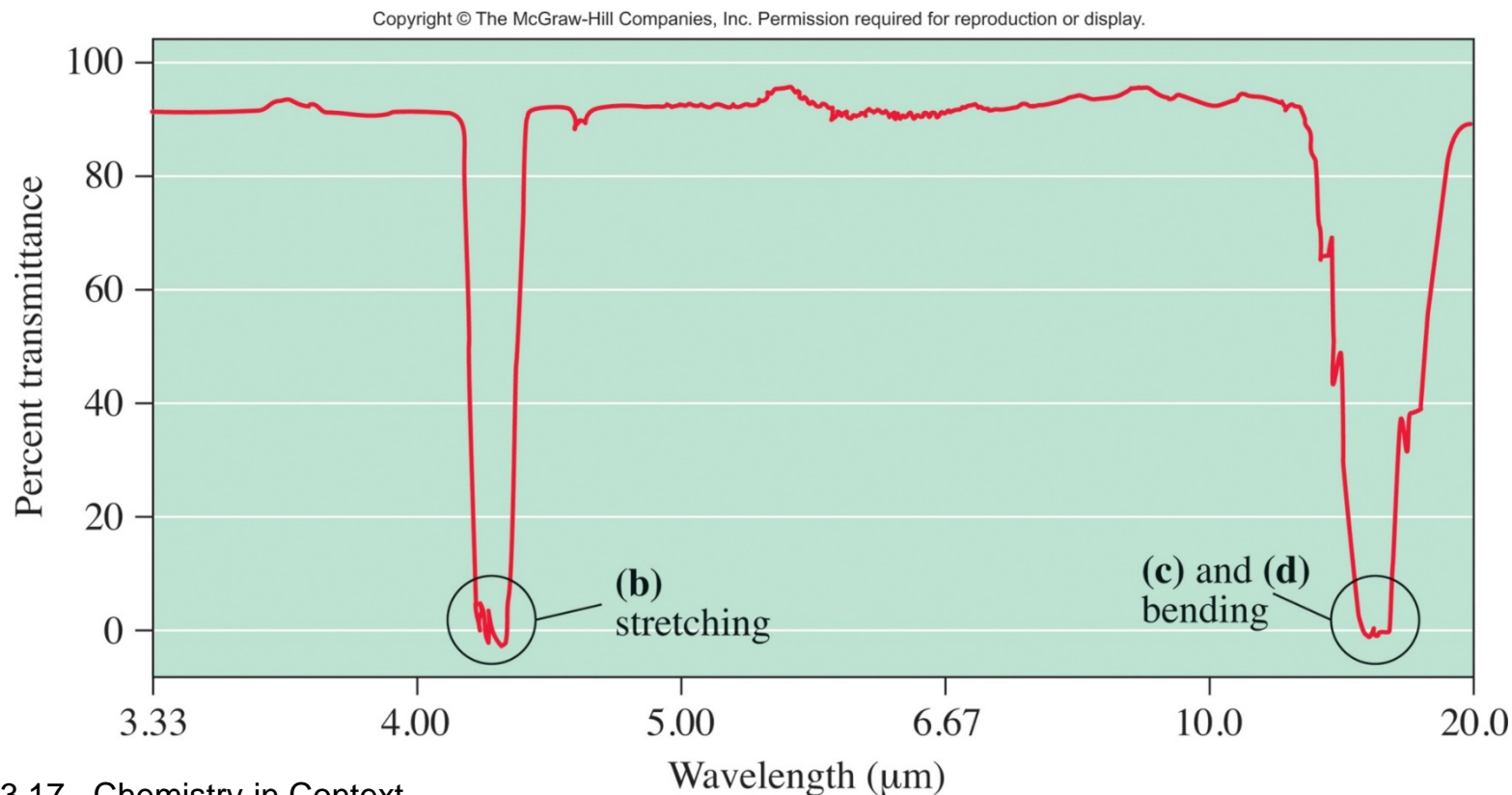


Fig 3.17, Chemistry in Context

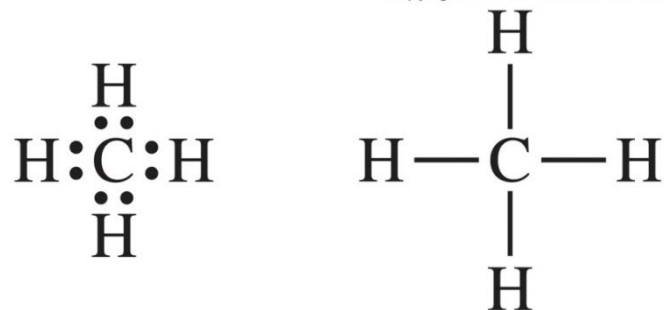
# Excitation of Molecules

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**CH<sub>4</sub> 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

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

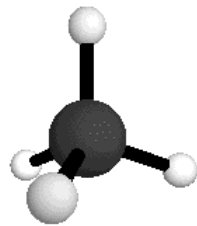
**Dipole moment**  $\Rightarrow$  product of magnitude of charges & distance of separation between charges:  
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**CH<sub>4</sub> has numerous vibrational modes, some of which interact with the IR field**

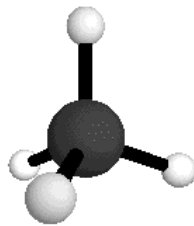
3 N – 6 freqs for non-linear molecules

Since CH<sub>4</sub> has 5 atoms, there are  $3 \times 5 - 6 = 9$  possible freqs

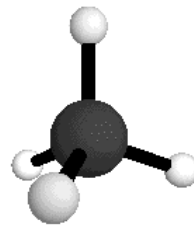
Due to the symmetry of the molecule, only 4 unique modes



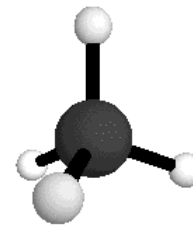
**#1**  
**3.31  $\mu\text{m}$**



**#2**  
**6.32  $\mu\text{m}$**



**#3**  
**3.17  $\mu\text{m}$**



**#4**  
**7.31  $\mu\text{m}$**

[http://www2.ess.ucla.edu/~schauble/MoleculeHTML/CH4\\_html/CH4\\_page.html](http://www2.ess.ucla.edu/~schauble/MoleculeHTML/CH4_html/CH4_page.html)

# Excitation of Molecules

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**H<sub>2</sub>O has a natural dipole moment !**

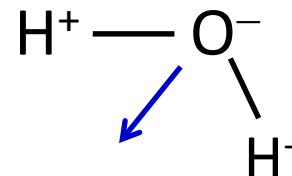
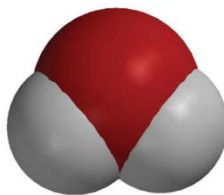
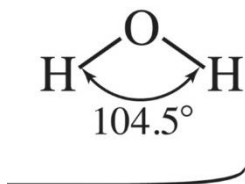
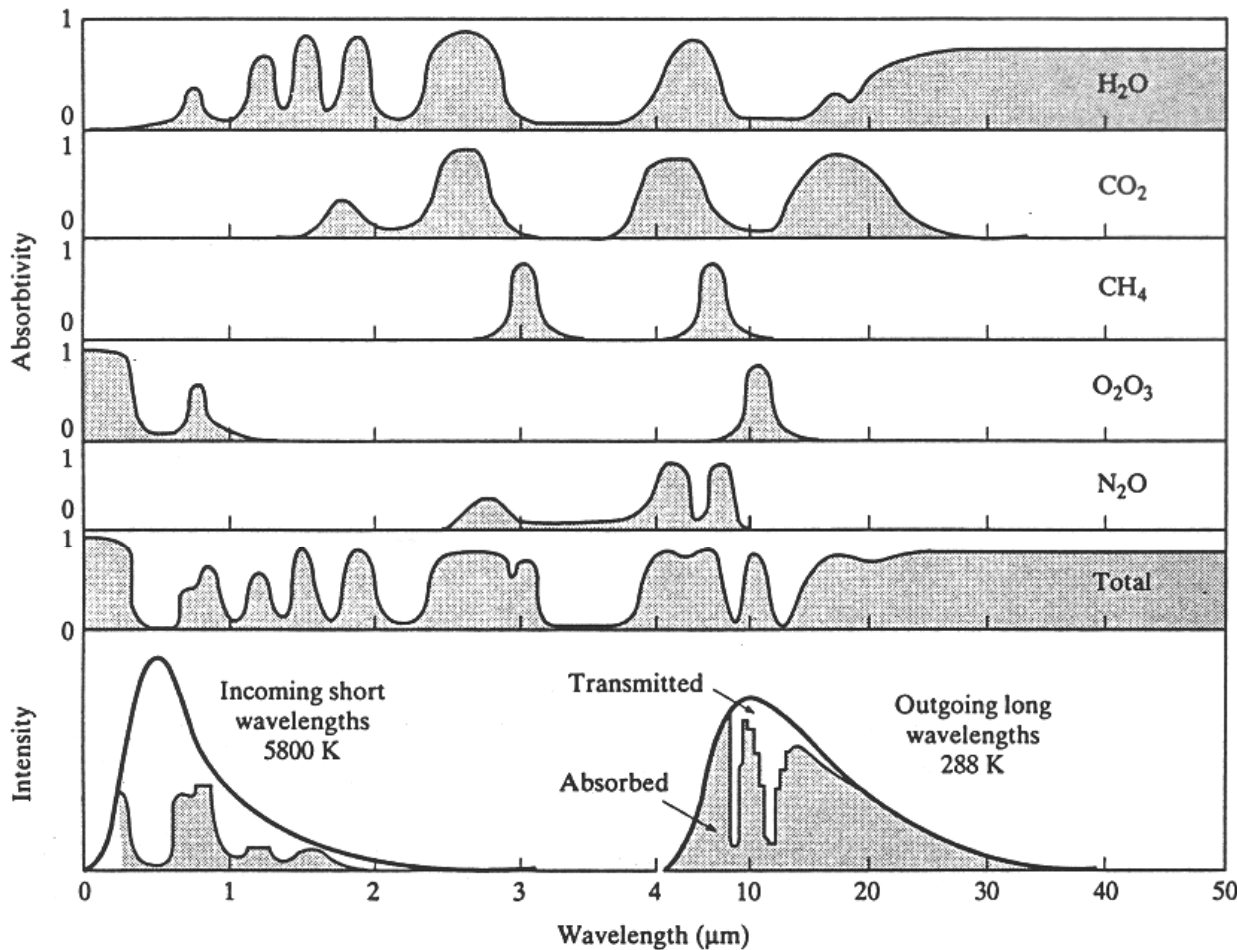


