Goals:

• Understanding interaction between gases and IR radiation

• Radiative forcing of greenhouse gases

• Radiative forcing of aerosols

Earth’s radiance as viewed from space
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
### Lecture 6

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

<table>
<thead>
<tr>
<th>Name and Chemical Formula</th>
<th>Preindustrial Concentration (1750)</th>
<th>Concentration in 2008</th>
<th>Atmospheric Lifetime (years)</th>
<th>Anthropogenic Sources</th>
<th>Global Warming Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon dioxide CO₂</td>
<td>270 ppm</td>
<td>388 ppm</td>
<td>50-200*</td>
<td>Fossil fuel combustion, deforestation, cement production</td>
<td>1</td>
</tr>
<tr>
<td>methane CH₄</td>
<td>700 ppb</td>
<td>1760 ppb</td>
<td>12</td>
<td>Rice paddies, waste dumps, livestock</td>
<td>21</td>
</tr>
<tr>
<td>nitrous oxide N₂O</td>
<td>275 ppb</td>
<td>322 ppb</td>
<td>120</td>
<td>Fertilizers, industrial production, combustion</td>
<td>310</td>
</tr>
<tr>
<td>CFC-12 CC₂F₂</td>
<td>0</td>
<td>0.56 ppb</td>
<td>102</td>
<td>Liquid coolants, foams</td>
<td>8100</td>
</tr>
</tbody>
</table>

*A single value for the atmospheric lifetime of CO₂ is not possible. Removal mechanisms take place at different rates. The range given is an estimate based on several removal mechanisms.*

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**Table 3.2**  
**Examples of Greenhouse Gases**
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)

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).


- 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.

$\text{CO}_2$ (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.

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![Diagram showing vibrational modes of CO2 molecule.](image)
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

![Diagram](image-url)

Fig 3.14, 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

**Symmetric Stretch: no dipole moment**

\[
\text{Symmetric stretch} \quad \begin{array}{c}
\text{O}^- \\
\text{C}^+ \\
\text{O}^-
\end{array} \\
\text{DP} = 0
\]

\[
\text{O}^- \quad \text{C}^+ \quad \text{O}^- \\
\text{DP} = 0
\]
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

**Anti-symmetric Stretch: dipole moment**

Anti-symmetric stretch

\[
\begin{align*}
O^- & \quad \rightarrow \quad C^+ \quad \rightarrow \quad O^- \\
\text{DP} &= 0
\end{align*}
\]

\[
\begin{align*}
O^- & \quad \rightarrow \quad C^+ \quad \rightarrow \quad O^- \\
\text{DP} &= \quad \rightarrow
\end{align*}
\]
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

3 N – 5 freqs for linear molecules,
N atoms: 4 freqs for CO₂

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

Wavenumber = 1 / Wavelength

\[
\frac{1}{2350} \text{ cm}^{-1} = 4.25\times10^{-4} \text{ cm} = 4.25\times10^{-6} \text{ m} = 4.25 \mu\text{m}
\]

\[
\frac{1}{666} \text{ cm}^{-1} = 1.50\times10^{-3} \text{ cm} = 15.0\times10^{-6} \text{ m} = 15.0 \mu\text{m}
\]

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

- 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

**CH₄** has numerous vibrational modes, some of which interact with the IR field

3 N – 6 freqs for non-linear molecules
Since **CH₄** has 5 atoms, there are 3x5 – 6 = 9 possible freqs
Due to the symmetry of the molecule, only 4 unique modes

3.31 µm  
6.32 µm  
3.17 µm  
7.31 µm

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

**H\(_2\)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, 2nd ed.
Fig. 2.9
The spectrum of the infrared energy emitted by the Earth. 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 CO₂ 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 N₂ and O₂ and can transfer some of the absorbed energy to those molecules, also as heat. Through both processes CO₂ “traps” some of the IR radiation emitted by the Earth … this is what makes CO₂ a greenhouse gas.
Radiative Forcing of Climate is Change in Energy reaching the lower atmosphere (surface to tropopause) as GHGs rise. “Back Radiation” is most important term.
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 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).

