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Finding Global Warming Potential of Greenhouse Gases Using Cross-Sectional Infrared Spectroscopy

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Infrared Spectra were taken of carbon dioxide gas to calculate Radiative Forcing (RF) through IR cross-section analysis, as a beginning of the creation of a new Physical Chemistry laboratory series that investigates Greenhouse Gases and leads students to calculate Global Warming Potential (GWP). The average RF value was 4.29×10^{-4} , compared to a literature³ value of $1.4 \times 10^{-5} \text{ W m}^{-2}$. Refinement of the experimental setup must occur as next steps in this research, in order to test more gases (nitrous oxide and methane) and to calculate their GWPs.

Background

The Earth emits radiation between 3 to 40 micrometers (μm) in the infrared (IR) range. The Earth's maximum emission is between 8 and 13 μm , commonly referred to as the atmospheric window region⁴; GHGs that absorb in this region often have a more severe effect on overall warming, especially when they absorb where water vapor and naturally occurring CO_2 do not. Some of this infrared radiation is trapped in the Earth's atmosphere by partially by Greenhouse Gases (GHGs) in the lower atmosphere, which absorb the energy and prevent it from escaping to space.

When molecular vibrations and rotations have energy level spacings equal to incoming IR radiation, they absorb the radiation, transfer the energy to other molecules through collisions, raising the overall thermal energy and therefore temperature of the system. Thus, molecules that absorb IR radiation and prevent it from escaping to space raise the temperature of the Earth's atmosphere. A molecule is IR active if it exhibits a change in its dipole moment of the course of a molecular vibration. Nonpolar diatomic or monatomic molecules, such as N_2 , O_2 , and Ar do not absorb IR energy and are not GHGs. CO_2 , CH_4 , N_2O , and O_3 , as well as atmospheric H_2O vapor, are the primary components of the atmosphere that are IR active. Water vapor, while a significant IR absorber and very prevalent in the atmosphere, is not the focus of discussion around climate change because it is not an anthropogenic GHG (is not produced by humans) and cycles effectively through the atmosphere through the natural water cycle.

Despite these 4 gases (CO₂, CH₄, N₂O, and O₃) being present in trace amounts in the atmosphere, they contribute greatly to atmospheric warming. Global Warming Potential (GWP) is a numerical value to quantify a gas's effect on warming and can explain why such small concentrations of gas can have detrimental impacts on atmospheric temperature (1). GWP depends on three factors⁴:

1. Which wavelengths a molecule absorbs. Molecules must absorb within the thermal IR and as mentioned previously, if they absorb within the window region of the atmosphere, they will be more impactful GHGs.
2. The atmospheric lifetime of a molecule. Longer-lived molecules will have greater warming impacts.
3. How strong a molecule absorbs. More energy absorbed on a per-molecule basis will mean more energy absorbed in any given concentration.

GWP is calculated for a particular time horizon, or amount of time to consider a GHG for, and it is always calculated in reference to CO₂. Therefore, CO₂ always has a GWP of 1. This value and those of the other gases involved in this research are listed in Table 1.

$$GWP = \frac{RF^{GHG} \times \left(\frac{1000}{MW^{GHG}}\right) \times \int_0^{TH} e^{-\frac{t}{LT^{GHG}}} dt}{RF^{CO_2} \times \left(\frac{1000}{MW^{CO_2}}\right) \times \int_0^{TH} e^{-\frac{t}{LT^{CO_2}}} dt} \quad (1)^1$$

Gas Name	Current Atmospheric Concentration	Lifetime (years)	Radiative Forcing (W m ⁻²)	GWP with Time Horizon 20 years	GWP with Time Horizon 100 years
Carbon Dioxide (CO ₂)	400 ppm	50-200 (env chem text)	1.4 x 10 ⁻⁵	1	1
Methane (CH ₄)	1800 ppb	12	3.7 x 10 ⁻⁴	72	25

Nitrous Oxide (N ₂ O)	325 ppb	114	3.03 x 10 ⁻³	289	298
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Table 1: Literature values for three select gases of interest³

Experimental Methods & Results

GWP is calculated with reference to 1 kg of CO₂ and with an exponential decay model. Exponential decay is a simplification of the real-world processes but serves as an effective estimate for this method. The lifetime of CO₂, while extremely variable, is taken as 150 in the GWP calculations¹. The precursor calculations for GWP are as follows. The average cross section σ (in cm² molecules⁻¹ cm⁻²) of a GHG spectrum is calculated using the integrated values over 10 cm⁻¹ intervals (A_{int}) in cm⁻¹, the path length of the IR cell in cm (l), and the number density of the gas in molecules cm⁻³ (n) (2)¹.

$$\sigma = \frac{A_{int}}{l n} \quad (2)$$

Radiative Forcing is a component of the GWP calculation; it quantifies the effect a singular gas has on the difference between outgoing radiation with and without the gas present per ppbv and is given in units of W m⁻² (3)³. Pinnock et al.² created a radiative forcing calculation through a “narrow band model” that breaks the spectrum of the average Earth sky into 10 cm⁻¹ segments (F_i). Later, the spectrum of a GHG will be broken into these same segments, all to allow for simple enough calculations that effectively estimate GWP. In this research, the range 500 to 2500 cm⁻¹ was used due to the limitations of the KBr gas cell windows on the low end and the tabulated F_i values in Pinnock et al.² on the high end. This makes 200 bands.

$$RF = \sum_{i=1}^{200} F_i \sigma_i \quad (3)$$

In the radiative forcing calculation, $F_{i\sigma}$ is radiative forcing per wavenumber per unit cross section in $\text{W cm m}^{-2} \text{cm}^{-2}$ molecule for each spectral band i . Sigma is the average cross section in molecules cm^{-3} for each spectral band (2). This calculation effectively weights the impact a GHG's absorption has when considering the window regions in the atmosphere.

