Greenhouse Gas and Climate Science Measurements

The SIM Metrology School
October 28 – November 1, 2013

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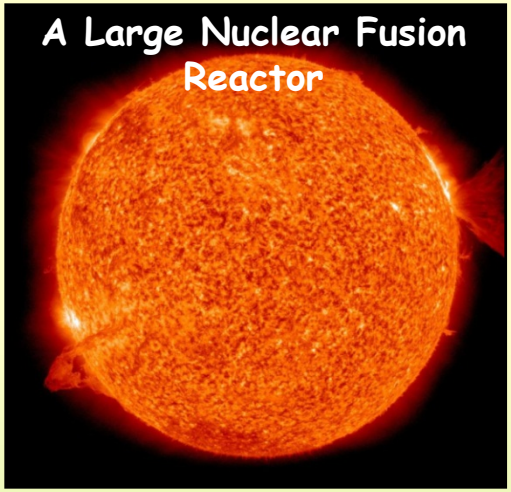
NIST
National Institute of Standards and Technology
U.S. Department of Commerce

Outline

- The Sun and The Earth
  - Protection Mechanisms for Life on the Surface
- Properties of Earth's Atmosphere
  - Earth's energy budget and greenhouse mechanisms
  - Greenhouses

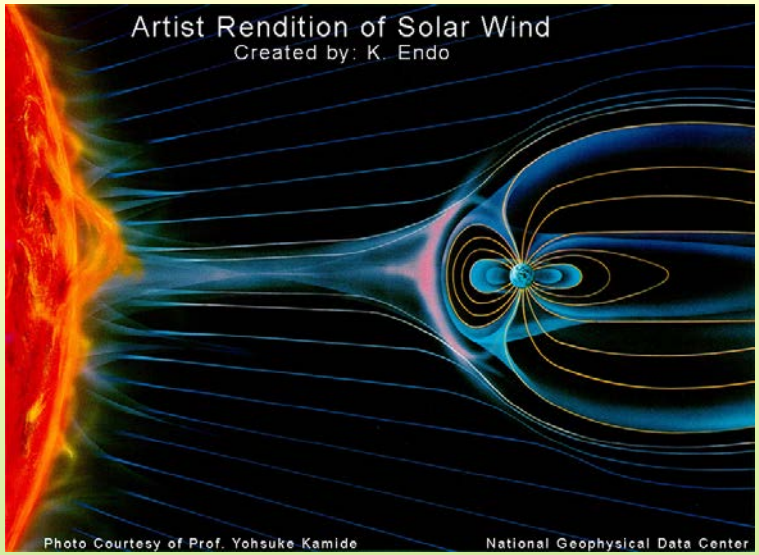
The Earth's Power House – The Sun

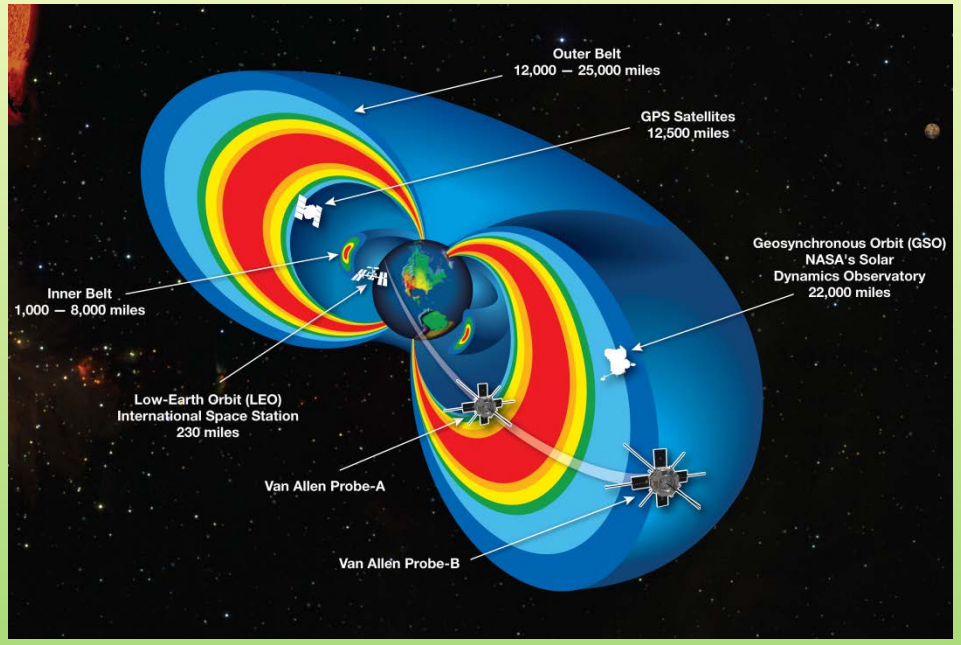


The Solar Wind

The sun emits a lot of intense short wavelength radiation. solar flares can be big and emit large quantities of energetic particles and radiation.

Earth's Properties and Characteristics Interact with Solar Radiation to Strongly Influence and Protect Its Surface

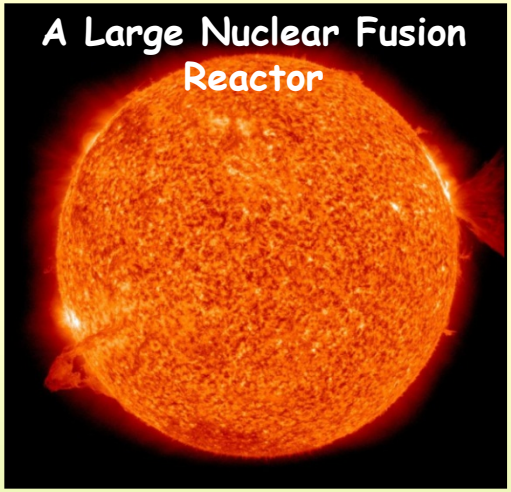




The Van Allen Belts

Earth's Magnetic Field Interacts with Charged Particles to Shield Its Surface from Damaging Effects of Particles impacting the Surface

The Earth's Power House – The Sun



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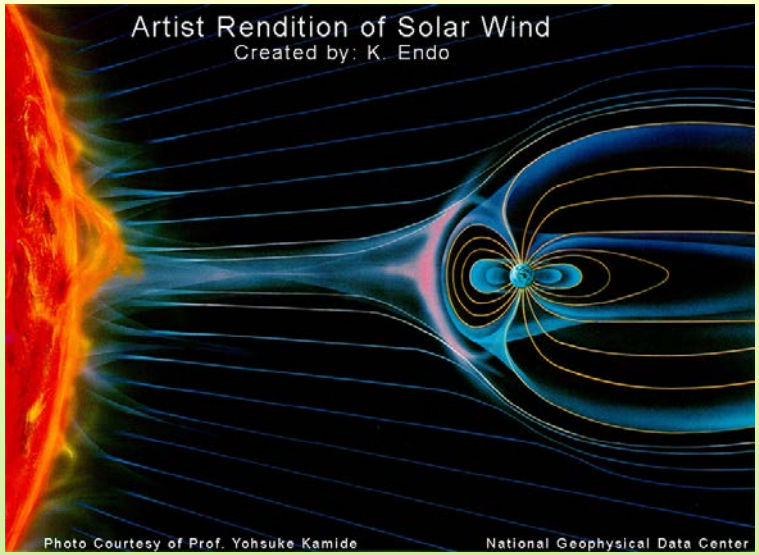
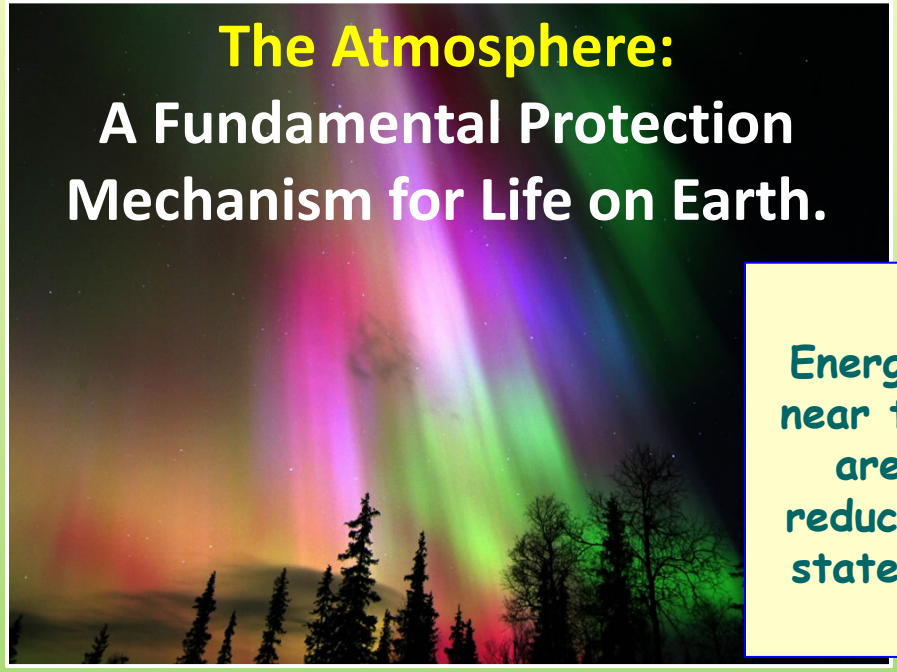




The Aurora Borealis

Energetic charged particles hit earth's atmosphere near the magnetic poles. Atmospheric gas molecules are impacted by the solar wind, absorbing and reducing the particle's energy. Electrons in excited states return to equilibrium by emitting the visible radiation the we see as the Aurora.