<table>
<thead>
<tr>
<th>Trace gas</th>
<th>Simplified expression</th>
<th>Radiative forcing, ΔF (Wm⁻²)</th>
<th>Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>ΔF = α ln(C/C₀)</td>
<td></td>
<td>α = 5.35</td>
</tr>
<tr>
<td>CH₄</td>
<td>ΔF = α(√(N - √N₀) - (√(M₀N₀) - √(M₀N₀)))</td>
<td></td>
<td>α = 0.036</td>
</tr>
<tr>
<td>N₂O</td>
<td>ΔF = α(√(N - √N₀) - (√(M₀N₀) - √(M₀N₀)))</td>
<td></td>
<td>α = 0.12</td>
</tr>
<tr>
<td>CFC-11a</td>
<td>ΔF = α(X - X₀)</td>
<td></td>
<td>α = 0.25</td>
</tr>
<tr>
<td>CFC-12</td>
<td>ΔF = α(X - X₀)</td>
<td></td>
<td>α = 0.32</td>
</tr>
</tbody>
</table>

ΔF = α ln(C/C₀)

ΔF = α(√(C) - √(C₀))

ΔF = α(C - C₀)
How does RF change with concentration?

<table>
<thead>
<tr>
<th>Gas</th>
<th>RF (in W m(^{-2}))</th>
<th>Constant (\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>(\Delta F = \alpha \ln\left(\frac{C}{C_0}\right))</td>
<td>5.35</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>(\Delta F = \alpha \left(\sqrt{M} - \sqrt{M_0}\right) - \left(f(M, N_0) - f(M_0, N_0)\right))</td>
<td>0.036</td>
</tr>
<tr>
<td>N(_2)O</td>
<td>(\Delta F = \alpha \left(\sqrt{N} - \sqrt{N_0}\right) - \left(f(M_0, N) - f(M_0, N_0)\right))</td>
<td>0.12</td>
</tr>
</tbody>
</table>

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

\[\Delta F = \alpha \left(\sqrt{C} - \sqrt{C_0}\right)\]

\[\Delta F = \alpha (C - C_0)\]
As the CH$_4$ and N$_2$O bands are not completely saturated (yet), we would expect the change in forcing from both species to be of the form:

\[
\Delta F = \alpha \left( \sqrt{(C)} - \sqrt{(C)_o} \right)
\]

where $C_o$ is the initial concentration (in ppb) and $\alpha$ is different for each species.
Change in RF: CH\textsubscript{4} and N\textsubscript{2}O:

\[ \Delta F_{\text{CH}_4} = 0.036 \text{ Wm}^{-2} \text{ ppb}^{-0.5} \left( \sqrt{(\text{CH}_4^{\text{FINAL}})} - \sqrt{(\text{CH}_4^{\text{INITIAL}})} \right) \]

\[ - (f(\text{CH}_4^{\text{FINAL}}, \text{N}_2\text{O}^{\text{INITIAL}}) - f(\text{CH}_4^{\text{INITIAL}}, \text{N}_2\text{O}^{\text{INITIAL}})) \]

\[ \Delta F_{\text{N}_2\text{O}} = 0.12 \text{ Wm}^{-2} \text{ ppb}^{-0.5} \left( \sqrt{(\text{N}_2\text{O}^{\text{FINAL}})} - \sqrt{(\text{N}_2\text{O}^{\text{INITIAL}})} \right) \]

\[ - (f(\text{CH}_4^{\text{INITIAL}}, \text{N}_2\text{O}^{\text{FINAL}}) - f(\text{CH}_4^{\text{INITIAL}}, \text{N}_2\text{O}^{\text{INITIAL}})) \]

where \( CH_4^{\text{INITIAL}}, CH_4^{\text{FINAL}}, N_2O^{\text{INITIAL}}, N_2O^{\text{FINAL}} \) 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\textsubscript{4} & \( N \) is N\textsubscript{2}O, again both in units of ppb