Fig 3.13, Chemistry in Context

# Absorption vs. Wavelength



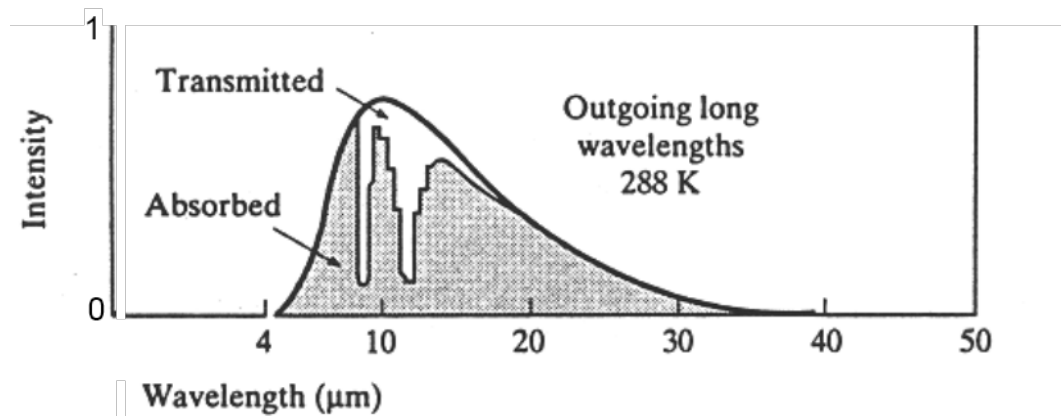
Gray shaded region denotes normalized absorptivity.

“0” – all radiation transmitted through atmosphere.

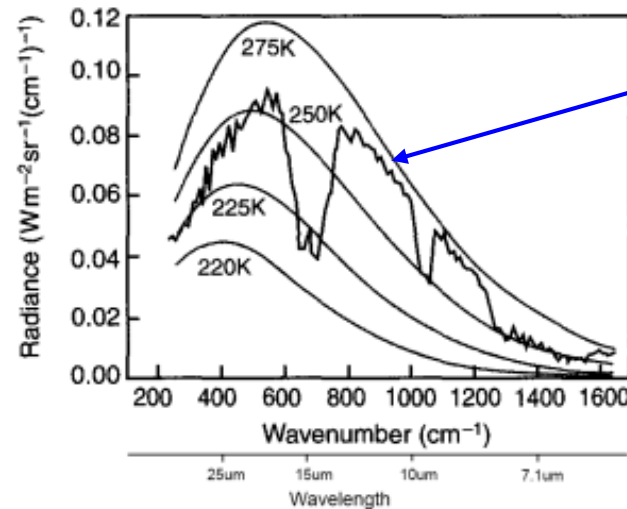
“1” – complete absorption.

Masters, Intro. to Environmental Engineering and Science, 2<sup>nd</sup> ed.





Masters, Intro. to Environmental Engineering and Science, 2<sup>nd</sup> ed.



Earth's radiance  
as viewed from space

**Fig. 2.9**

The spectrum of the infrared energy emitted by the Earth.<sup>32</sup> The various features are the absorption/emission bands of atmospheric gases, especially water vapour, ozone, and carbon dioxide (Fig. 2.5). The area under the Earth's spectrum, when averaged over latitude, longitude, and time, and integrated over wavelength, is about the same as the area obtained by integrating the Planck function (represented at four different temperatures by the smooth curves) for a temperature of 255K. At this temperature, the thermal infrared emission from the Earth just balances the incoming solar radiative energy at shorter UV, visible, and near-infrared wavelengths.

<https://scienceofdoom.files.wordpress.com/2010/03/radiation-earth-from-space-taylor-499px.png>

# The Greenhouse Effect

Molecules of CO<sub>2</sub> 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 like N<sub>2</sub> and O<sub>2</sub> and can transfer some of the absorbed energy to those molecules, also as heat. Through both processes CO<sub>2</sub> “traps” some of the IR radiation emitted by the Earth ... this is what makes CO<sub>2</sub> a greenhouse gas,

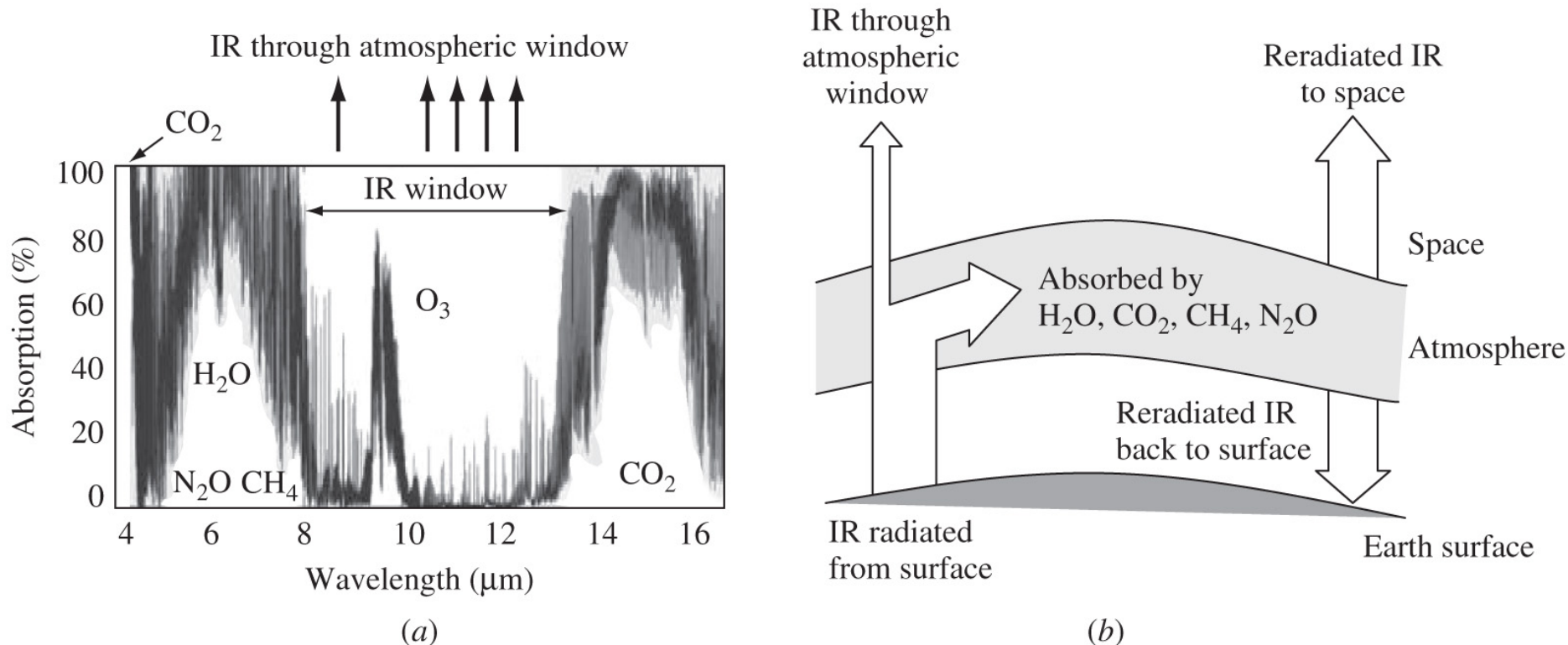
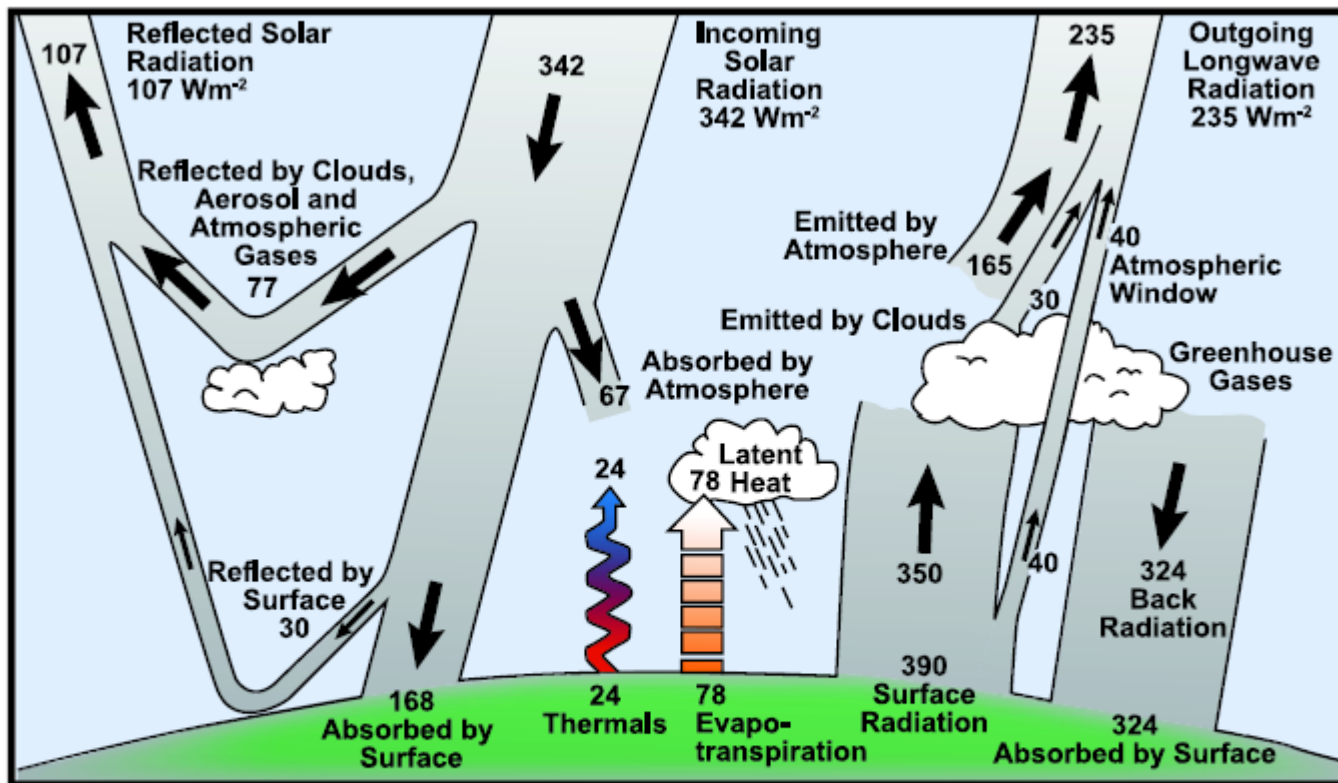