Observing the Sun and Solar/Earth Interactions

- How do we measure the amount of solar radiation?
  - Planck's Radiation Law
  - The Earth as a Blackbody, Thermal Radiation, and the Atmosphere
- What's this got to do with Greenhouse Gases and Climate?
  - What does Earth's atmosphere do
    - Radiative effects – Selective Absorption
    - How does the greenhouse effect work?
    - What's the impact of atmospheric trace gases
    - Greenhouses and Earth's energy budget and Atmospheric processes
    - Monitoring the atmosphere and the Oceans

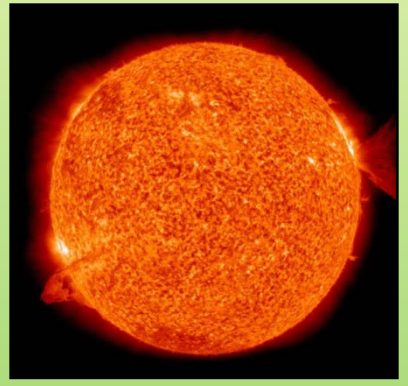
Planck's Radiation Law

$$B_\nu(T) = \frac{2h\nu^3}{c^2}\frac{1}{e^{\frac{h\nu}{k_B T}} - 1}, \text{ or } B_\lambda(T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

where for a body (blackbody):

- B – its spectral radiance,
- T – absolute temperature,
- k_B – the Boltzmann constant,
- h – the Planck constant,
- c – the speed of light,
- λ - wavelength , and
- γ - frequency.

- Planck's law describes the electromagnetic radiation that pervades any medium, whatever its constitution, that is in *thermodynamic equilibrium* at a definite *temperature*.
  If the medium is homogeneous and isotropic, the radiation is homogeneous, isotropic, unpolarized, and incoherent.
  - Composed of fundamental physical constants - applicable to all physical systems and observational parameters
- Radiance
  - the quantity of radiation that passes through or is emitted from a surface and falls within a given solid angle in a specified direction
  - SI Units – watts per (steradian – cubic meter) ($W \cdot sr^{-1} \cdot m^{-3}$)
- Allows measurement of solar radiation emitted
  - What's needed to measure solar surface temperature?
    - Spectral Radiance
    - Wavelength or frequency of the radiation
    - Assumes that the sun's surface is uniform



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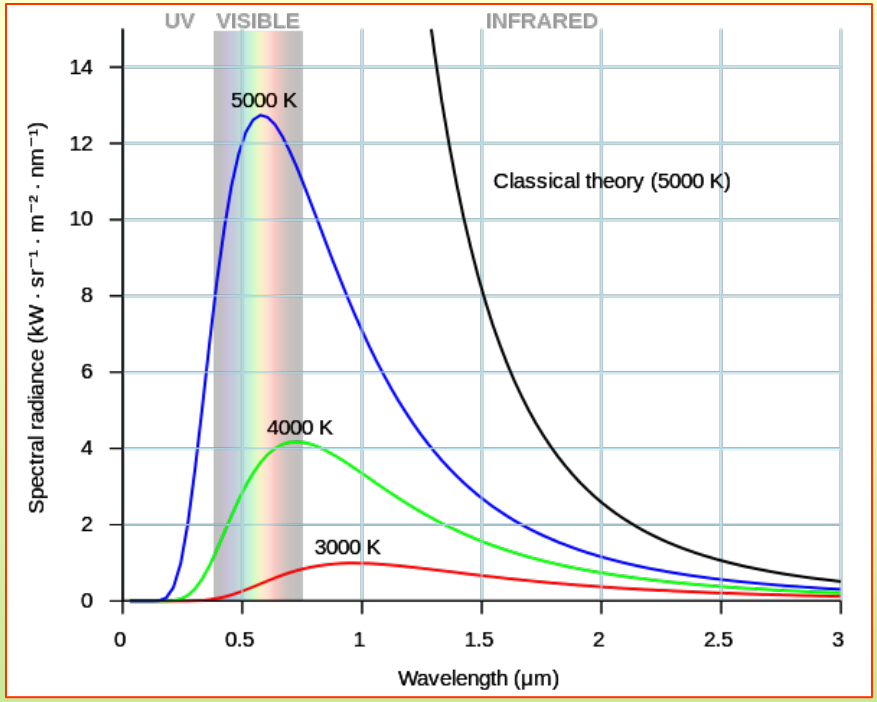
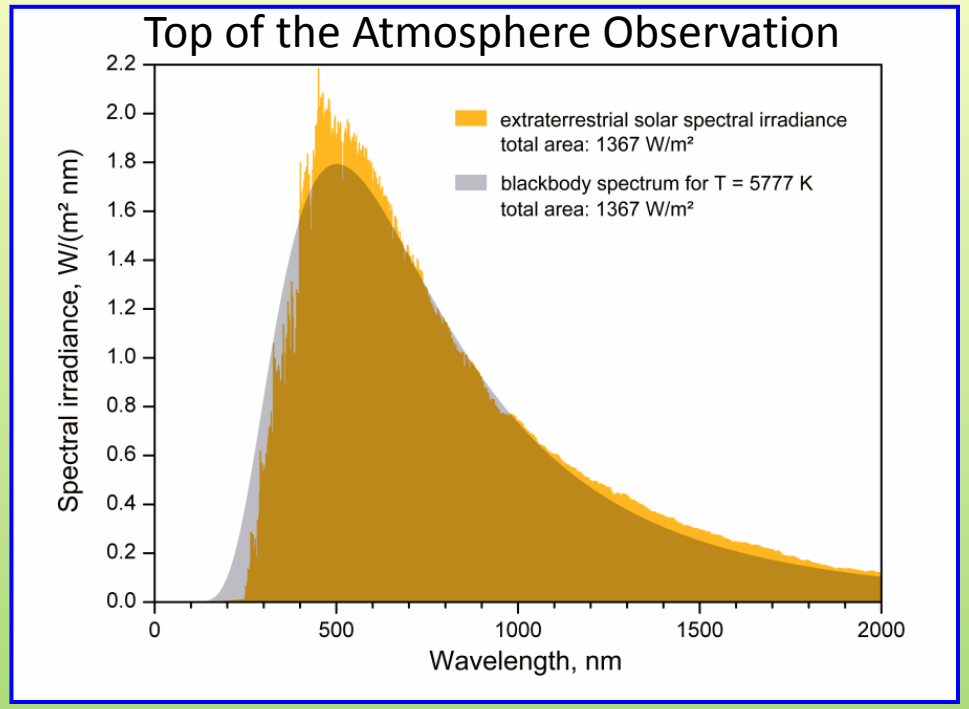




- **Theory vs. Observation**
- **Sun can be approximated by a blackbody having a uniform surface Temperature of ~5,777 K with a spectral irradiance of ~1,361 W/m^2**
- **Variation near T_{max} cause differing estimated values of peak temperature**