The experimental setup is shown in Figure 1. Its components are listed below.

- A. Stainless steel 10 cm vacuum-capable gas cell with KBr windows
- B. Pressure gauge (torr)
- C. 1/4" NPT male to 3/8" NPT female adaptor
- D. 3/8" NPT male to 1/4" Swagelok male
- E. 1/4" Swagelok compression fitting
- F. 1/4" Swagelok metering valve
- G. 1/4" NPT female hose barb for 1/4" ID tubing

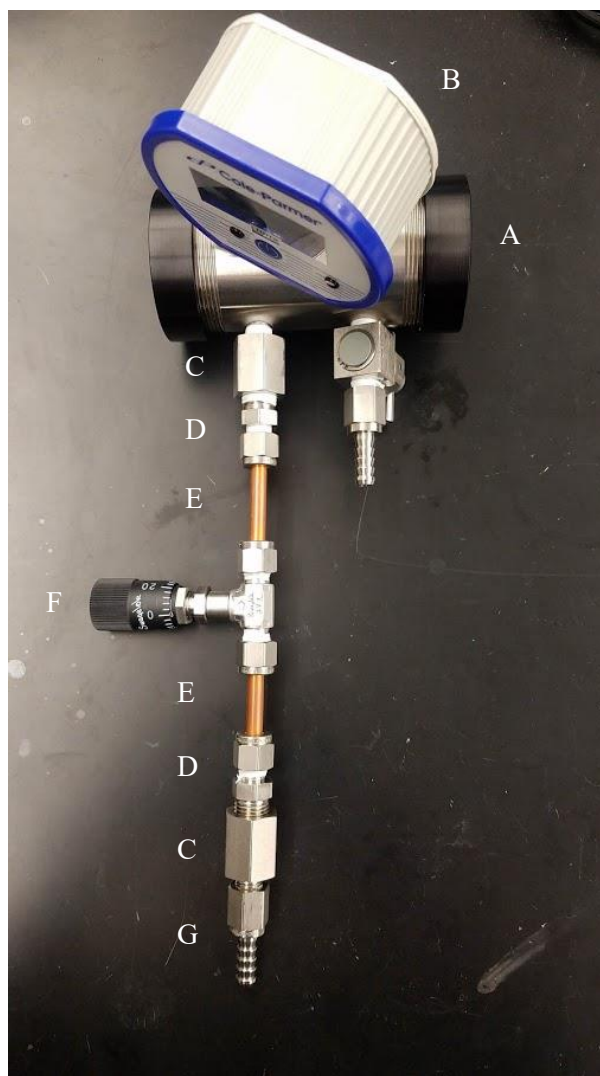


Figure 1: IR cell experimental setup

CO₂ was tested by adding approximately 10-20 torr above atmospheric pressure of Nitrogen. N₂ was flushed into the cell for 8 minutes before adding the small pressure of CO₂ using the metering valve. In between trials, the KBr windows were removed for 5 minutes before repeating the process by refilling the cell with N₂. The data was processed using both an Excel template and using a Python script. Both methods take data and variable input and they output calculated values. The progress at this point in the research is to output RF, but in the future both methods will output GWP when gases other than CO₂ are tested. The literature³ value for the Radiative Forcing of CO₂ is $1.4 \times 10^{-5} \text{ W m}^{-2}$. Data is not reported for 2 trials where the pressure

was similar to the successful trials but the CO₂ peaks in the spectra were inexplicably weak and almost indistinguishable from the areas with no absorption.

Trial	Pressure (torr)	Radiative Forcing (W m ⁻²)
1	9	5.34 x 10 ⁻⁴
2	15	2.37 x 10 ⁻⁴
3	20	5.17 x 10 ⁻⁴
Average		4.29 x 10 ⁻⁴

Table 2: Results of RF calculations for CO₂

There is room for improvement on the experimental setup; the inlet port could be reduced to have less leakage points in order to potentially take spectra at vacuum pressure, or to hold above atmospheric pressure better. Additionally, the method needs to be replicated to see how consistent of results it produces. If the issue with weak peaks persists, troubleshooting and adjustment must occur. A first troubleshooting step would be to re-take backgrounds and find how often the background needs to be refreshed. Also, CH₄ and N₂O might require higher pressures than CO₂ did, so the cell setup may need to be adjusted if it cannot hold pressures much higher than atmospheric pressure. Once these next two gas spectra have been taken, it will be easier to see whether the values are accurate with the current experimental setup and procedure.

Conclusion

In this project, an IR gas cell setup was created to take spectra of Greenhouse Gases, and Radiative Forcing values were calculated using Excel and Python. CO₂ spectra were taken and the RF was calculated to be an average of 4.29 x 10⁻⁴ between 3 trials, compared to a literature³ value of 1.4 x 10⁻⁵ W m⁻². The next steps of this research include taking spectra of N₂O and CH₄. Using these spectra, integration values and GWP can be calculated. It remains to be seen how

accurate these GWP values will be given how the RF of CO₂ is an order of magnitude from the literature value. Once the experimental setup and method is replicable and GWP values for these two gases are close enough to literature, an investigative laboratory series can be written to lead Physical Chemistry students to understanding of how GHGs work and how GWP is calculated. In the future, these laboratory materials could be expanded to take spectra of other GHGs, such as a lab-safe HCFC.

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