12.335 Experimental Atmospheric Chemistry

A practical guide to write your report for this section.

Lab 2: First principles of the green house effect - Using infrared spectra of CO₂ and H₂O to assess their roles on radiative forcing.

• In this section, we measure infrared spectrum of CO₂ and H₂O and discuss why they are the most important greenhouse gasses. Main goal is to use the observed spectrum to estimate radiative forcing of CO₂, and compare the value with that estimated by IPCC. We will mostly follow the article by Wilson and Gea-Banadoche (2012). Hereafter it is called W&G.

• Your lab report will describe what you did in a following format:
  1. Abstract: summarize what you did, why you did it, and the main findings.
  2. Introduction: the goal of the study, why it is important, and a brief summary of the structure of the report. Introduction may refer to numbers in two figures attached in this document (radiation budget and IPCC reports of radiative forcing).
  3. Method: how you did it. This part will contain both 1) experimental method and 2) description of the model.
  4. Results: describe your findings.
  5. Discussion: discuss your findings. In this report, you will compare your results to models, e.g., Stefan-Boltzmann radiation budget or IPCC values of radiative forcing. Discuss if they match well or do not match well, if not, discuss possible reasons why.
  6. Conclusions: summarize main findings.

The report will contain questions in this documents (Q1, Q2, etc.). Some questions are optional, and are suggestions for those interested in deeper understanding. Feel free to ask additional questions you may find.

Infrared spectra of CO₂ and H₂O
Using the FTIR instrument, we measured infrared spectra of CO₂ and H₂O between 550 and 4500 cm⁻¹. We estimate the mixing ratio of CO₂ in the gas cell, and path length (10 cm). We can calculate the absorption cross section by using Beer-Lambert law.

\[
\text{Transmission} = \frac{I}{I_0} = \exp(-\sigma n L)
\]

We saw two absorption band systems of CO₂ in the observed region, one corresponding to the bending mode of vibration, and the other corresponding to stretching, centered around 670 cm⁻¹ and 2350 cm⁻¹, respectively. The center of the band corresponds to fundamental vibrational energy and the fine structures around them are due to rotational energy levels.
We also tested for H2O by injecting 10 mL of water-saturated air to the absorption cell.

Q1: Calculate cross section (σ) as a function of wavenumber for CO2, and plot them. A MATLAB® file is provided for this(CO2calc.m).

Q2: Calculate cross section for water. Assume our flask air was saturated with H2O. You can do this by modifying CO2calc.m

1) Radiation model without atmosphere

Following the Stefan-Boltzmann law,

\[ \sigma_{SB} \times 4\pi R_e^2 = (1 - \alpha) I_0 \times \pi R_e^2 \]

We roughly estimated that the greenhouse effect should be about 150 W m⁻² (see Willon and Gea-Banacloche, 2012). IPCC suggests CO2 radiative forcing is 1.66 Wm⁻² (the important figure is attached below). IPCC radiative forcing is defined as the change in greenhouse effect due to CO2 and compared to preindustrial time (defined as year 1750, and mCO2 at 280 ppm). Thus, CO2 radiative forcing is about 1 % of the total greenhouse effect (1.66/150). But how does the IPCC estimate radiative forcing?

The goal of this section, thus, is to see if we can reproduce IPCC number by a very simple model, and using our own observation of infrared spectra of two most important greenhouse gasses (H2O and CO2). First we test the very simple model assuming homogeneous atmosphere, and then move on to a bit more involved model.

2) 1st order model: a non-radiating homogeneous atmosphere

First, we use the simplest possible model that assumes homogeneous atmosphere, and does not radiate back. Our first goal is to calculate how much radiation escapes to space with or without CO2, the difference should be greenhouse effect.

The pressure of the atmosphere decreases exponentially with altitude. We can solve this from hydrostatic equation (see Seinfeld and Pandis, Chapter 1), assuming that temperature is relatively constant.

\[ p = p_0 \exp (-z/L) \]

Where, L is called the scale height. This is the height of a hypothetical atmosphere that is homongeneous in terms of temperature and pressure.
Mixing ratio of CO$_2$ is fairly constant (there is no major reactions within troposphere and stratosphere unlike CH$_4$ and N$_2$O). Assuming that the mixing ratio is constant at 400 ppm in our homogeneous atmosphere, calculate column density of CO$_2$. That is,

$$C_{D_{CO2}} = m_{CO2} \times n_0 \times L$$

Column density has a unit per area, e.g., # of molecules per cm$^2$. The $n_0$ is the total number density of our homogeneous atmosphere. The first task is to calculate cross section ($\sigma$) using Beer-Lambert law from our FTIR data, and then apply it to calculate the transmission (as a function of wavelength) of our homogeneous atmosphere.

The next step is to set up a formula for the Planck’s law. This is from equation (14) of W&G (2012).

$$B(\nu, T) = \frac{2\pi h \nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1},$$

You will note that the radiation peaks at around 600 cm$^{-1}$, and this is where bending vibration of CO$_2$ is located.