The Earth as a Blackbody

The Stefan-Boltzmann Law

Treating Earth as a Blackbody

- **Assume a uniform surface temperature**
- **Emits thermal radiation**
- **Equate incoming solar and outgoing thermal radiation**
- **Earth's Surface Temperatures**
  - **Completely absorbing ~279 K (+6 °C)**
  - **Clouds reflect ~30% ~255 K (-18 °C)**
- **Radiative physics theories based on simple assumptions about the earth's surface do not explain observed Earth surface temperature of ~300 K (27 °C)**
- **Additional explanation needed**

$$j = \sigma T^4$$

j – radiant exitance (W/m^2)
power emitted / square meter

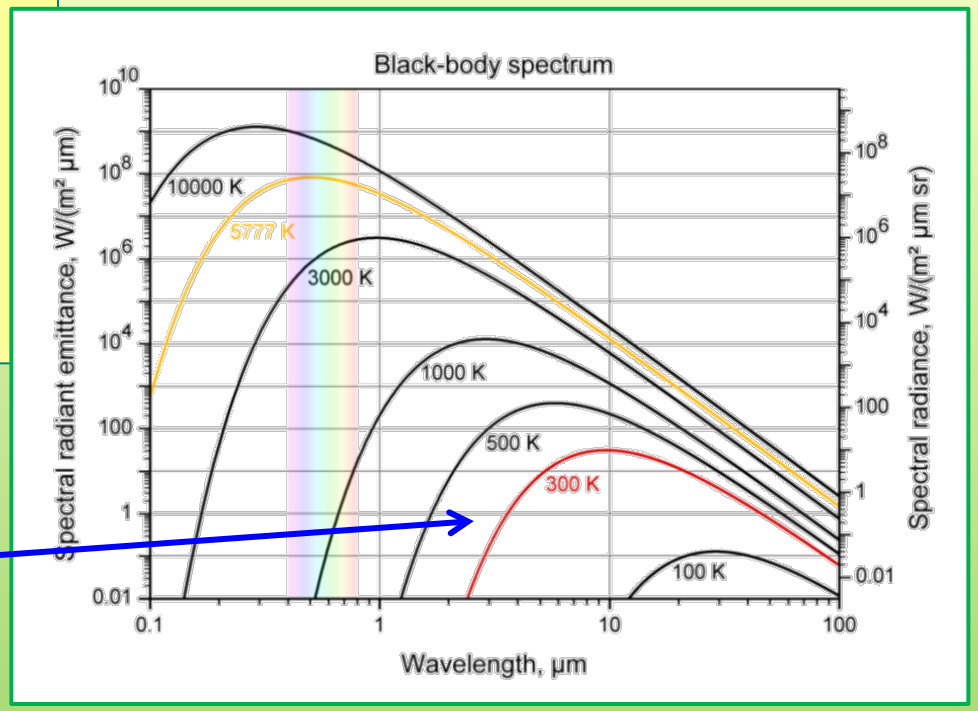
$$\sigma = \frac{2\pi^5 k^4}{15 c^2 h^3} = 5.670400 \times 10^{-8}\,\mathrm{J\,s^{-1}m^{-2}K^{-4}}$$

Wein's Approximate to Planck's Law

$$\lambda_{\max} = \frac{hc}{x}\frac{1}{kT} = \frac{2.89776829\ldots \times 10^6\ \mathrm{nm}\cdot K}{T}.$$

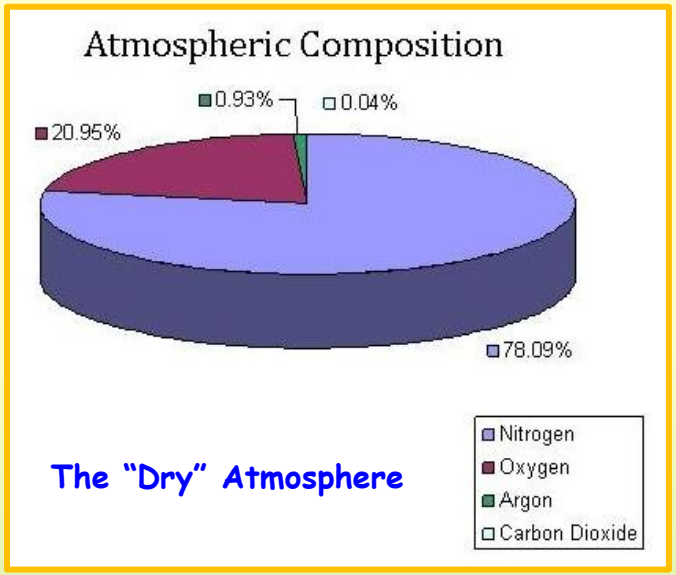
For T = 300K

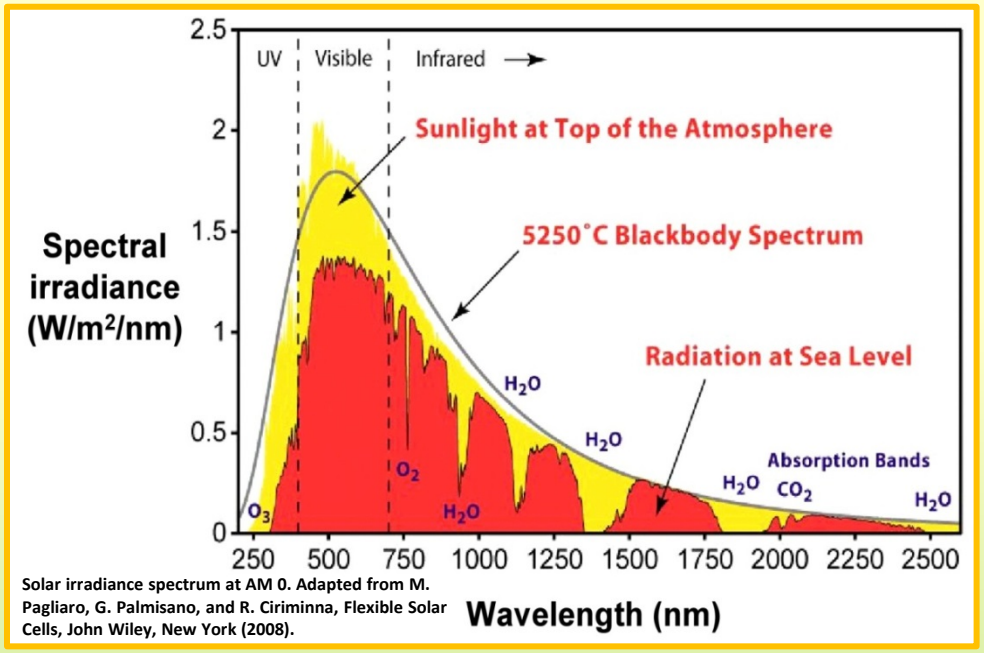
λ_m = 9659 nm = 9.659 µm



Composition of the Atmosphere & Solar Irradiance

Atmospheric Absorption Processes





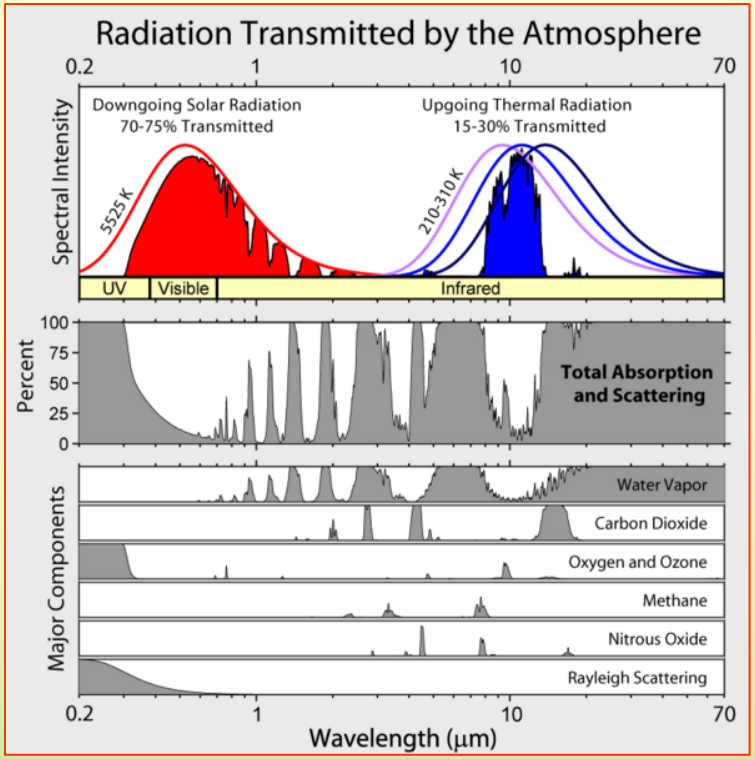
Solar irradiance spectrum at AM 0. Adapted from M. Pagliaro, G. Palmisano, and R. Ciriminna, Flexible Solar Cells, John Wiley, New York (2008).