Figure: 08-11

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

## Radiative Forcing

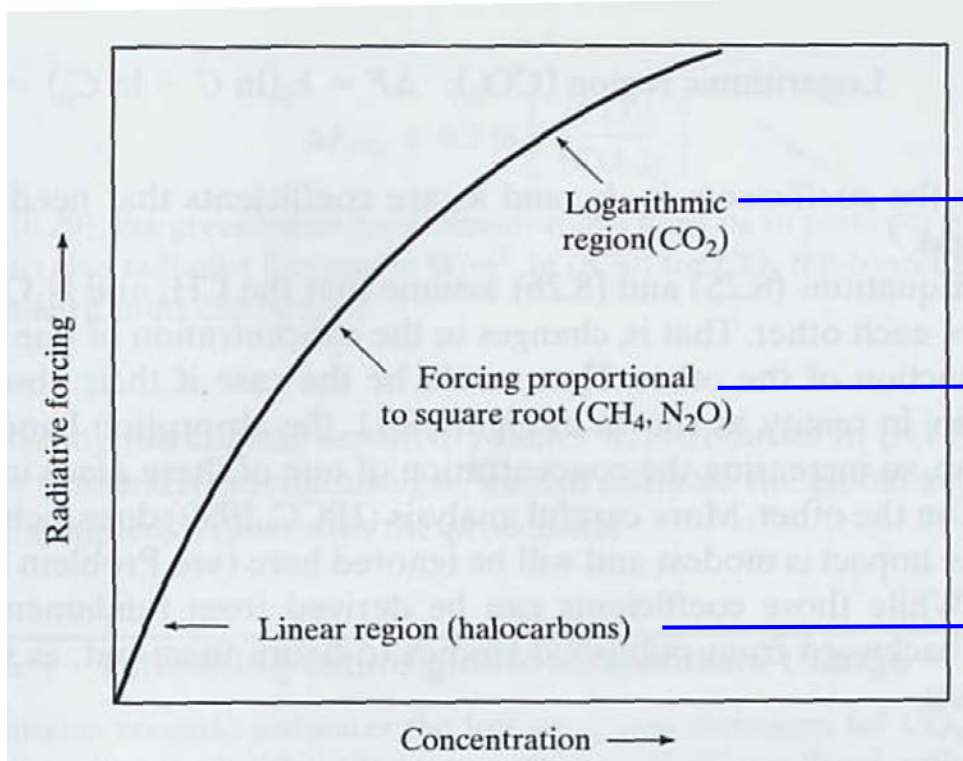


FAQ 1.1, Figure 1. Estimate of the Earth's annual and global mean energy balance. Over the long term, the amount of incoming solar radiation absorbed by the Earth and atmosphere is balanced by the Earth and atmosphere releasing the same amount of outgoing longwave radiation. About half of the incoming solar radiation is absorbed by the Earth's surface. This energy is transferred to the atmosphere by warming the air in contact with the surface (thermals), by evapotranspiration and by longwave radiation that is absorbed by clouds and greenhouse gases. The atmosphere in turn radiates longwave energy back to Earth as well as out to space. Source: Kiehl and Trenberth (1997).

Question 1.1, IPCC, 2007

**Radiative Forcing of Climate is Change in Energy**  
 reaching the lower atmosphere (surface to tropopause) as GHGs rise.  
 "Back Radiation" is most important term.

# How does RF change with concentration?



Wigley (1987)

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

$$\Delta F = \alpha (\sqrt{C} - \sqrt{C_o})$$

$$\Delta F = \alpha (C - C_o)$$

Masters, Introduction to Environmental Engineering and Science, 1998

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?

**Table 6.2:** Simplified expressions for calculation of radiative forcing due to CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and halocarbons.

The first row for CO<sub>2</sub> lists an expression with a form similar to IPCC (1990) but with newer values of the constants. The second row for CO<sub>2</sub> is a more complete and updated expression similar in form to that of Shi (1992). The third row expression for CO<sub>2</sub> is from WMO (1999), based in turn on Hansen *et al.* (1988).

Trace gas	Simplified expression Radiative forcing, ΔF (Wm <sup>-2</sup> )	Constants
CO <sub>2</sub>	ΔF = α ln(C/C <sub>0</sub> )	α = 5.35
CH <sub>4</sub>	ΔF = α(√M - √M <sub>0</sub> ) - (f(M, N <sub>0</sub> ) - f(M <sub>0</sub> , N <sub>0</sub> ))	α = 0.036
N <sub>2</sub> O	ΔF = α(√N - √N <sub>0</sub> ) - (f(M <sub>0</sub> , N) - f(M <sub>0</sub> , N <sub>0</sub> ))	α = 0.12
CFC-11a	ΔF = α(X - X <sub>0</sub> )	α = 0.25
CFC-12	ΔF = α(X - X <sub>0</sub> )	α = 0.32

$$\Delta F = \alpha \ln\left(\frac{C}{C_0}\right)$$

$$\Delta F = \alpha (\sqrt{C} - \sqrt{C_0})$$

$$\Delta F = \alpha (C - C_0)$$

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

C is CO<sub>2</sub> in ppm

M is CH<sub>4</sub> in ppb

N is N<sub>2</sub>O in ppb

X is CFC in ppb

The constant in the simplified expression for CO<sub>2</sub> 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.

<sup>a</sup> 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).

# How does RF change with concentration?

**Table 8.SM.1** | Supplementary for Table 8.3: RF formulae for CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O.

Gas	RF (in W m <sup>-2</sup> )	Constant $\alpha$
CO <sub>2</sub>	$\Delta F = \alpha \ln(C / C_0)$	5.35
CH <sub>4</sub>	$\Delta F = \alpha (\sqrt{M} - \sqrt{M_0}) - (f(M, N_0) - f(M_0, N_0))$	0.036
N <sub>2</sub> O	$\Delta F = \alpha (\sqrt{N} - \sqrt{N_0}) - (f(M_0, N) - f(M_0, N_0))$	0.12

$$\Delta F = \alpha \ln\left(\frac{C}{C_0}\right)$$

$$\Delta F = \alpha (\sqrt{(C)} - \sqrt{(C_0)})$$

Acronym, Common Name or Chemical Name	Chemical Formula	Lifetime (Years)	Radiative Efficiency (W m <sup>-2</sup> ppb <sup>-1</sup> )
CFC-11	CCl <sub>3</sub> F	45.0	0.26
CFC-12	CCl <sub>2</sub> F <sub>2</sub>	100.0	0.32

$$\Delta F = \alpha (C - C_0)$$

Notes:

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

C is CO<sub>2</sub> in ppm.

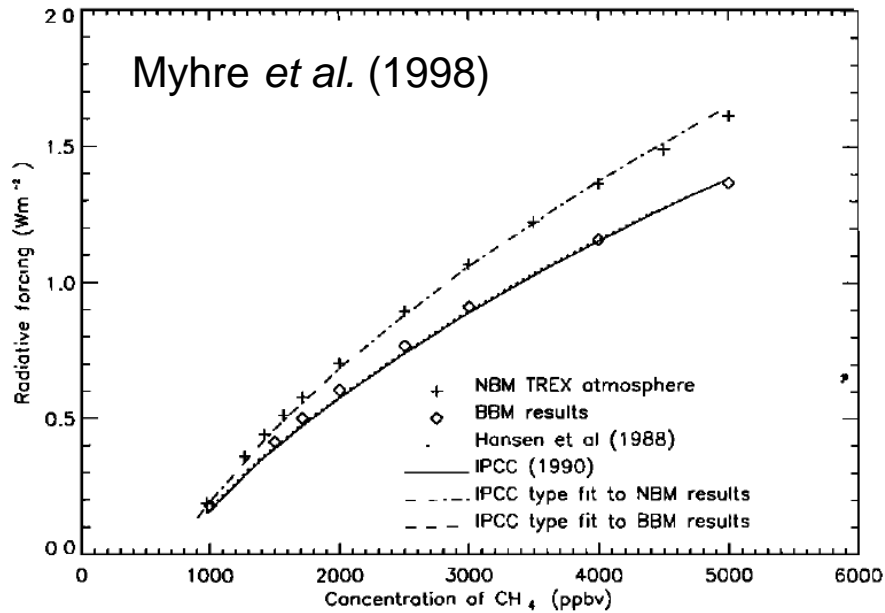
M is CH<sub>4</sub> in ppb.

N is N<sub>2</sub>O in ppb.

The subscript 0 denotes the unperturbed molar fraction for the species being evaluated. However, note that for the CH<sub>4</sub> forcing N<sub>0</sub> should refer to present-day N<sub>2</sub>O, and for the N<sub>2</sub>O forcing M<sub>0</sub> should refer to present-day CH<sub>4</sub>.