Table 6.2, IPCC 2001
Table 8.SM.1, IPCC 2013
Graphical representation of change in RF: CH₄ and N₂O
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 affect on the radiative flux. As such, CFCs have a linear affect on forcing:

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

\[ \Delta F = 0.25 \text{ Wm}^{-2} \text{ ppb}^{-1} (C - C_o), \text{ CFC - 11} \]
Aerosol RF Terms

Human Activities

Well-mixed GHGs

Ozone

Stratospheric Water

Contrails

Surface Albedo

Total Aerosol

Total Anthropogenic

Natural Processes

ΔRF (W m⁻²)

ΔRF Terms

Well-mixed GHGs

Ozone

Stratospheric Water

Contrails

Surface Albedo

Total Aerosol

Total Anthropogenic

Natural Processes

ΔRF Terms

Well-mixed GHGs

Ozone

Stratospheric Water

Contrails

Surface Albedo

Total Aerosol

Total Anthropogenic

Natural Processes

ΔRF (W m⁻²)

Large uncertainty in aerosol RF

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

Figure 1-4, Paris Beacon of Hope
**Tropospheric Aerosol RF**

![Graph showing radiative forcing over time for different aerosols](image)

**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 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)

- **BC direct effects**
  - Atmosphere absorption & scattering
  - Estimate (Uncertainty range): 0.71 (0.08, 1.27)
  - LOSU: Med

- **BC cloud indirect effects**
  - Combined liquid cloud
    - (semi-direct, albedo, and lifetime)
  - Semi-direct effect (-0.10)
  - Estimate (Uncertainty range): -0.2 (-0.61, 0.1)
  - LOSU: Low

- **BC snow and sea ice effects**
  - BC snowpack effective forcing
  - Estimate (Uncertainty range): 0.10 (0.014, 0.30)
  - LOSU: Med

- **Total climate forcing**
  - BC only
  - Estimate (Uncertainty range): 1.1 (0.17, 2.1)
  - LOSU: Med

- **BC + co-emitted species**
  - (BC-rich sources only)
  - Estimate (Uncertainty range): -0.06 (-1.45, 1.29)

**Total Climate Forcing, Black Carbon Aerosols (W m\(^{-2}\))**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta RF, BC)</td>
<td>0.1 (0.03 to 0.3)</td>
<td>0.2 (0.1 to 0.4)</td>
<td>0.2 (0.05 to 0.35)</td>
<td>0.4 (0.05 to 0.80)</td>
</tr>
</tbody>
</table>

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

http://www.grida.no/climate/IPCC_tar/wg1/253.htm#fig67
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).


Santa María

Agung

El Chichón

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

where

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

\[ 1+\gamma = \left\{ 1 - \Sigma \text{(Feedback Parameters)} / \lambda_p \right\}^{-1} \]

\text{NAA RF} = \text{net RF due to anthropogenic aerosols}

\text{SOD} = \text{Stratospheric optical depth}

\text{TSI} = \text{Total solar irradiance}

\text{ENSO} = \text{Multivariate El Niño South. Osc Index}

\text{Q}_{\text{OCEAN}} = \text{Ocean heat export}

Volcanoes drive modest, temporary cooling, because stratospheric sulfate aerosols reflect sunlight.
Global Temperature, 1900 to present

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

where

- \( \lambda_p = 3.2 \text{ W m}^{-2} / ^\circ \text{C} \)
- \( 1+\gamma = \left\{ 1 - \Sigma \text{(Feedback Parameters)} / \lambda_p \right\}^{-1} \)
- NAA RF = net RF due to anthropogenic aerosols
- SOD = Stratospheric optical depth
- TSI = Total solar irradiance
- ENSO = Multivariate El Niño South. Osc Index
- Q_{OCEAN} = 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)