- **Earth's Atmosphere, ~99%, is nitrogen and oxygen with some other gases in trace amounts**
  - Observation of the solar spectrum through Earth's atmosphere shows large gaps
  - Caused by absorption of specific molecular gases
  - Ozone (O_3) absorption protects the Earth's surface from ultraviolet radiation that damages biological organisms
  - Ozone and oxygen absorb in the visible and near infrared.
  - The greenhouse gases absorb thermal radiation throughout the infrared region in bands dependent upon wavelength

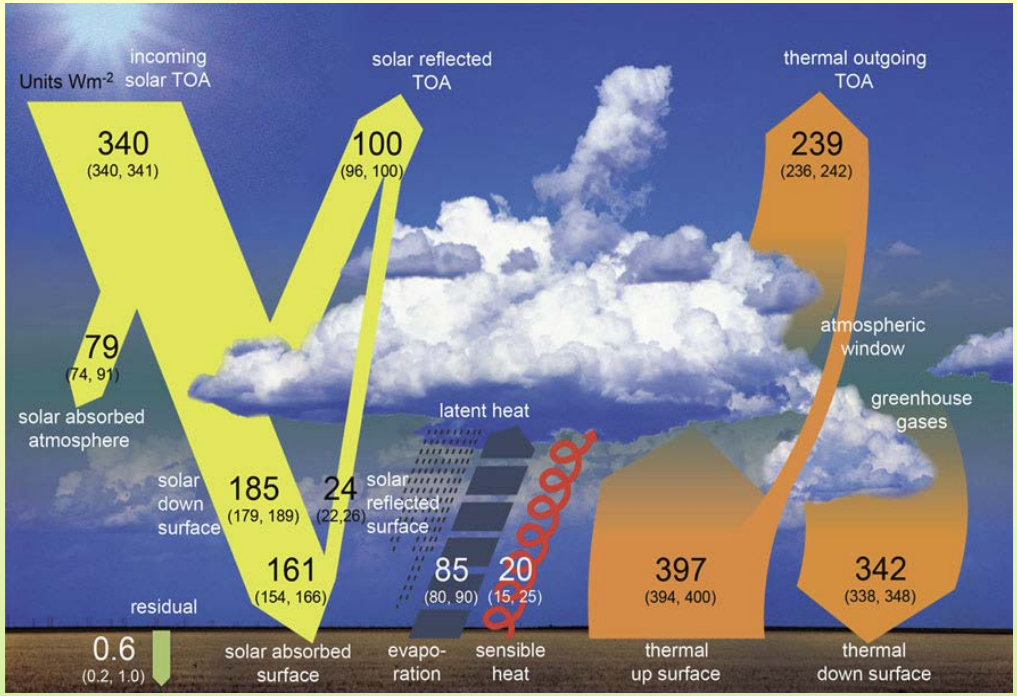
Global Atmospheric Concentrations of Greenhouse Gases

CO_2 – Carbon Dioxide	400 μmoles/mole
CH_4 – Methane	1.8 μmoles/mole
N_2O – Nitrous Oxide	0.32 μmoles/mole

The Atmosphere as Window and Absorber & The Earth's Energy Budget



Earth's Energy Budget



Wild, Folini, Schar, Fold, Loeb, König-Langlom. Clim Dyn (2013) 40:3107–3134

- The atmosphere transmits and selectively absorbs radiation
- Many mechanisms interact with incoming short wavelength radiation to reflect it back to space, absorb it by both atmospheric gases the surface
- Radiation absorbed by atmospheric gases raise Earth's temperature.
- Main greenhouse gases: water vapor, CO_2, CH_4, and N_2O)

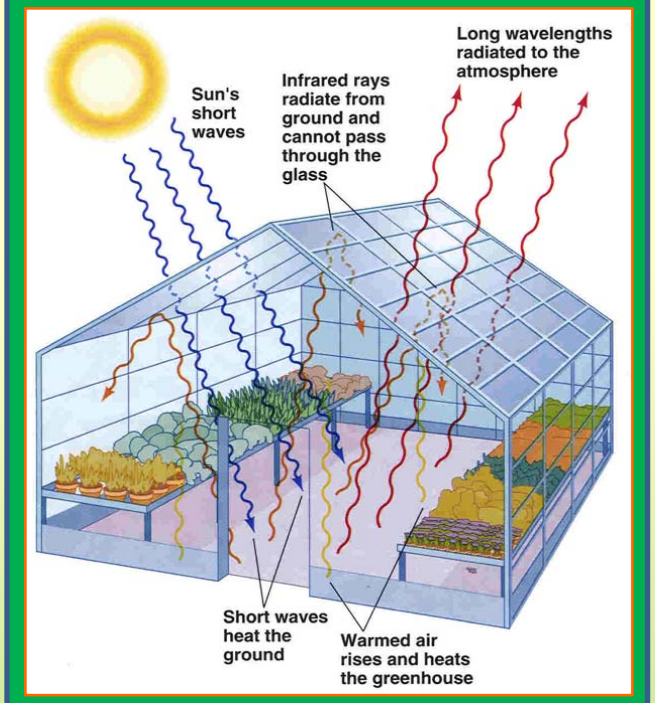
Earth's Greenhouse

Driven by Selective Absorption of Solar & Earth's Radiation

Selective Absorption Warms Atmospheric Gases

- Earth's surface emits thermal radiation in the infrared spectral region.
- Molecular gases, CO_2, CH_4, N_2O, & H_2O strongly absorb thermal radiation: ~ 1.5 – 30μm
- Small concentrations of greenhouse gases have large effects because their absorption strength is much larger, 100X to 10,000X, than nitrogen and oxygen (~99% of the atmosphere).
- Molecular collisions quickly transfer absorbed thermal energy to oxygen and nitrogen.
- Earth's land and oceans are warmed by the overlying atmosphere which transfer energy (heat) to surfaces convectively and radiatively
- CO_2, CH_4, & N_2O: significant man-made (Anthropogenic) sources and sinks
- Some water vapor emissions are anthropogenic, but they are a very small fraction of the quantities involved in evaporation and condensation in the oceans and on land.
- Atmospheric Greenhouse warms Earth ~ 35 to 40 °C

Earth's Greenhouse

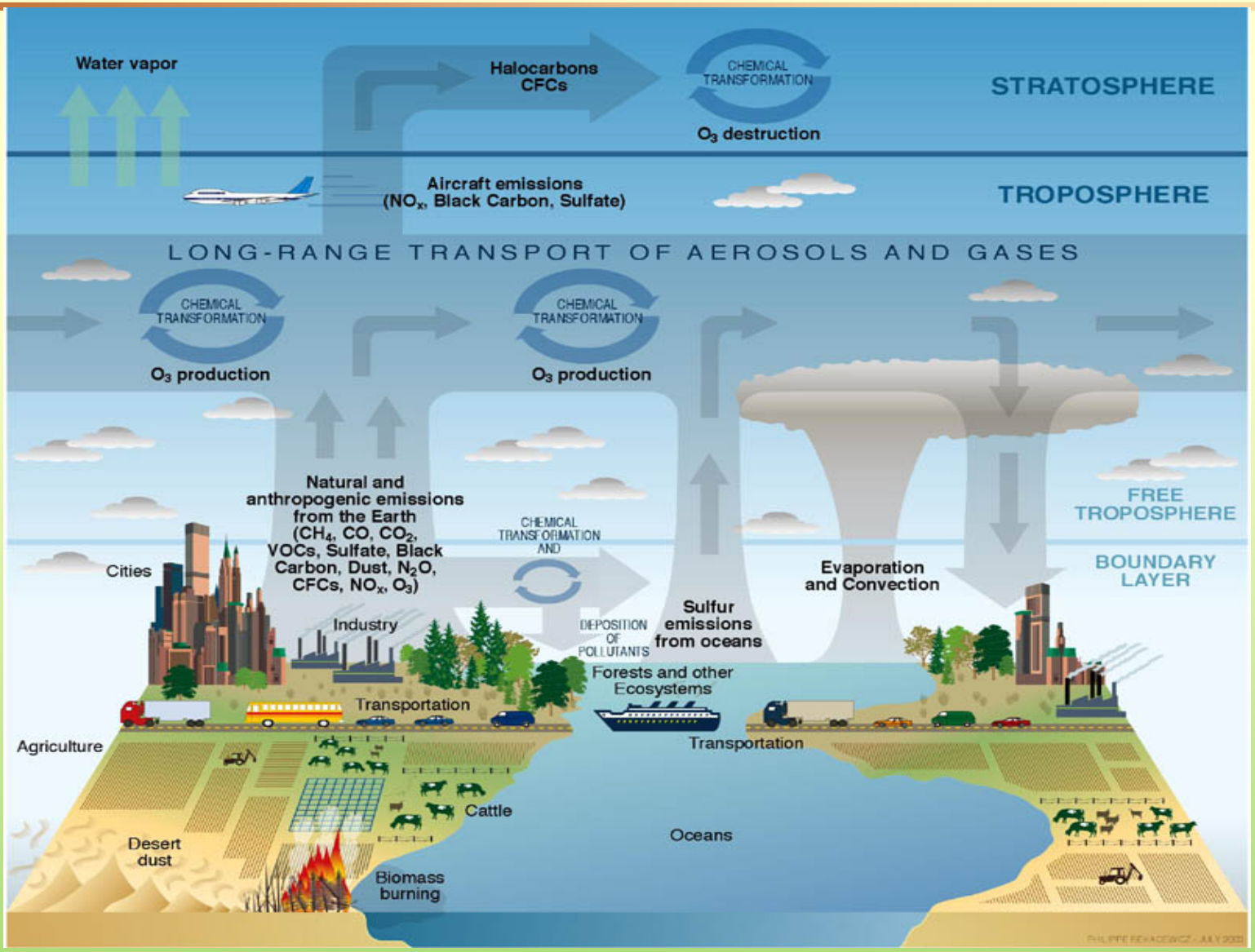


Approximate Global Average Concentrations of Greenhouse Gases in the Atmosphere

CO_2 – Carbon Dioxide	400 μmoles/mole
CH_4 – Methane	1.8 μmoles/mole
N_2O – Nitrous Oxide	0.32 μmoles/mole