IPCC Fifth Assessment Report, 2013

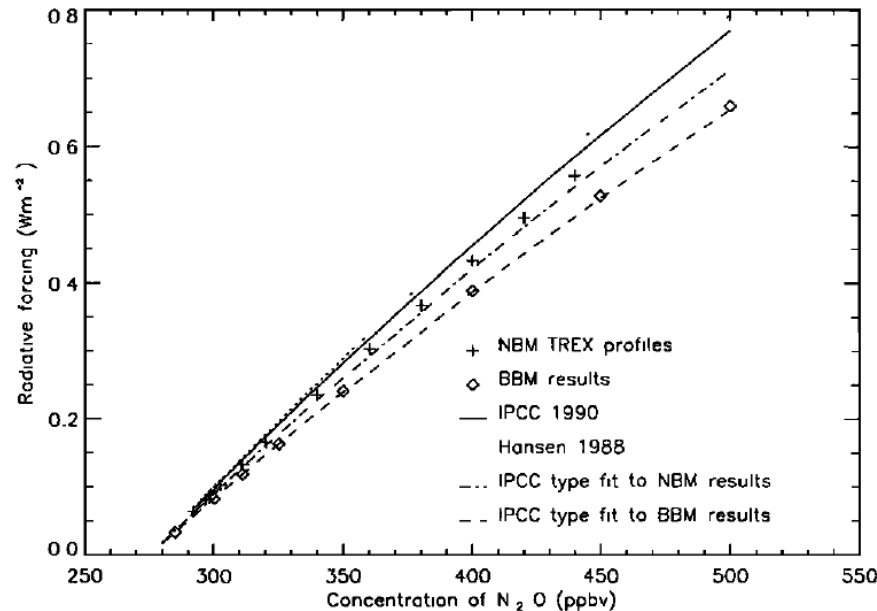
# Change in RF: CH<sub>4</sub> and N<sub>2</sub>O



As the CH<sub>4</sub> and N<sub>2</sub>O bands are not completely saturated (yet), we would expect the change in forcing from both species to be of the form:

$$\Delta F = \alpha (\sqrt{(C)} - \sqrt{(C)_o})$$

where  $C_o$  is the initial concentration (in ppb) and  $\alpha$  is different for each species.



# Change in RF: CH<sub>4</sub> and N<sub>2</sub>O

Accounting for the overlap between CH<sub>4</sub> and N<sub>2</sub>O:

$$\Delta F_{\text{CH}_4} = 0.036 \text{ Wm}^{-2} \text{ ppb}^{-0.5} \left( \sqrt{(\text{CH}_4^{\text{FINAL}})} - \sqrt{(\text{CH}_4^{\text{INITIAL}})} \right) \\ - \left( f(\text{CH}_4^{\text{FINAL}}, \text{N}_2\text{O}^{\text{INITIAL}}) - f(\text{CH}_4^{\text{INITIAL}}, \text{N}_2\text{O}^{\text{INITIAL}}) \right)$$

$$\Delta F_{\text{N}_2\text{O}} = 0.12 \text{ Wm}^{-2} \text{ ppb}^{-0.5} \left( \sqrt{(\text{N}_2\text{O}^{\text{FINAL}})} - \sqrt{(\text{N}_2\text{O}^{\text{INITIAL}})} \right) \\ - \left( f(\text{CH}_4^{\text{INITIAL}}, \text{N}_2\text{O}^{\text{FINAL}}) - f(\text{CH}_4^{\text{INITIAL}}, \text{N}_2\text{O}^{\text{INITIAL}}) \right)$$

where CH<sub>4</sub><sup>INITIAL</sup>, CH<sub>4</sub><sup>FINAL</sup>, N<sub>2</sub>O<sup>INITIAL</sup>, N<sub>2</sub>O<sup>FINAL</sup> are all in units of ppb

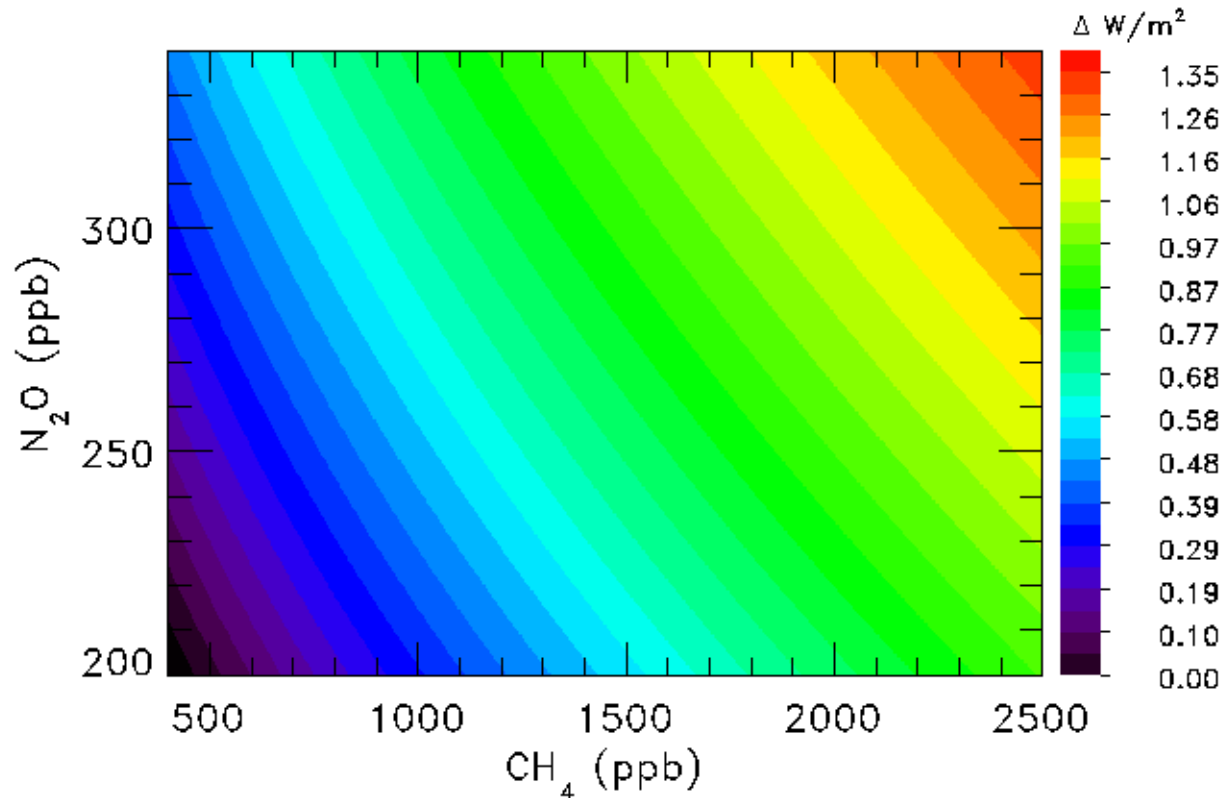
and  $f(M, N) = 0.47 \ln(1 + 2.01 \times 10^{-5} (MN)^{0.75} + 5.31 \times 10^{-15} M(MN)^{1.52})$ ,

where M is CH<sub>4</sub> & N is N<sub>2</sub>O, again both in units of ppb

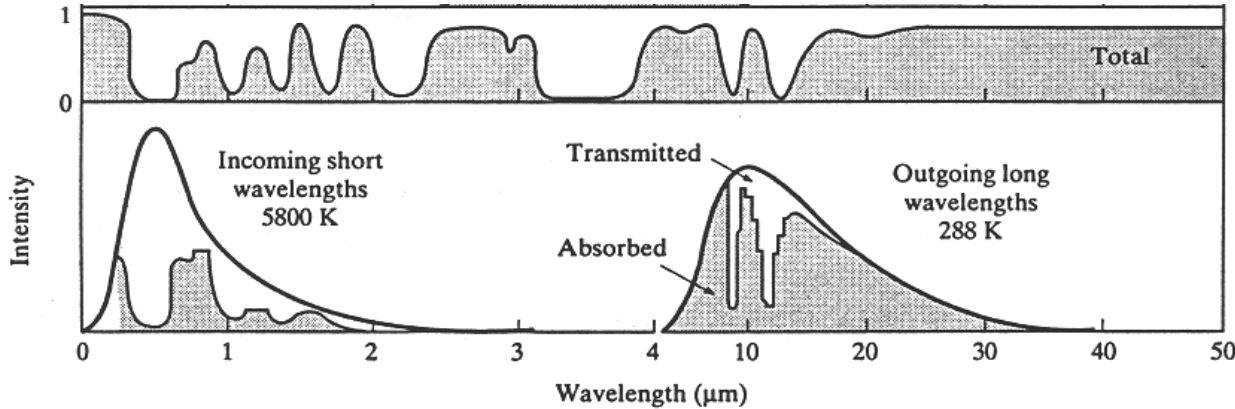
**Table 6.2, IPCC 2001**  
**Table 8.SM.1, IPCC 2013**



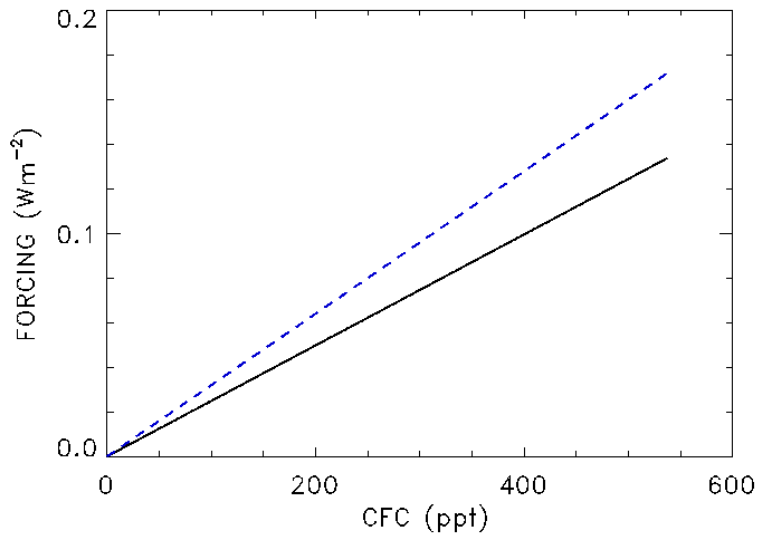
# Graphical representation of change in RF: CH<sub>4</sub> and N<sub>2</sub>O



# Change in RF: CFCs



CFCs absorb in wavelength regions that are relatively unaffected by other species (i.e. the atmospheric window is clear). The addition of absorbing species at these wavelengths can have a strong effect on the radiative flux. As such, CFCs have a linear effect on forcing:



$$\Delta F = 0.32 \text{ Wm}^{-2} \text{ ppb}^{-1} (C - C_o), \text{ CFC-12}$$

$$\Delta F = 0.25 \text{ Wm}^{-2} \text{ ppb}^{-1} (C - C_o), \text{ CFC-11}$$

Masters, Intro. to Environmental Engineering and Science, 2<sup>nd</sup> ed.