In our homogeneous atmosphere, what we want to know is how much radiation is blocked by the CO$_2$ or how much radiation can escape out of the atmosphere. This can be done by multiplying the transmission of the atmosphere ($T(\nu)$) and Planck’s blackbody radiation ($B(\nu, T)$). Then, the upward radiation at the top of our homogeneous atmosphere will be:

$$I_{TOP}(\nu) = \exp(-\sigma(\nu)C_{D_{CO2}})B(\nu, T)$$

Q3: Run the MATLAB file, “radiation1.m” and test this. This m-file numerically integrates across wavenumber and give radiation in W/m$^2$. How much does CO$_2$ contribute to the radiation budget? I have got 54 W/m$^2$, this is about the third of our first analysis (of 150 W) based on the Stefan-Boltzmann Law.

Q4 (Optional): if you include water, would you get the rest 100 W of greenhouse effect? How much water is in the air? Try out different quantities. It is hypothetical since water mixing ratio changes with altitude so that our hypothetical atmosphere doesn’t really work here but this will give us a ballpark number.

Q5: Now you can change the mixing ratio of CO$_2$ from 400 to 280 ppm (which is the mCO$_2$ in 1750), and see how radiation budget changes. Can we get a RF value somewhat reasonable compared to IPCC estimate? IF not, suggest why, and try improving the model. Some ways of improving the model are described below.
Spectrum resolution and saturation

You may realize that one of the limit for our approach is in the FTIR data. The instrument is not particularly sensitive around 600 cm\(^{-1}\). There is a very strong absorption at the center of the band system but data is very noisy.

- Q6: Show that our FTIR instrument is not very sensitive at 600 cm\(^{-1}\) from baseline measured by our instrument. IR source is more like a black body, and the detector (our detector is DTGS) has a characteristic sensitivity across IR regions.
- Q7: Would an experiment with higher mCO\(_2\) help? Why or why not?
- Q8 (optional): Implement triangle approximation for your spectrum (Figure 1, W&G) in the radiation model, and test if you get more reasonable radiative forcing.

Another limit is the spectrum resolution. Our FTIR (Thermo Nicolet is5) has 0.8 cm\(^{-1}\) resolution. Ro-vibrational line width in a real atmosphere is much narrower. Two factors contribute to the line width: Doppler and pressure broadening. Doppler line width is a function of the molecular weight, temperature and the frequency of transition, and is very narrow compared to the spectrum resolution of our FTIR (~0.001 cm\(^{-1}\)). Pressure broadening also contributes to the line broadening. HITRAN database uses an empirical formula to account for this. The line broadening parameters for CO\(_2\) bending are around 0.075 to 0.08 cm\(^{-1}\)/atmosphere. Thus, at surface pressure of 1 atmosphere, pressure broadening (called Lorentzian) line width is about 0.08 cm\(^{-1}\) (this is in half width at half maximum). These are wider than the Doppler line width but still very narrow, compared to our spectrometer’s resolution.

Instrument resolution, however, does not affect (theoretically) the integrated cross section (i.e., low resolution instrument give shorter and broader absorptions but the area should be the same). The line strength is also a function of temperature. A sophisticated radiative-transfer model takes account line width and strength as a function of T and P. We ignored them entirely.

3) 2nd order model. Model with a radiating atmosphere

CO\(_2\) absorbs photons at around 660 cm\(^{-1}\), but the absorbed energy can eventually radiate back, roughly half radiates back towards the ground, and half towards the space. There may be half the chance of the trapped energy radiates upward at each absorption step. In a real atmosphere, though, molecular collision happens much faster, at a time scale on the order of nano-seconds. Collisions transfer energy to surrounding molecules and this process warms up the air. Thus, the next model takes account the radiation from the atmosphere itself.
A fundamental equation for the radiative transfer model is called Schwarzchild’s equation.

\[ \frac{dI_{up}}{dz} = -n\sigma(v)\left(I_{up} - B(v, T(z))\right) \]

See equation 15 from W&G, 2012. We are interested in the upward radiation \( I_{up} \) at the top of the atmosphere, and want to compare that at ground level. Thus, we’ll need to integrate \( dI_{up} \) from the surface to the top of the atmosphere. W&G paper solves this by approximating \( n \) (number density) and \( T \) (temperature) as a function of altitude \( (z) \).

- Q9: Use MATLAB file rad2.m to calculate equation (22) of W&G. Modify it and see what radiative forcing you get form here.
- Q10: Test mCO\(_2\) at 400 ppm (roughly today) and 280 ppm and see what radiative forcing you get.

References:
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).
Figure SPM.2. Global average radiative forcing (RF) estimates and ranges in 2005 for anthropogenic carbon dioxide (CO2), methane (CH4), nitrous oxide (N2O) and other important agents and mechanisms, together with the typical geographical extent (spatial scale) of the forcing and the assessed level of scientific understanding (LOSU). The net anthropogenic radiative forcing and its range are also shown. These require summing asymmetric uncertainty estimates from the component terms, and cannot be obtained by simple addition. Additional forcing factors not included here are considered to have a very low LOSU. Volcanic aerosols contribute an additional natural forcing but are not included in this figure due to their episodic nature. The range for linear contrails does not include other possible effects of aviation on cloudiness. \(2.9, \text{Figure 2.20}\)

from IPCC-4\textsuperscript{th} report