Major Mechanism of the Earth's Atmosphere

GHG Sources, Sinks, and Transport

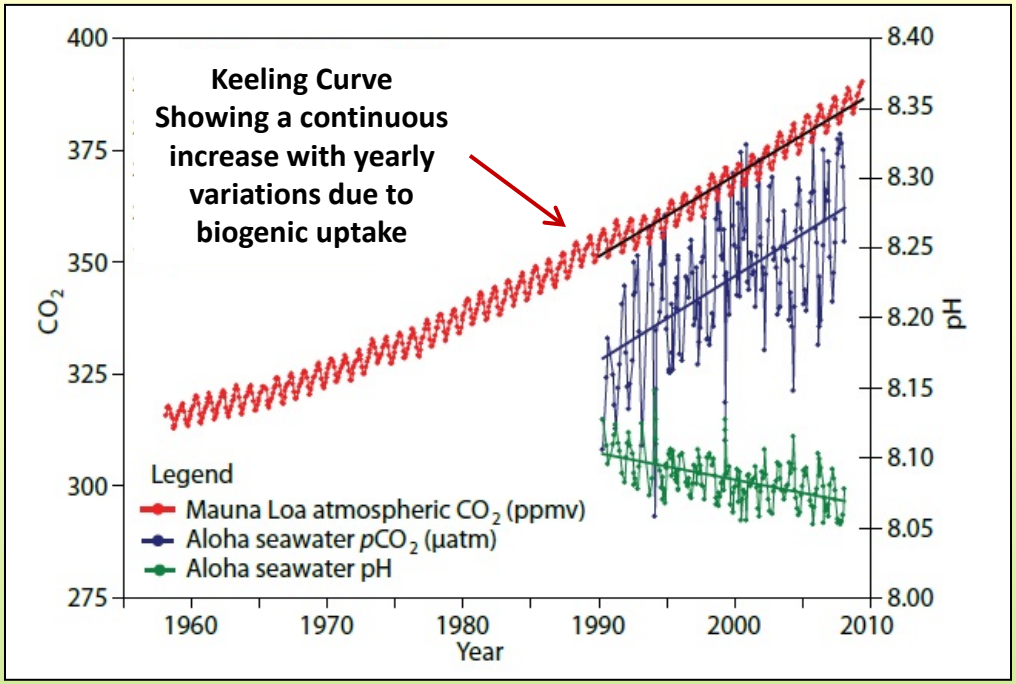


http://www.climatescience.gov/Library/stratplan2003/final/ccspstratplan2003-chap3.htm

Increases in Atmospheric CO_2 Concentrations

Impact the Oceans – Ocean Acidification

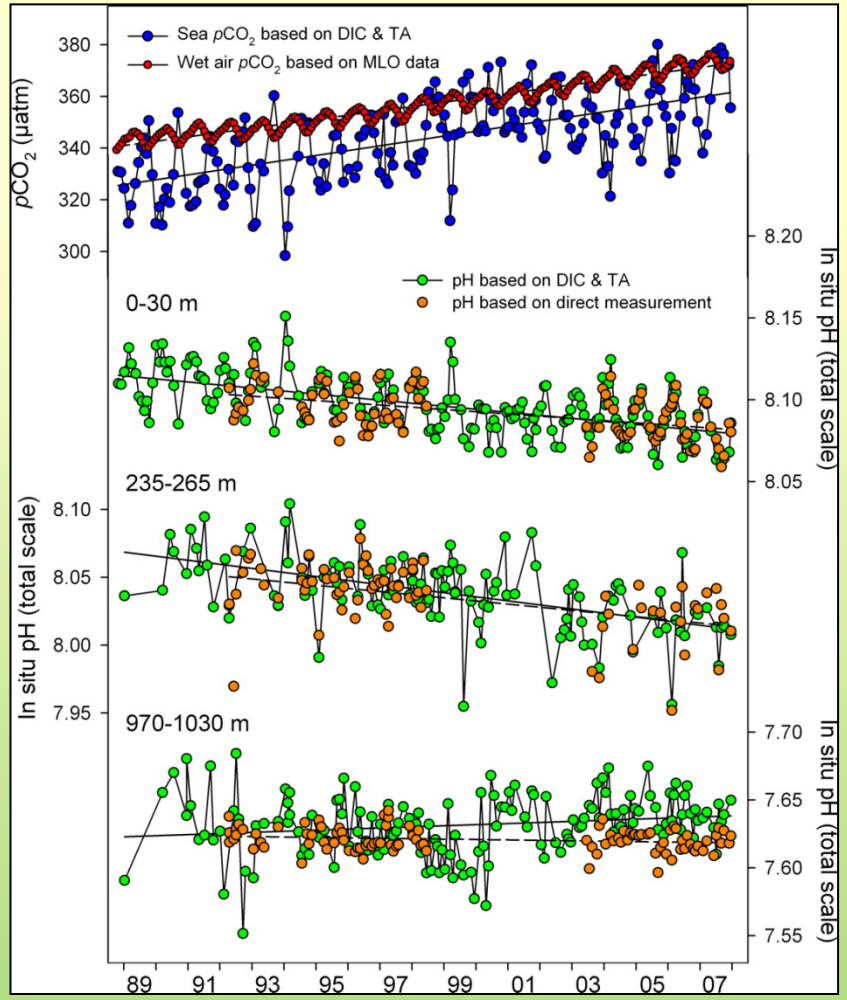
CO_2, pH, and pCO_2 Time Series



Time series of atmospheric CO_2 at Mauna Loa (in parts per million volume, ppmv; red), surface ocean pCO_2 (µatm; blue) and surface ocean pH (green) at Ocean Station ALOHA in the subtropical North Pacific Ocean. Note that the increase in oceanic CO_2 over the past 17 years is consistent with the atmospheric increase within the statistical limits of the measurements.

Mauna Loa data courtesy of Pieter Tans, National Oceanic and Atmospheric Administration/Earth System Research Laboratory ; Hawaii Ocean Time-Series (HOT)/ALOHA data courtesy of David Karl of University of Hawaii ; see also Dore et al., 2009

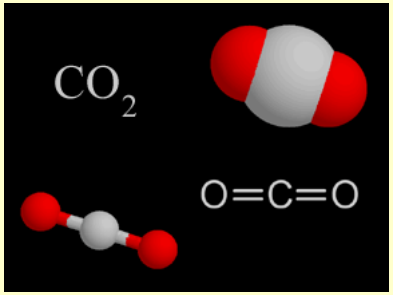
pH & pCO_2 Time Series



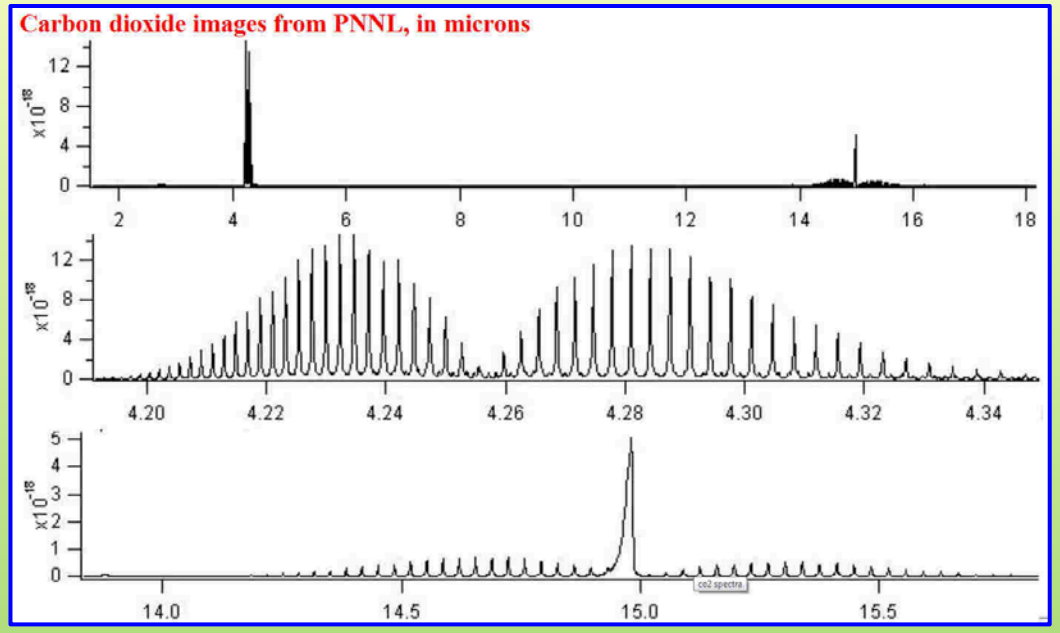
SPECTROSCOPY OF GREENHOUSE GASES AND OBSERVATIONS