# Radiative Forcing of Climate, 1750 to 2011

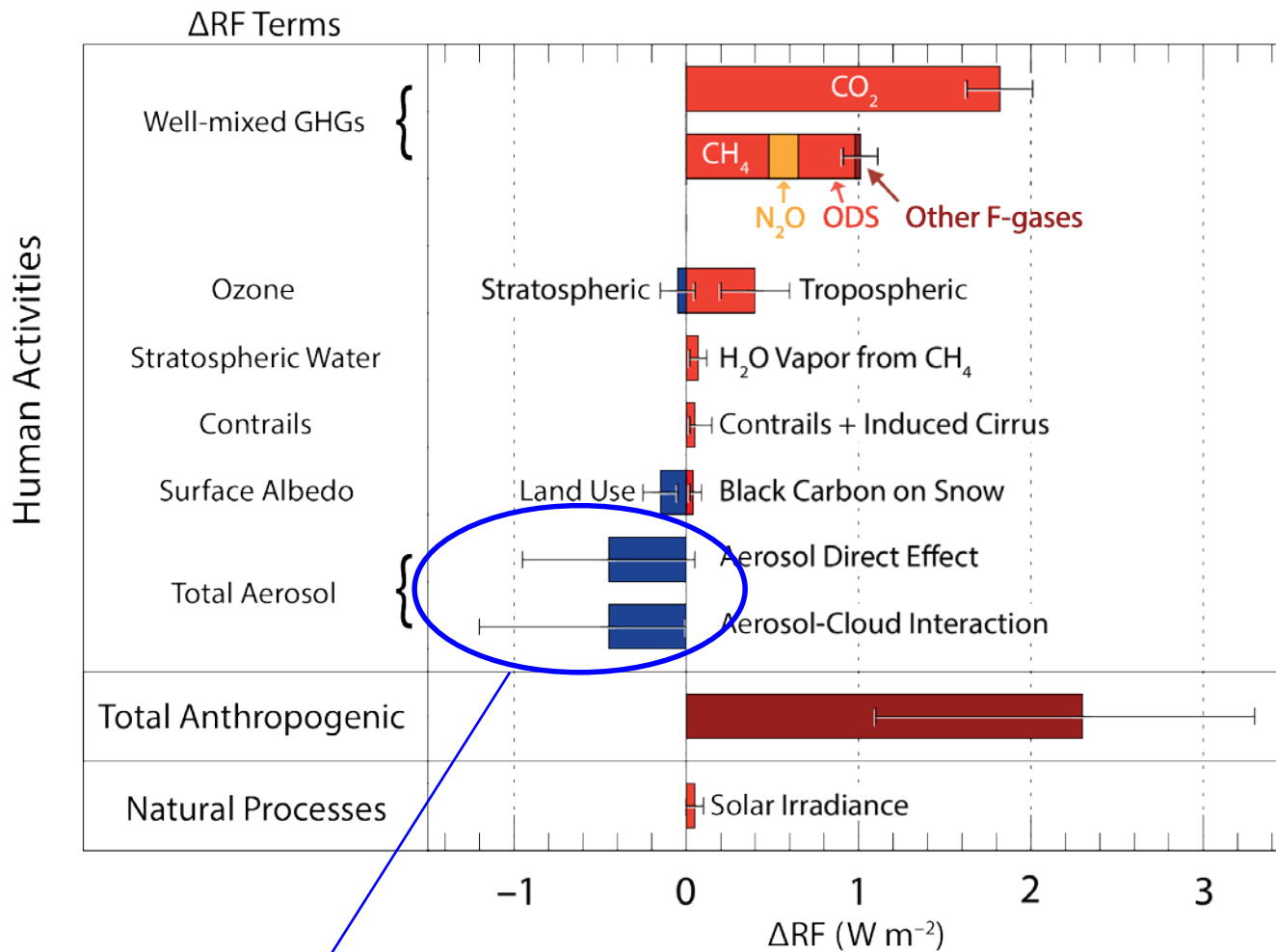
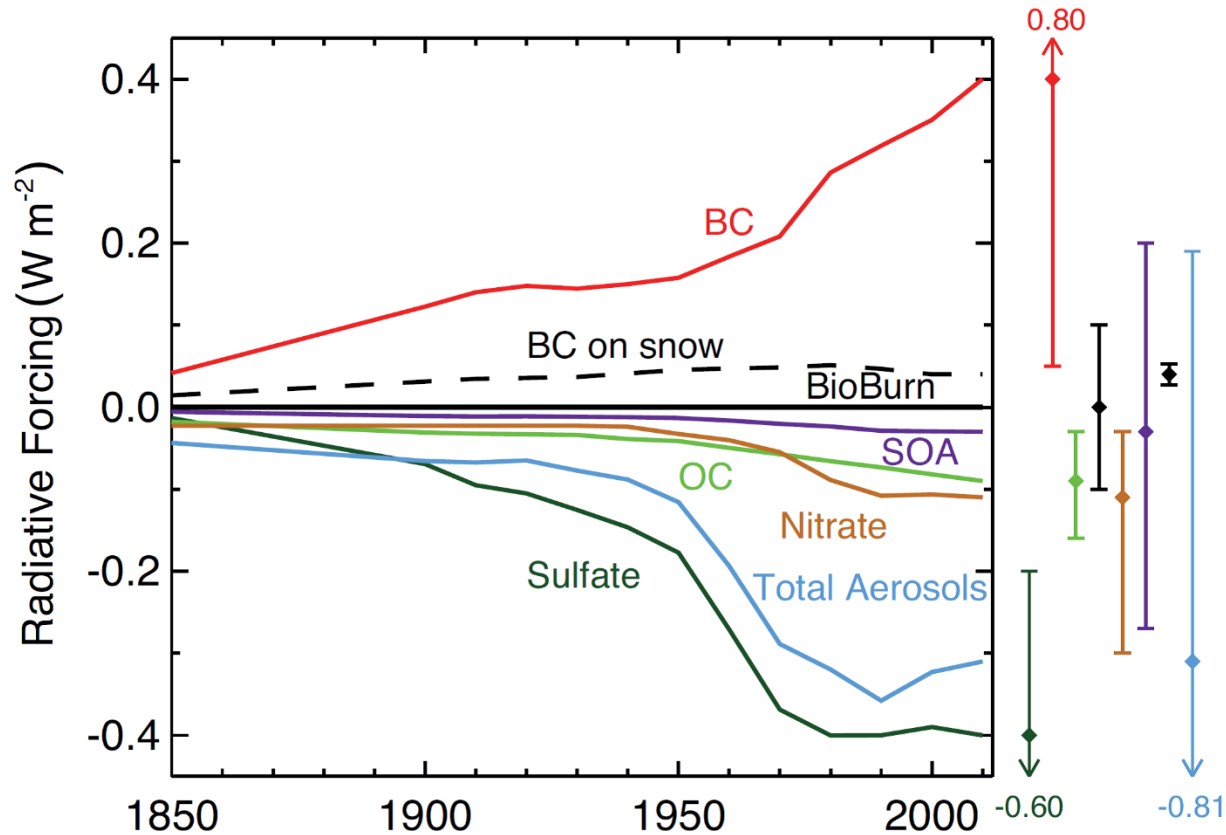


