Cars versus Cows:

Comparing the greenhouse effects of CO2 and CH4

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1 Introduction

Global climate change is a complicated problem. In order to finish calculations in a period less than the age of the universe, climate simulations running on some of the world's best supercomputers have to break up the planet into massive 10,000 square kilometer grids in order to account for the 510 million square kilometer Earth [1]. To say the atmosphere is a complex system is an understatement, and at these scales, it is difficult to even account for variations in the clouds. This is why climate scientists study large scale phenomenon and variations in the weather over time.

One ubiquitous phenomenon relating to climate change is the process by which the Earth's heat is trapped by greenhouse gasses. These gases collectively represent less than 1% of the atmosphere however they are responsible for keeping the Earth above freezing temperatures. There is a wide range of greenhouse gasses but if you were to search "climate change" or "greenhouse effect" on the internet, you'd find that carbon dioxide (CO_2) dominates the discussion [10]. You'd probably also find seemingly conflicting information reporting that Methane (CH_4) is anywhere from 30 to 84 times more potent than carbon dioxide [6, 5]. This paper analyzes the similarities and differences between carbon dioxide and methane in order to explore why CO2 is the main culprit of climate change and how despite this, methane may be considered more potent.

2 Black Body Radiation

In order to understand the mechanism for the behavior of greenhouses gases we will first introduce the physical model of a black body radiator. This is an object that absorbs all incident radiation and then re-radiates energy that is characteristic to that object. The following diagram illustrates how the Earth behaves as a back body and showcases the trapping effect of greenhouse gases:

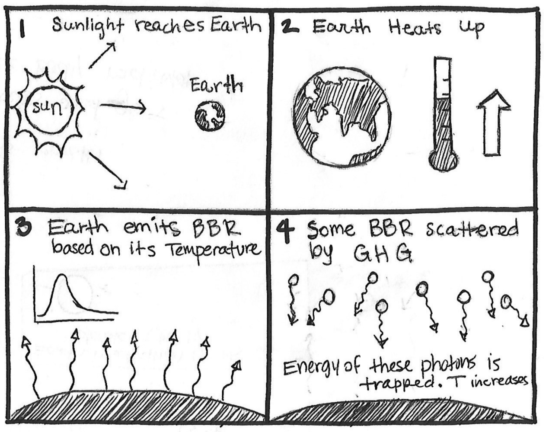

Figure 1: *Earth absorbs radiation from the sun and emits black body radiation (BBR)*

The equation governing how much light intensity is emitted as a function of wavelength is given as a result of solving for the allowable energies for thermal radiation confined to a cavity. It is:

$$I(\lambda) = \frac{2\pi hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_b T}} - 1} \tag{1}$$

Using the surface temperature of the Earth [3], we can calculate what the spectral intensity of light should be coming from the Earth's surface. Figure two below shows a graph of this spectrum:

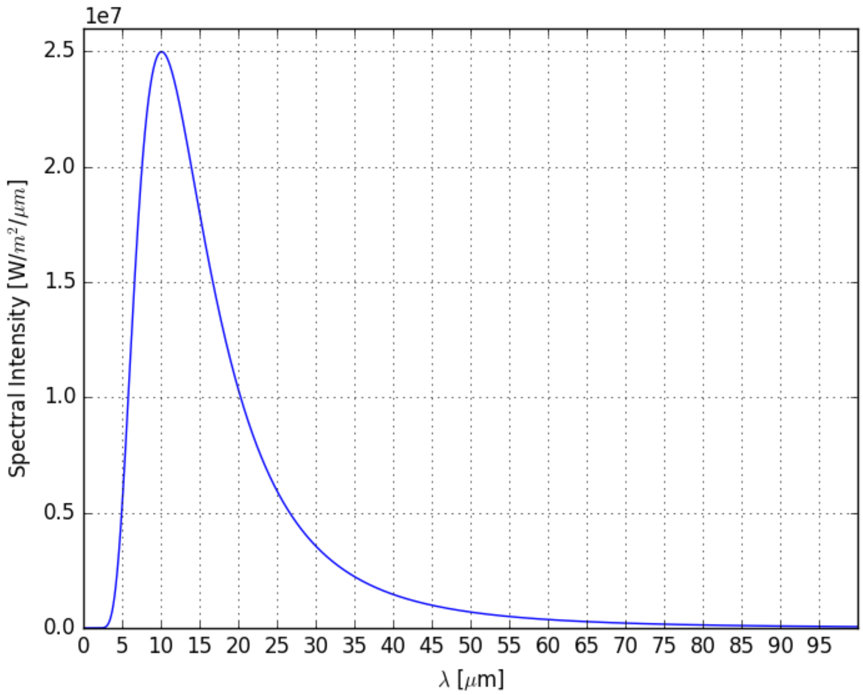

Figure 2: *The black body spectrum of the Earth from equation 1 using the surface temperature T = 287 K*

When this spectrum is compared to those captured by satellites in orbit around the Earth there are some inconsistencies (visually, they appear as dips) that leads us to suspect that not all of this radiation is able to escape the Earth's atmosphere. The following graph is taken from NASA's FIRST project (Far-Infrared Spectroscopy of the Troposphere).