Measuring GHG Gas Concentration

Spectroscopy-Based Approaches for CO_2, CH_4, & N_2O



- **GHG's absorb thermal radiation selectively**
  - Molecular absorption throughout the infrared region of the spectrum, from ~1 to ~20 µm
  - Spectra arise from the quantum mechanical behavior of the inter-molecular dynamics of gases
  - Quantized rotations and vibrations around the molecular center of mass
  - CO_2 has strongly absorbing bands at ~4.3 and ~14.9 µm
  - Weakly absorbing bands ~1.5 and ~2.07 µm Near Infrared – NIR
- **Measuring concentrations can be based on the same physical principles, selective absorption, as those causing the Earth's greenhouse**



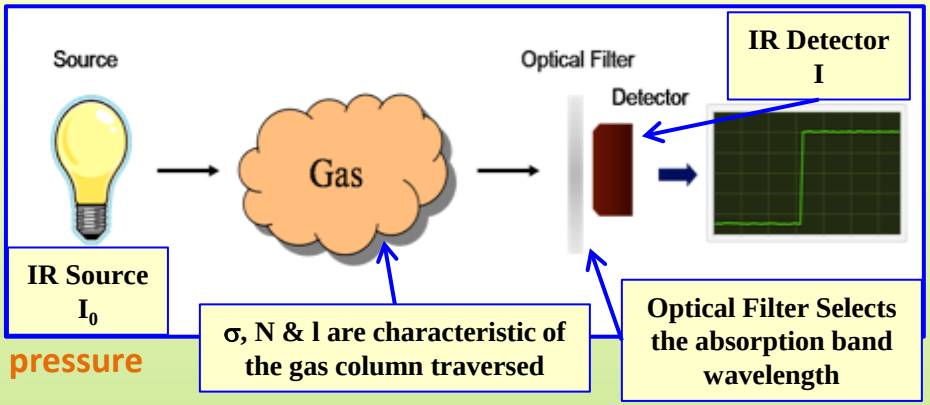
Measuring GHG Gas Concentration

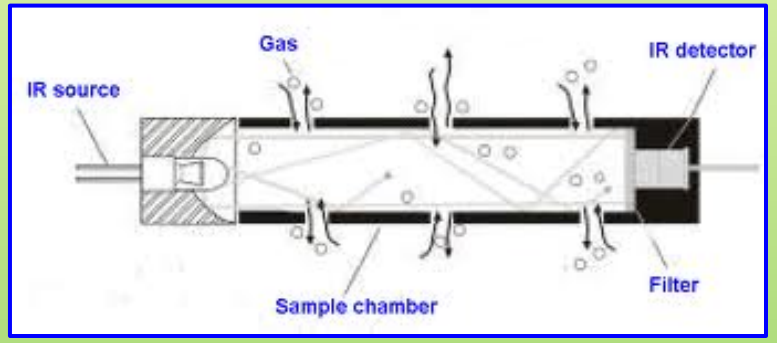
Spectroscopy-Based Approaches for CO_2, CH_4, & N_2O

$$I = I_0 e^{-\sigma N l}$$

σ – abs. cross section
N – number density
l – path length

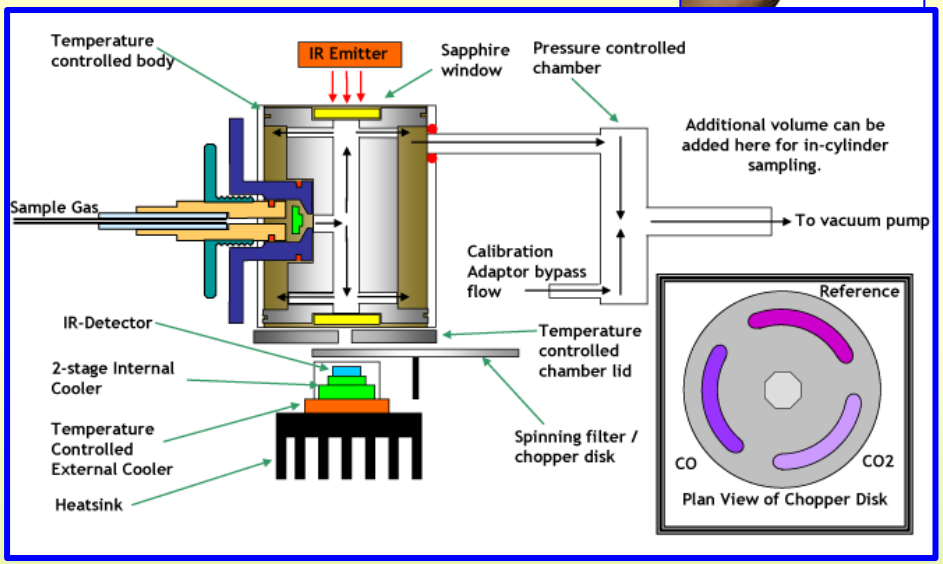
- **Beer – Lambert Law**
  - Describes the exponential dependence of the intensity of light transmitted by an absorber – the greenhouse gas
  - Absorption cross section – describes the capability of a species of gas molecule to absorb a photon – wavelength dependent
  - Number density – how many molecules will lie in the path of the photons traversing the gas column having the path length l
- **Non-Dispersive Infrared (NDIR) Instrumentation**
  - Observed or measured values need for an instrument:
    - Initial and attenuated intensity
    - Number density – compute this for known gas pressure
    - The path length
    - Absorption cross section – reference data, but assumes one gas is doing the absorbing
  - measuring all of these to the desired accuracy for practical instruments is difficult
  - How to eliminate drift and ensure accuracy?

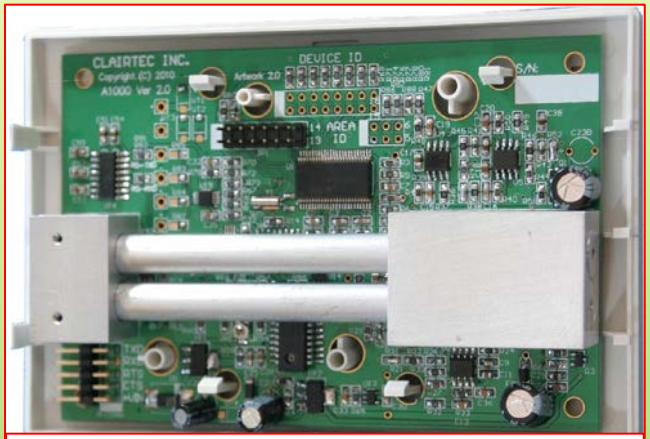




NDIR's come in Many Shapes and Forms

- Widely used & relatively inexpensive
- Can have good sensitivity, but have well-recognized drift behavior
- Signal drift characteristics are well know for Infrared detectors and sources (lamps)
- How is accuracy obtained with NDIR-based instruments?
  - Use of gas concentration standards
    - Typically a zero absorbing gas and a 'span' gas having a concentration value at the top end of the desired range
    - Achieving the highest level of instrument performance may utilize several calibration gases to minimize instrument response non-linearity.
  - An important gas standards requirement that drives gas metrology programs at National Metrology Institutes