Figure 1-4, *Paris Beacon of Hope*

## Large uncertainty in aerosol RF

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

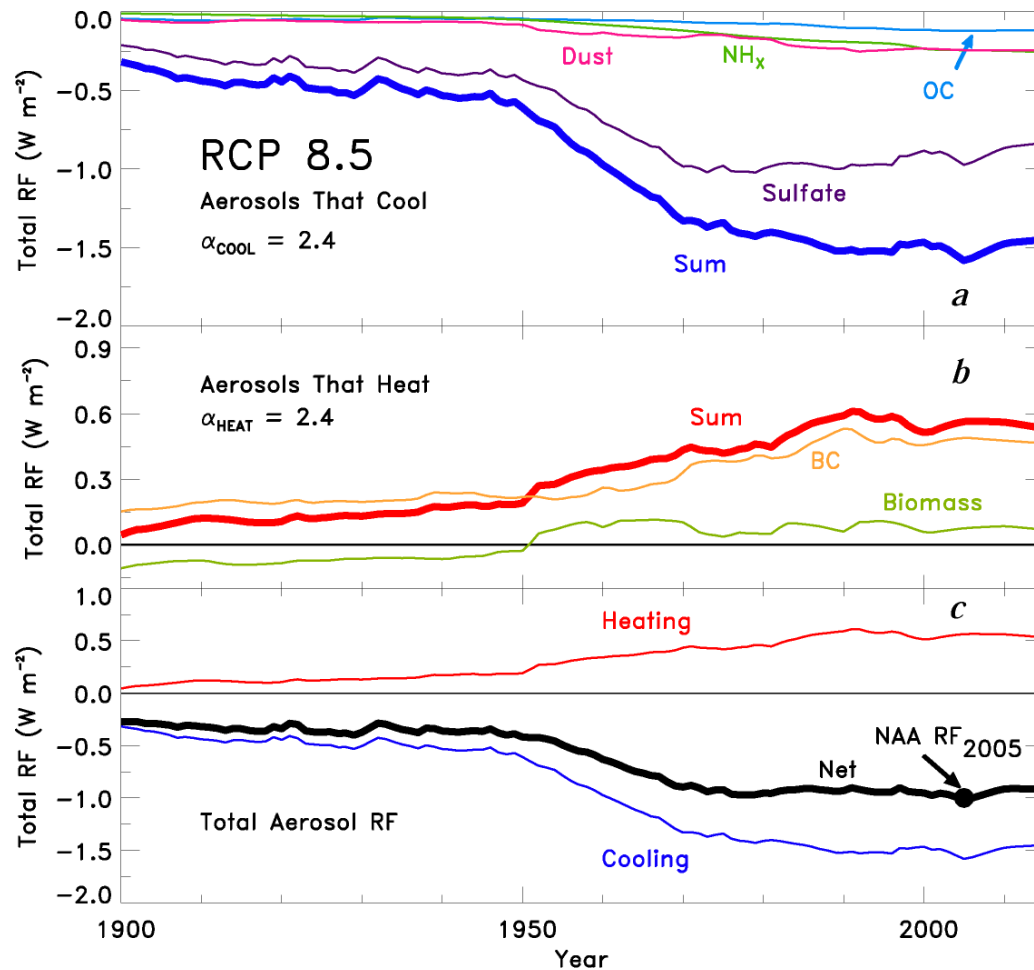
# Tropospheric Aerosol RF



**Figure 8.8 |** Time evolution of RF due to aerosol–radiation interaction and BC on snow and ice.

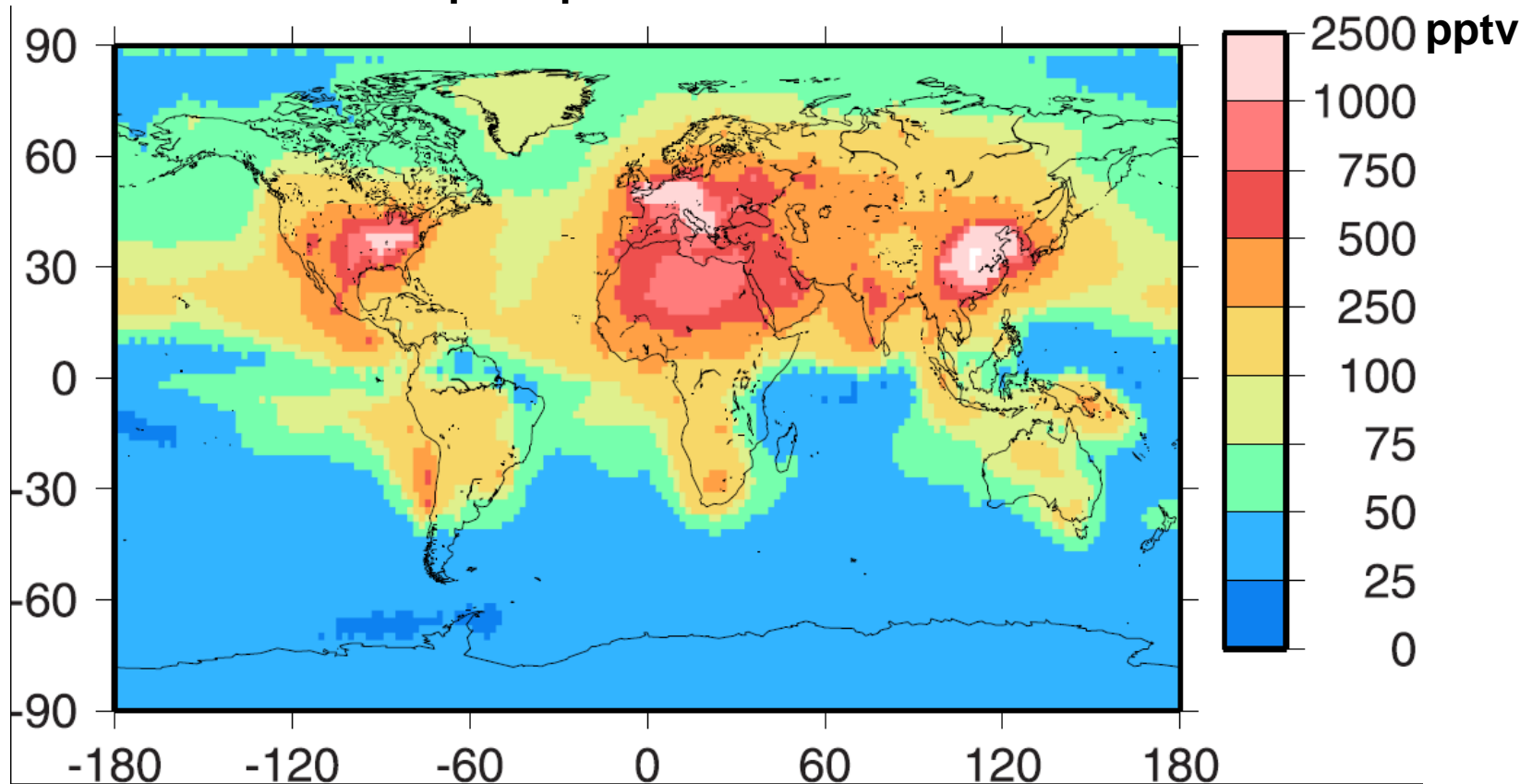
**Fig 8.8, IPCC 2013: Only Direct RF of aerosols considered here**

# Tropospheric Aerosol RF



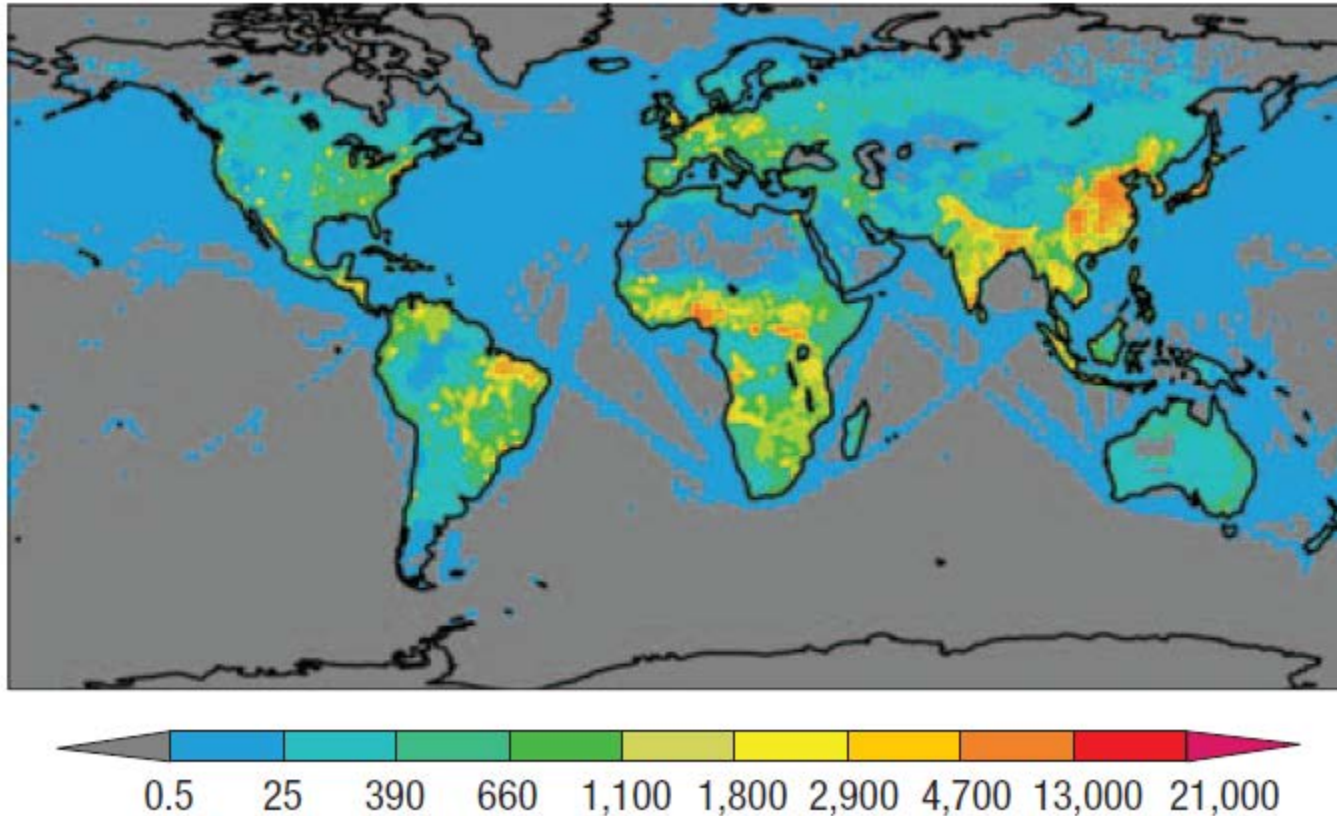
**Fig 3, Canty et al. 2013: Direct & Indirect RF of aerosols considered here !**

# Tropospheric Sulfate aerosols



Modeled surface concentration of sulfate (ppt)  
(Koch *et al.*, *JGR*, 2007)