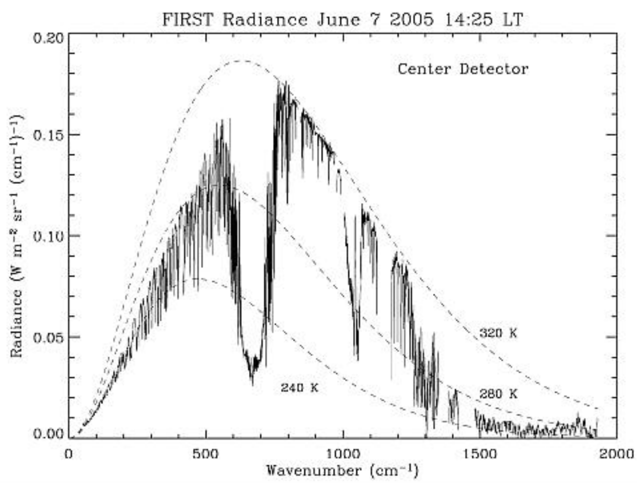

Figure 3: *Radiance spectrum vs Wavenumber for the Earth taken in June 2005 by NASA's FIRST project. Black body spectra for different temperatures are overlaid for reference.*

Figure 3 shows a graph of the Radiance of light coming from the Earth (proportional to Intensity) versus wavenumber (related to wavelength λ). While the general shape appears to follow the curve for a black body, there are very clear dips that suggest that some of the light being radiated by the Earth can not escape the atmosphere to reach the satellites taking this data. As it turns out, the wavelength ranges corresponding to the dips in this spectrum relate to the resonant frequencies of greenhouse gases like carbon dioxide and methane.

3 Carbon Dioxide

Carbon Dioxide (CO_2) is a colorless, odorless gas whose molecules are made up of two oxygen atoms covalently bonded to a central carbon atom. CO_2 is important for many reasons including it's vital role in the respiration processes for life Atmospheric CO_2 exists as a trace gas making up roughly 0.04 percent of the atmosphere by volume [7]. This percentage is steadily increasing due to the burning of hydrocarbon fossil fuels (gasoline, air fuel, etc...) which follows the combustion formula:

$$\mathrm{C}_x\mathrm{H}_{y(\mathrm{g})} + (x + \frac{y}{4})\mathrm{O}_{2(\mathrm{g})} \rightarrow (\frac{y}{2})\mathrm{H}_2\mathrm{O}_{(\mathrm{g})} + x\mathrm{CO}_{2(\mathrm{g})} + \mathrm{Heat}$$

Here the values of x and y determine the type of hydrocarbon fuel being burnt. More importantly though is that the combustion of *any* hydrocarbon always results in the production of CO_2.

4 Methane

Methane (CH_4) is another colorless, odorless gas. Its chemical structure consists of one carbon atom covalently bonded to four hydrogen atoms. Methane is naturally produced through the decomposition of plant and animal matter as well as through the digestive processes of many animals. It is also occurs as a byproduct of many industrial processes and is sought after as a fuel through the fracking industry.

Currently, atmospheric concentrations of methane are estimated to be around 1.8 parts per billion (ppb) [2] which is significantly less than carbon dioxide at around 0.0002 $\%$ of the atmosphere. Due to increased efforts to reach natural gas stores underground and due to increasing agricultural demand, emissions of methane are also increasing. It is clear that there is significantly more CO_2 than methane in the atmosphere. The question remains: why might methane be more potent than carbon dioxide?

5 Analysis

To evaluate which gas has the greatest impact on the climate, we will consider the following three points:

1. The absorption cross section for each molecule as a way to quantify how much light each scatters.

2. The energy of the photons in each element's absorption peak. If the photons being scattered have more energy then that gas will heat the Earth more.

3. The atmospheric lifetime of each gas.

5.1 Absorption Cross Sections

Molecules are collections of atoms whose valence shell electrons imbue them with interesting electrical properties. When subjected to an alternating electric field, like those of electromagnetic radiation, the slight separations of charge between bonded atoms results in oscillations. Similar to a system like an LRC circuit or a string mass, the properties of these molecules lead to natural frequencies. If incident light has an electric field oscillating at these frequencies, the molecules respond by absorbing the photon. In order to return to it's ground state, the molecule then emits a photon and thus the incident radiation has been scattered.