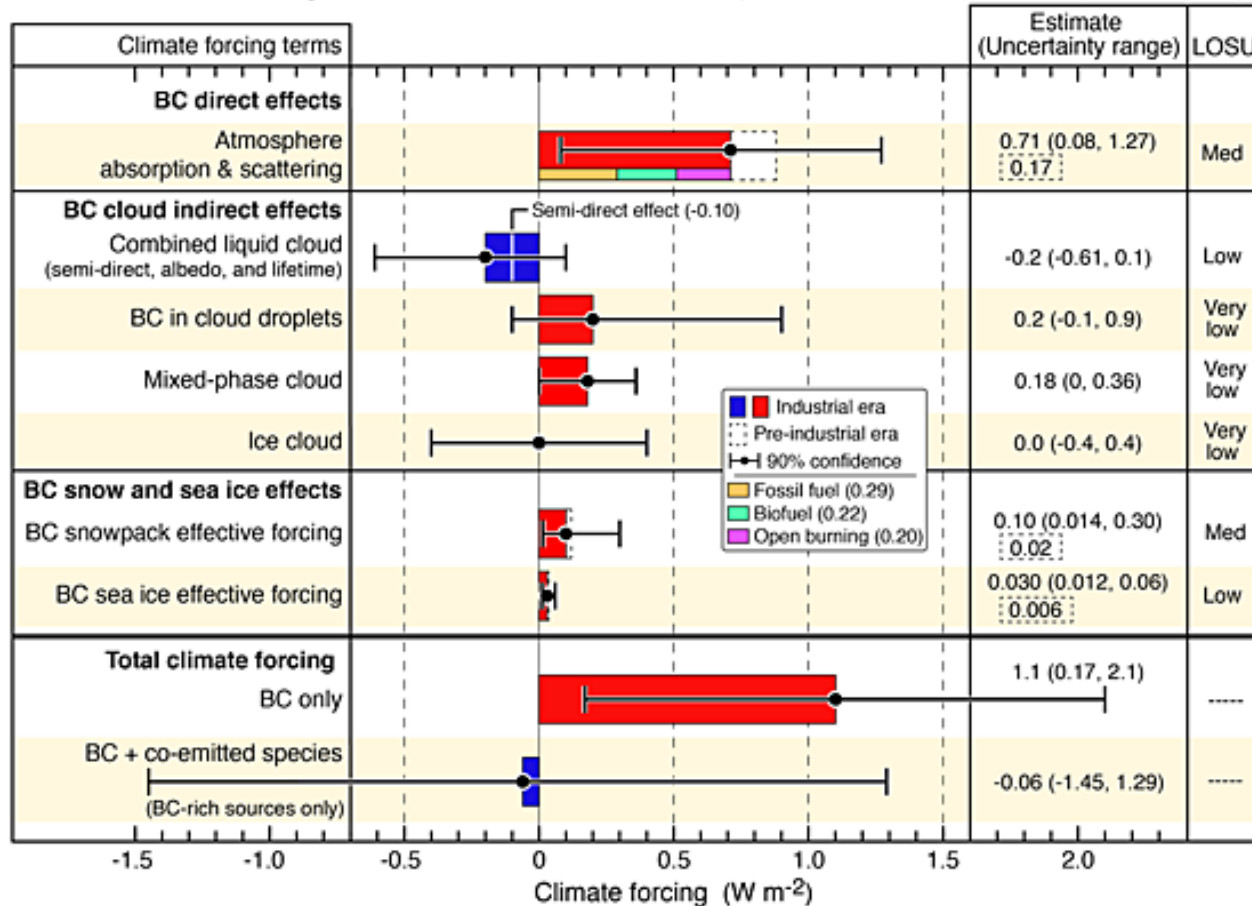
# Black Carbon Aerosols



Black Carbon emissions (ton/yr) for 1996. Includes emissions from fuel combustion (fossil fuels and biofuels) and open biomass burning (forest fires, savanna burning and outdoor cooking)  
(Ramanathan and Carmichael, *Nature*, 2009)

# Black Carbon Aerosols

Global climate forcing of black carbon and co-emitted species in the industrial era (1750 - 2005)



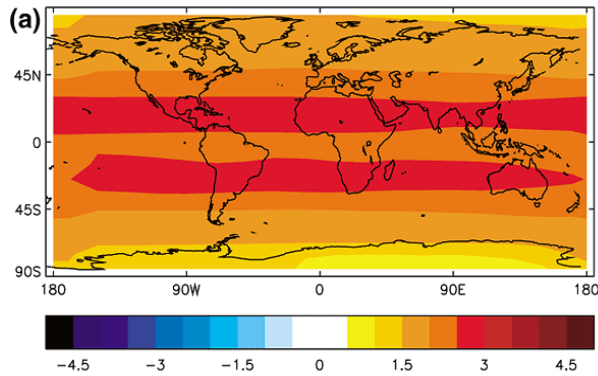
Bond *et al.*, Bounding the role of black carbon in the climate system: A scientific assessment, *JGR*, 2013

	Total Climate Forcing, Black Carbon Aerosols ( $W m^{-2}$ )			
Report	IPCC (1995)	IPCC (2001)	IPCC (2007)	IPCC (2013)
$\Delta RF, BC$	0.1 (0.03 to 0.3)	0.2 (0.1 to 0.4)	0.2 (0.05 to 0.35)	0.4 (0.05 to 0.80)

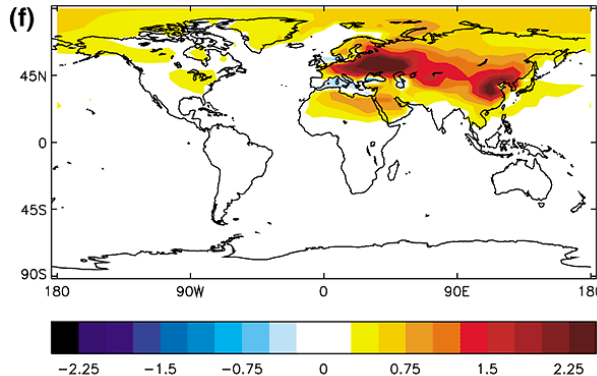


# Global View

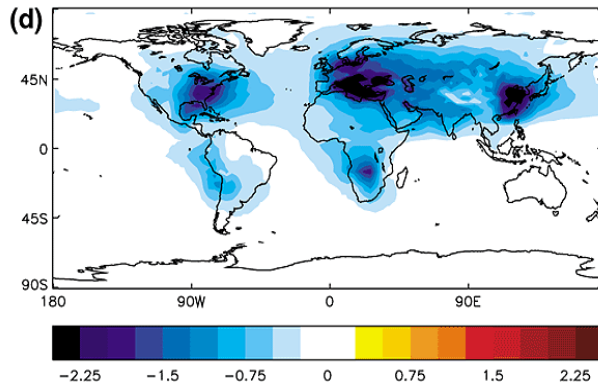
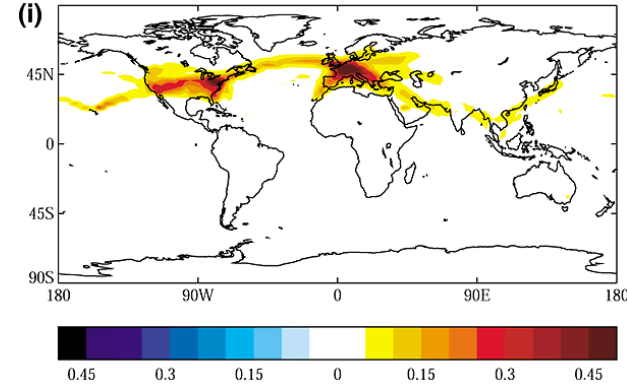
All forcings (1750-2000) are in  $Wm^{-2}$



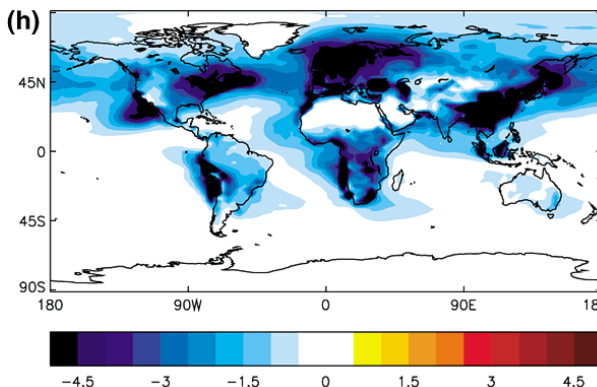
Greenhouse gases



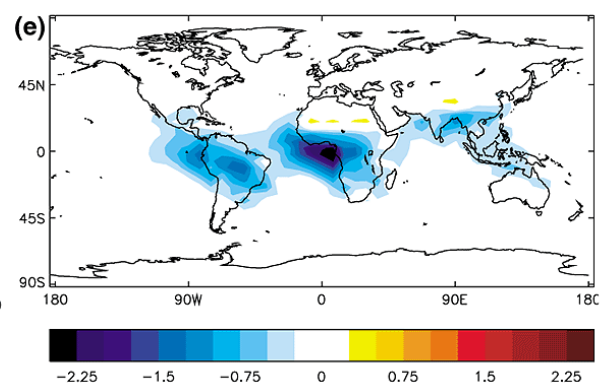
Organic and black carbon from fossil fuel burning