A useful metric that describes the probability of a scattering event is called the absorption cross section. Though it is typically given in units cm^2, the cross section σ is used to denote what percentage of photons will make it a given distance through a particular concentration of gas. For example, imagine light emitted by the Earth at a particular resonant frequency for a greenhouse gas. We can treat this light as a wavefront of area A. The area of light absorbed (denoted A') after traveling a distance L is obtained by computing:

$$\rho AL\sigma = A' \tag{2}$$

Where ρ denotes the concentration of molecules given in $[\frac{particles}{m^3}]$.

The following graphs compare the absorption cross sections for carbon dioxide and methane as a function of wavelength:

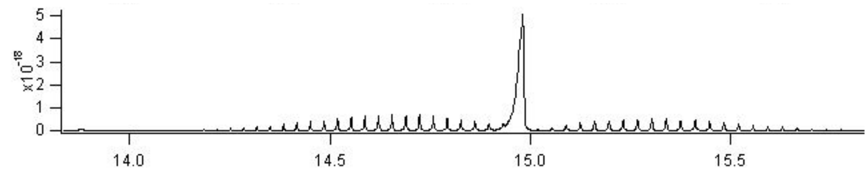

Figure 4: *Absorption cross section of CO2 as a function of wavelength. Vertical axis is in* cm^2 *and Horizontal is in* μm *[8]*

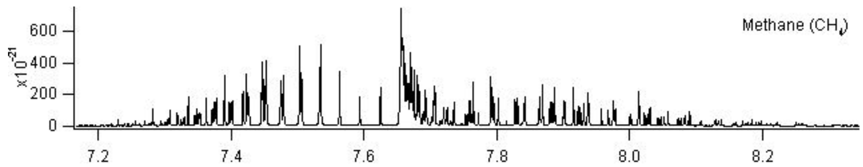

Figure 5: *Absorption cross section of CH4 as a function of wavelength. Vertical axis is in* cm^2 *and Horizontal is in* μm *[9]*

There are a few interesting characteristics to note from these graphs. The first is that for CO2 there is one sharp, tall peak where as for methane, there are many peaks of nearly the same height.The second point to notice is that for carbon dioxide the peak occurs at about 14.95 μm where methane is centered around about 7.65 μm. This will be important later when we consider the energy of the photons reflected by each gas.

Now we want to consider how the gasses differ in the amount of light they absorb. For this calculation consider a box of area A and length 10m. We want to know how much light will be scattered after passing through this box. First we need values for the concentration of each gas which shall be denoted ρ_1 and ρ_2 for CO2 and CH4 respectively.

If we assume the atmospheric gasses to be ideal then we can solve for the concentration of particles in the atmosphere using the ideal gas law:

$$\rho_{atm} = \frac{1}{k_b T} \tag{3}$$

1 atmosphere is roughly 10^5 Pascals so we have:

$$\begin{aligned}\rho_{atm} &= \frac{10^5}{1.38 \cdot 10^{-23} \cdot 287} \\ &= 2.4 \cdot 10^{25} \quad \frac{particles}{m^3}\end{aligned}$$

Now if we multiply each of these by the percentages we listed earlier we will have the needed values.

$$\rho_1 = \rho_{atm} \cdot 400 \cdot 10^{-6} \approx 10^{20} \quad \frac{particles}{m^3}$$
$$\rho_2 = \rho_{atm} \cdot 1800 \cdot 10^{-9} \approx 4.3 \cdot 10^{19} \quad \frac{particles}{m^3}$$

Now using these values we can find the percentage of scattering through the 1 meter long box:

$$\frac{A'}{A} = \rho_1 \cdot 10 \cdot 5 \cdot 10^{-22} = 0.5 = 50\%$$
$$\frac{A'}{A} = \rho_2 \cdot 10 \cdot 800 \cdot 10^{-25} = 0.035 = 3.5\%$$

The results of these calculations show that after 10 meters of travel, 50 percent of the light on resonance with CO2 is absorbed in contrast the much smaller 3.5 percent of light on resonance with methane. As you may have expected, the larger atmospheric concentration of CO2 as well as the larger absorption cross section leads to the carbon dioxide being absorbed much earlier in the atmosphere than methane.