Direct effect from sulphate aerosols



Indirect effect from sulphate aerosols

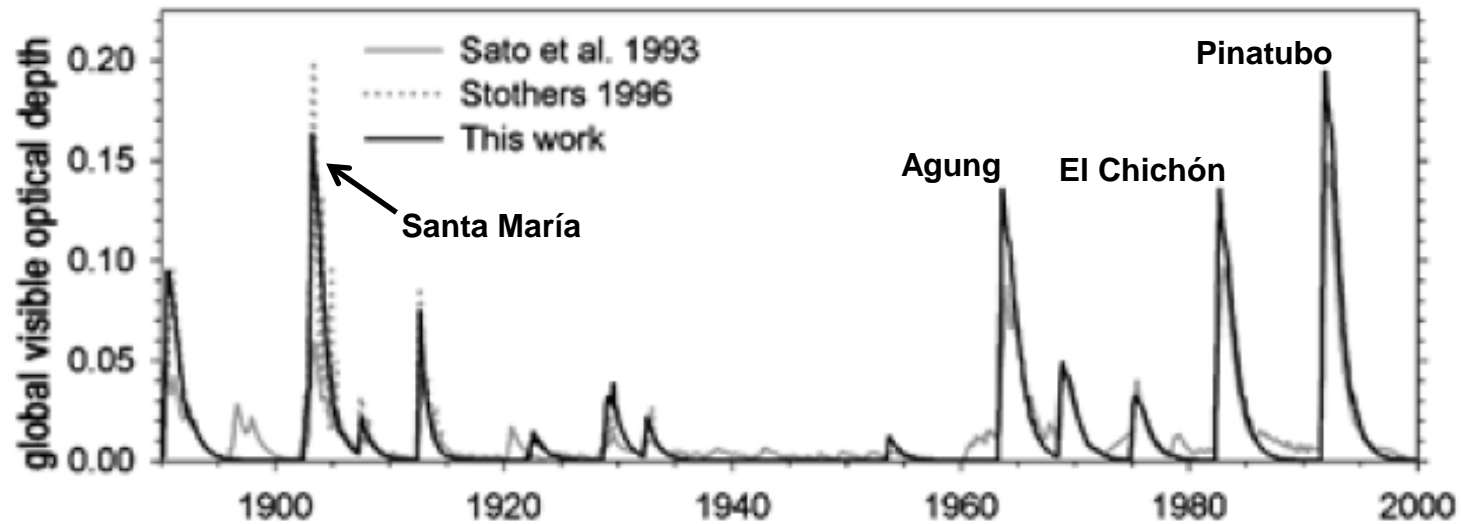


Organic and black carbon from biomass burning

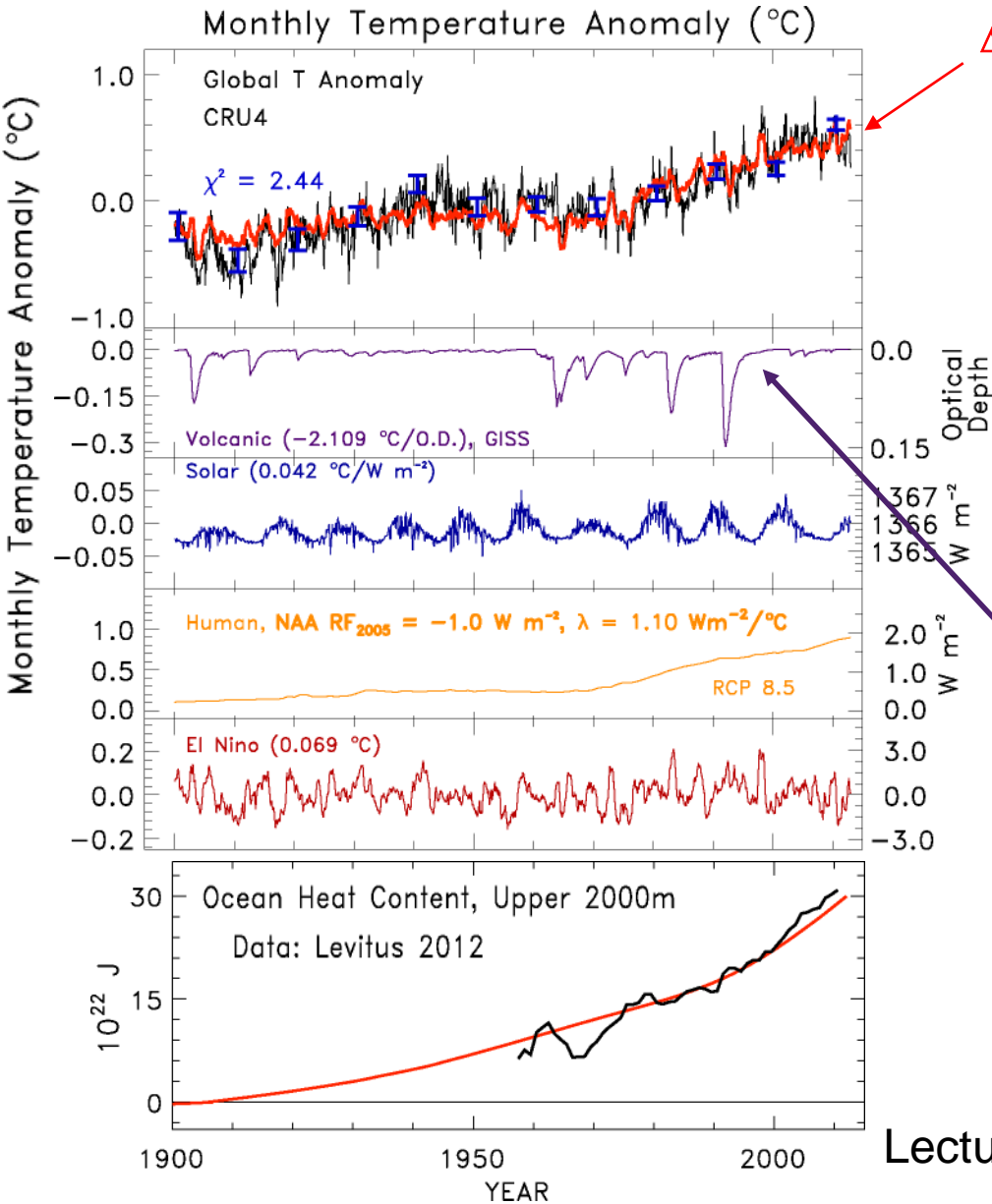
# Volcanic aerosols

Volcanoes may add massive amounts of aerosols to upper atmosphere, effects may last years.

Current aerosol optical depth in stratosphere is low (stratosphere is relatively free of aerosols).



[Ammann et al., Geophys. Res. Lett., 2003](#)



$$\Delta T_{MDL\ i} = (1 + \gamma) (\text{GHG RF}_i + \text{NAA RF}_i) / \lambda_P + C_0 + C_1 \times \text{SOD}_{i-6} + C_2 \times \text{TSI}_{i-1} + C_3 \times \text{ENSO}_{i-2} - Q_{\text{OCEAN}\ i} / \lambda_P$$

where

$$\lambda_P = 3.2 \text{ W m}^{-2} / ^\circ\text{C}$$

$$1 + \gamma = \{ 1 - \Sigma(\text{Feedback Parameters}) / \lambda_P \}^{-1}$$

NAA RF = net RF due to anthropogenic aerosols

SOD = Stratospheric optical depth

TSI = Total solar irradiance

ENSO = Multivariate El Niño South. Osc Index

Q<sub>OCEAN</sub> = Ocean heat export

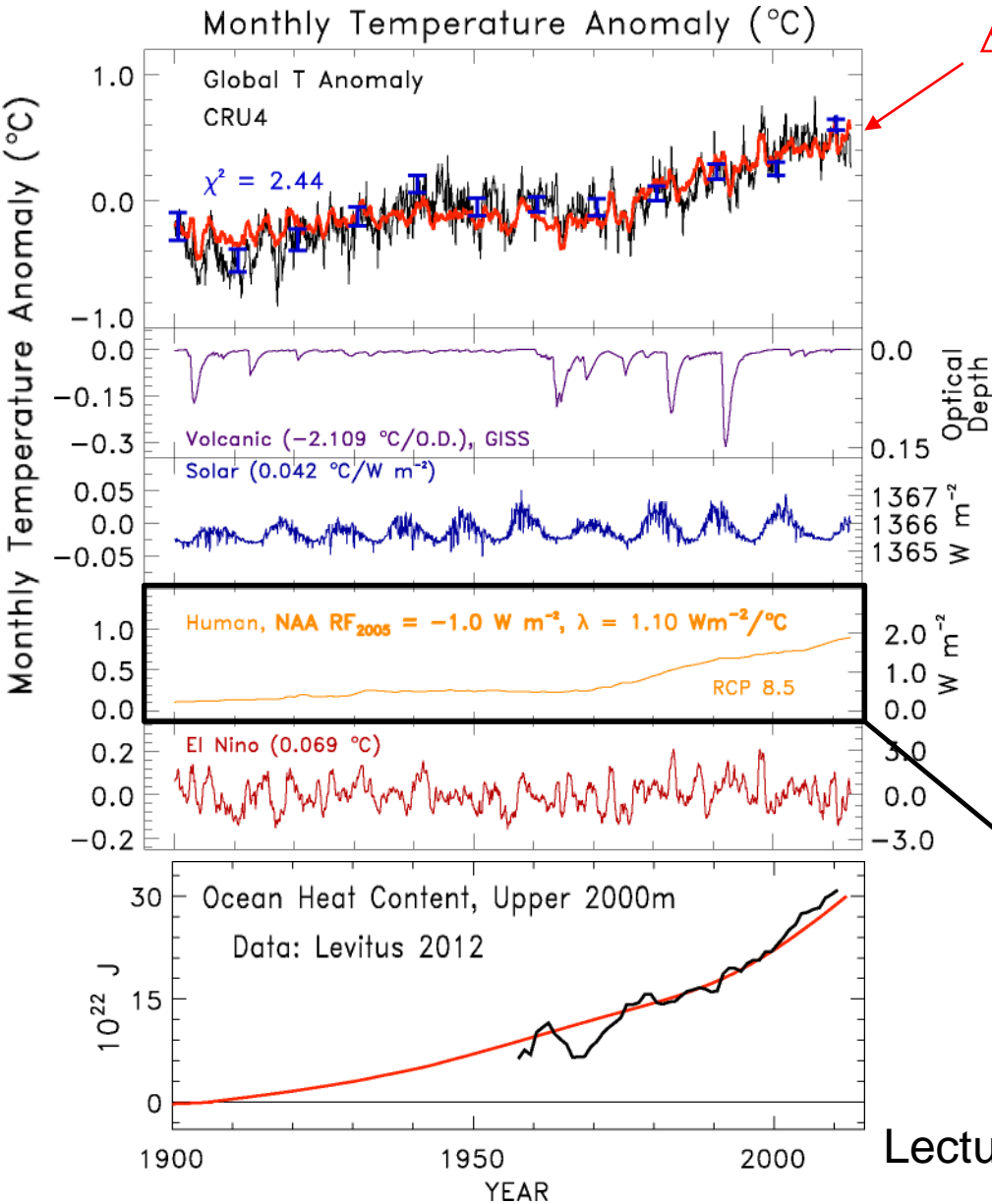
**Volcanoes drive modest, temporary cooling, because stratospheric sulfate aerosols reflect sunlight**

## Lecture 2

Canty et al., *ACP*, 2013

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$$\Delta T_{MDL\ i} = (1 + \gamma) (\text{GHG RF}_i + \text{NAA RF}_i) / \lambda_p + C_0 + C_1 \times \text{SOD}_{i-6} + C_2 \times \text{TSI}_{i-1} + C_3 \times \text{ENSO}_{i-2} - Q_{\text{OCEAN}\ i} / \lambda_p$$

where

$$\lambda_p = 3.2 \text{ W m}^{-2} / ^\circ\text{C}$$

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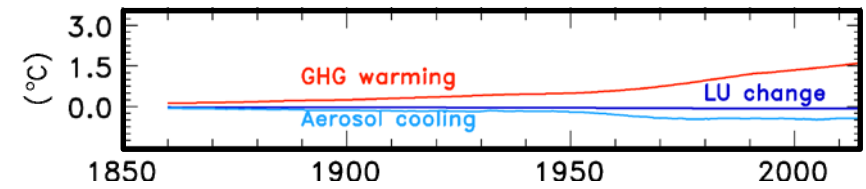
SOD = Stratospheric optical depth

TSI = Total solar irradiance

ENSO = Multivariate El Niño South. Osc Index

Q<sub>OCEAN</sub> = Ocean heat export

**Total Human RF of climate reflects balance of GHG warming (well known) tropospheric aerosol cooling (poorly known) & climate feedback  $\gamma$  (also not well known; subject of next lecture)**



## Lecture 2

Canty et al., ACP, 2013

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