5.2 Energy of the photons

Next let's consider the difference in wavelengths between CO2 and CH4. Planck's law for the energy of a photon is:

$$E = h\nu = \frac{hc}{\lambda} \tag{4}$$

Using this equation for the 14.95μm CO2 peak and 7.65μm CH4 peak we find:

$$E_{CO_2} = \frac{hc}{14.95 \quad \mu m} = 0.083 \quad eV$$
$$E_{CH_4} = \frac{hc}{7.65 \quad \mu m} = 0.162 \quad eV$$

This shows that the light being absorbed by methane has about twice as much energy as the light absorbed by carbon dioxide. This gives a little more credence to the idea of methane being more potent than carbon dioxide. Also if we revisit our first calculation, we found that 3.5 percent of the light on resonance for methane's peak is absorbed in 10 meters. If we extend this to 100 percent we have that it would only take 285 meters for the light to be absorbed by methane. Considering that the atmosphere is many thousands of meters tall, it stands to reason that this difference in absorption cross section isn't significant that significant with regard to how much energy the gases trap.

clearly the light that methane traps has more energy but how much of that light is being radiated by the Earth? It doesn't matter how much energy methane can trap if the Earth doesn't emit any in this wavelength range. To quantify this we will revisit equation 1, the spectral intensity of black body radiation. Plugging in our two wavelengths 14.95 μm and 7.65 μm we can compare how much light is available to trap:

$$I(\lambda_{CO_2}) \approx 1.81 \cdot 10^7 \quad \frac{W}{m^2 \cdot \mu m}$$
$$I(\lambda_{CH_4}) \approx 2.03 \cdot 10^7 \quad \frac{W}{m^2 \cdot \mu m}$$

Thus the light that methane traps has more energy and there is slightly more of it being radiated by the Earth. So if we were to account for the multiple absorption peaks (instead of just one) as well as weighting those energies by their relative spectral intensities, it seems reasonable why many different sources conclude that methane is a more potent greenhouse gas than carbon dioxide. The differences in how much more potent is likely due to differences in how the various ranges of light are weighted when calculating the total amount of energy trapped.

6 Atmospheric Lifespan

Up to this point, we've shown how there is more available light for methane to trap and that light at wavelengths which make methane resonate have more energy than those for CO2. Now we want to consider the atmospheric lifespan of each gas, i.e. how long it is effectively in the atmosphere from the moment it is produced. This will illustrate why CO2 is the main contributor to climate change despite methane being more potent.

Scientists have had a difficult time identifying the atmospheric lifespan of CO2 due to the countless processes it is involved in. Estimates suggest that somewhere between 65 and 80% of atmospheric CO2 dissolves into the ocean over a period of 20 to 200 years. Other processes that make use of CO2 are much slower including chemical weathering and rock formation. So once in the air, Carbon Dioxide can persist for hundreds of years [4]. The

Carbon Dioxide Information Analysis Center (CDIAC) lists the atmospheric lifetime for CO2 at 100-300 years. They describe this number as the time for a input pulse of gas to decay to $\frac{1}{e}$ of its original volume [2].

Methane on the other hand is part of a much less complicated cycle. Removal of methane from the atmosphere occurs through its oxidation by the hydroxyl radical ($^*OH$).

$$CH_4 +^* OH \rightarrow^* CH_3 + H_2O \tag{5}$$

This process leads to a much shorter atmospheric lifespan estimated to be about 12.4 years [2]. Thus it is due to the complicated processes of the carbon cycle that CO2 remains in the atmosphere to trap the Earth's heat for much longer than methane.

7 Conclusion

First, we introduced the idea that the Earth behaves as a black body, radiating the energy it receives from the sun back towards space. This radiated light is not emitted equally for all wavelengths. Instead, as we showed using equation (1), the Spectral Intensity varies with a peak that is governed by the temperature of the body.

This model was then tested by scientists who used satellites and weather balloons in the upper atmosphere and in orbit to analyze the spectrum of infrared light being emitted by the Earth. The data shows that overall, the light radiated by our planet nearly follows the line for a black body at a temperature between 280-300K. However, the dips and spikes in this spectrum necessitated our consideration of greenhouse gasses - principally carbon dioxide and methane which are said the be two of the most potent greenhouse gases along with water vapor.

We developed an intuition for why methane is more ”potent” by showing that despite is smaller absorption cross section, methane traps light that has nearly twice as much energy as that of CO2. Looking back to the black body spectrum we also realized that more light (higher intensity) is put out in the range of methane’s natural frequency than for carbon dioxide. Thus reports of methane being more a potent greenhouse gas appear to be correct.

Finally, we considered the processes by which CO2 and methane are removed from the atmosphere. Due to the complex intricacies of the carbon cycle and the slow process of dissolving into water, CO2 has the potential to live for hundreds of years in our atmosphere as opposed to methane’s decade scale. This is the reason why CO2 garners so much more attention as a greenhouse gas. Emissions today do not just affect us or our children but many generations down the line.

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