2 Channel NDIR
- A 'zero' channel
- Note housing for temperature control

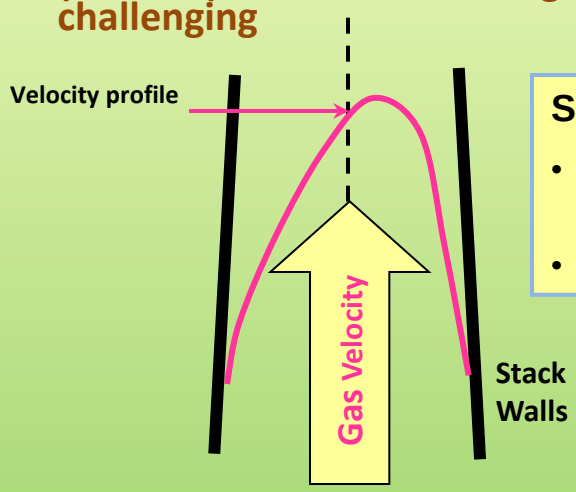
Stationary/Point Emission Source Metrology

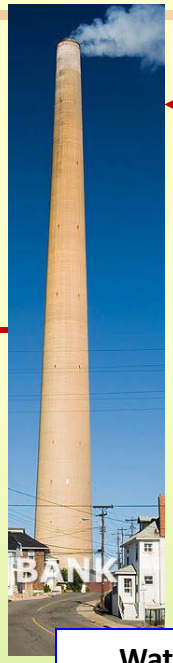
Continuous Emission Monitoring (CEMs) – Industrial Energy Generation

GHG Emission = Total Gas Mass Flow rate X GHG (CO_2) Conc.
= Mass of GHG (CO_2) /Time

Gas Mass Flow in Smoke Stacks
Continuous Emission Monitoring (CEM) Technology

- Infrared spectrometry – gas concentration
- Stacks have complex gas flows
  - Significant measurement challenges to achieve accuracies desired
  - CO_2 concentration and total velocity are key measurements
  - Highly turbulent stack flow conditions make accurate (<1 – 2%) determination of gas mass flow rate challenging





Total Stack Gas Mass Flow Rate Measurement

Ultrasonic flow rate measurements are becoming more widely used in U.S. plants

Gas Extraction

Water Extraction

Gas Concentration by NDIR

Calibration Gases

Stack Probes
- Velocity Profile
- Temperature

Continuous Emissions Monitoring System

CO_2 Emission Flux (kg/hr)

Point Source Metrology:

Comparing Fuel Calculations and Direct Measurements

Examination of U.S. CO_2 Emission Data

Question:

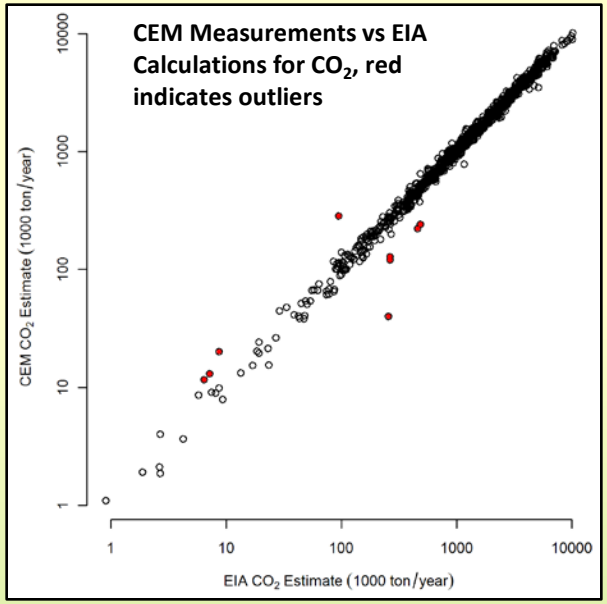
What is the Agreement Between CO_2 Emissions Based on Reported Information?

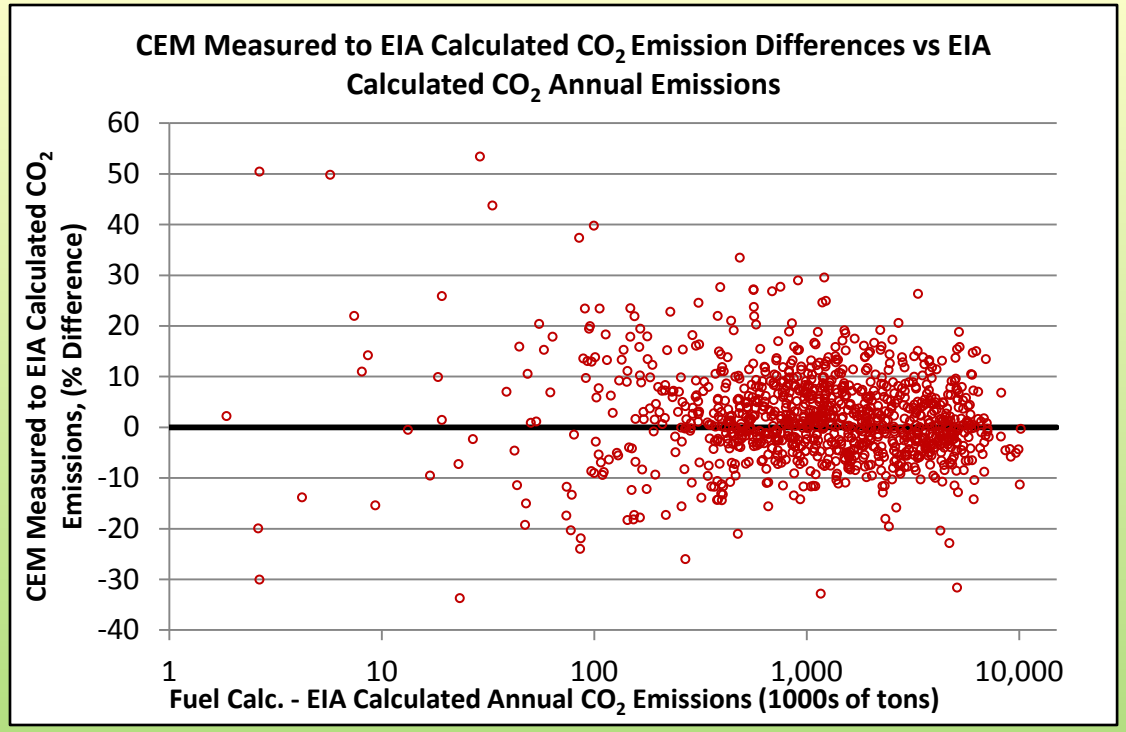
- Fuel Calculation vs. Continuous Emissions Monitoring (CEMs) Methods

- Fuel Consumption and Measured CO_2 Emissions Data – 2007 U.S. Reporting
  - Pre-Combustion
    - Amount of carbon burned and converted to CO_2
    - Dept. of Energy – Energy Information Agency
      - Annual Steam-Electric Power Plant Design Data Fuel Type & Quantity
      - Carbon factor or Fuel Carbon Content (kg CO_2/mmBTU)
  - Post-Combustion
    - Direct Measurement (CEMs Data) and Reporting of CO_2, SO_2, NO_x Required by U.S. EPA
- eGRID and EIA 767 databases contain >4866 entries
  - 1664 with appropriate primary fuel and annual CO_2 emissions with CEM measurements.
  - 1066 have all necessary information in Fuel type and composition database

Comparative Analysis:

Fuel Calculation CO_2 – CEMs CO_2





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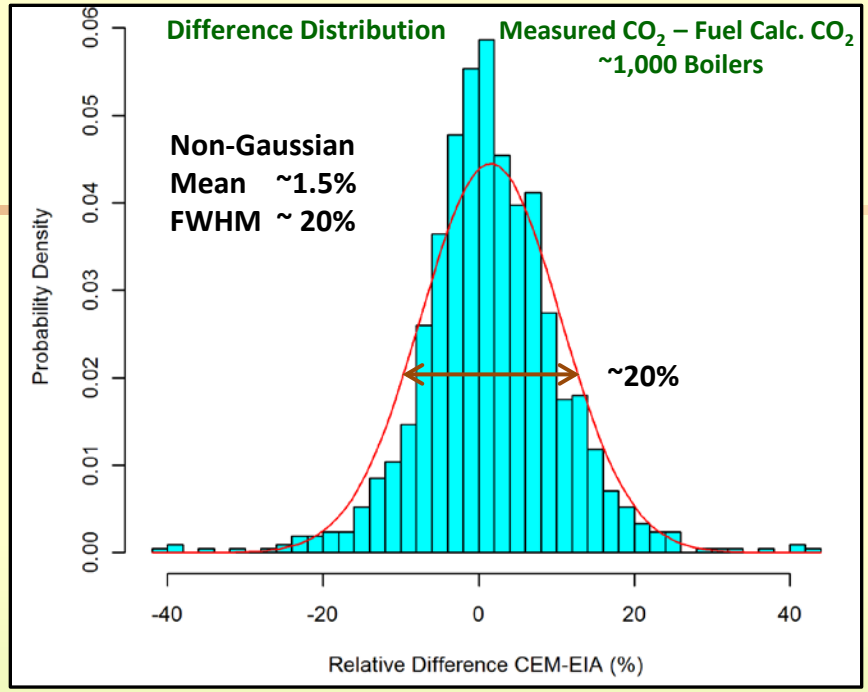
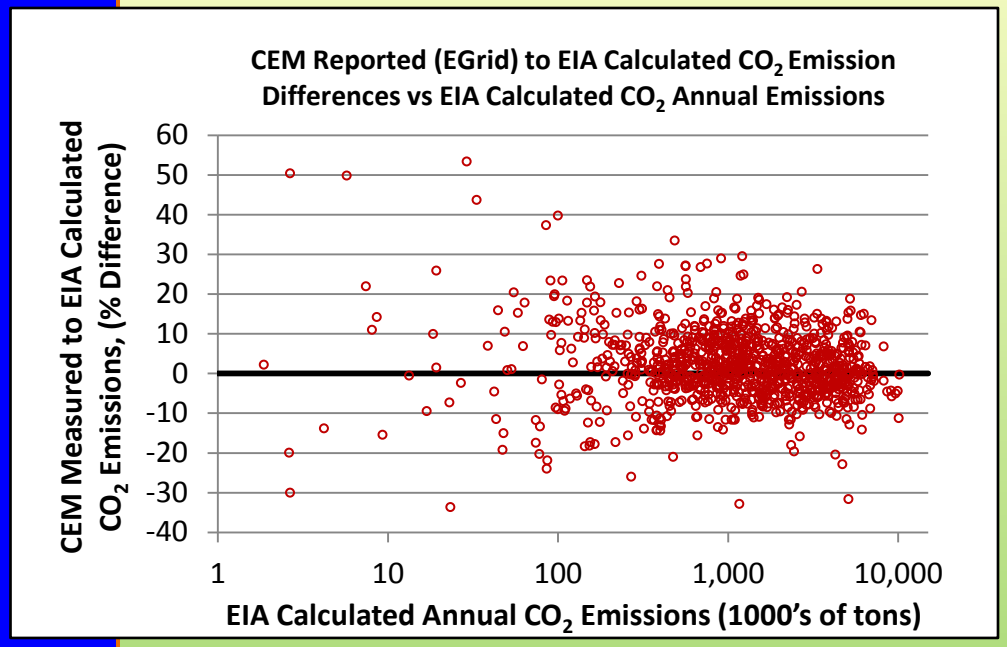
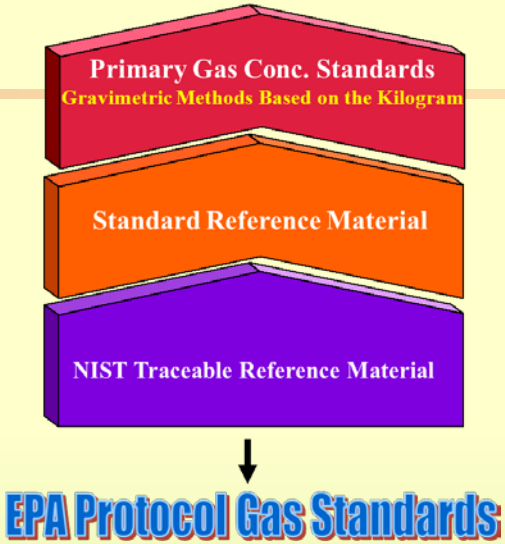


Accuracy Improvement Potential

- **Continuous Emissions Monitoring (CEM)**
  - Improve stack gas mass flow measurement
  - Reduce gas concentration uncertainty
    - Current EPA regulations allow ± 2% unc. for uncertainty
    - NIST Traceable Reference Material Program meets this need
- **Fuel Based Calculations**
  - Increase fuel carbon (energy content) accuracy
    - Calorimetry and sampling issues
  - Improved mass determination
    - 2 phase flow issue
- **NIST's Investment in Pt. Source Metrology**
  - Improved stack flow measurements
  - Large Fire Facility – large scale CO_2 emissions test bed



Gas Metrology



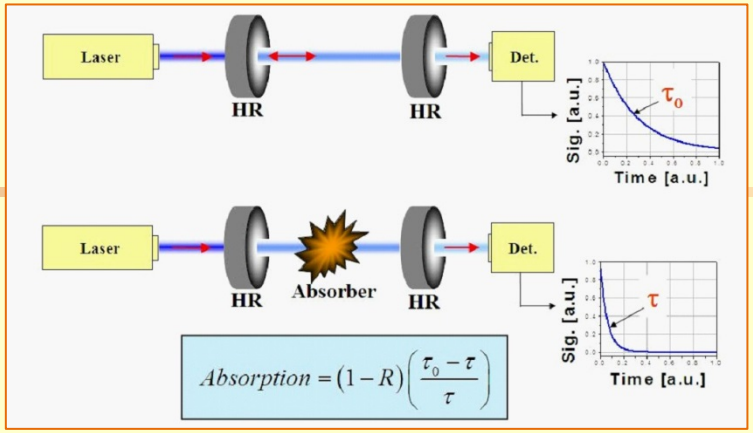
- **Gas Concentration Measurements Are Ubiquitous to Accurate GHG Measurements in All Settings**
- **NIST Gas Concentration Standards Support:**
  - **CEM systems**
    - High Concentrations typical of combustion flue gases
    - Gases are mandated by EPA for all electrical and manufacturing power generation plants
    - NIST Traceable Materials Program
      - Quality assurance program with U.S. specialty gas manufacturers
      - ~ 150,000 standard gas cylinders / year required in the U.S. for in-situ calibration of stack gas concentration instruments (non-dispersive IR)
    - EPA uncertainty requirements (±2% relative) are modest relative to the state-of-the-art in standards provision
  - **Atmospheric Monitoring**
    - World Meteorological Org. trace gas concentration uncertainties are at or very near the state-of-the-art
    - WMO Central Calibration laboratory for CO_2, CH_4, N_20 – NOAA's Earth Systems Research Lab
    - SRM 1720 (Northern Hemisphere) and SRM 1721 (Southern Hemisphere) will be certified for these gases in air and will meet or exceed WMO Data Quality Objectives
    - Close collaboration with NOAA-ESRL – Support linkage to WMO's CCL for these

WMO Atmospheric Trace Gas Monitoring Requirements

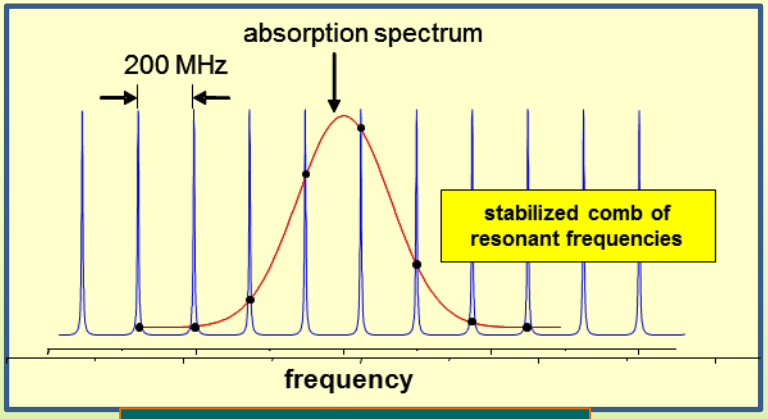
	Nominal Concentration	GAW Data Quality Obj.
CO_2	380 – 420 (µmol/mol)	±0.1 (µmol/mol)
CH_4	1800 – 2000 (nmol/mol)	±2 (nmol/mol)
N_2O	310 – 320 (nmol/mol)	±0.1 (nmol/mol)
CO	10 – 500 (nmol/mol)	±2 (nmol/mol)
SF_6	6 - 8 (pmol/mol)	±0.02 (pmol/mol)

Long Path Length Methods

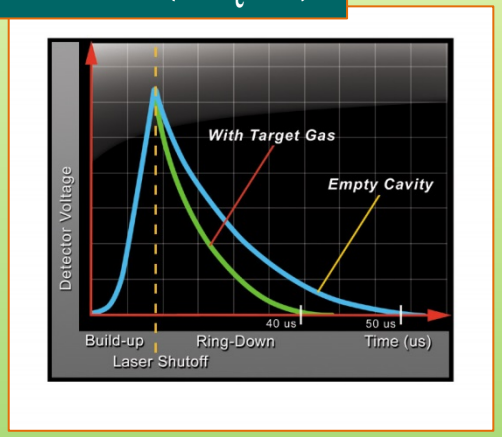
Cavity Ringdown Spectroscopy



- Based on optical cavities made using high reflectivity mirrors (R ~ 0.999900)
- The cavity acts as a very selective optical filter that rejects light except at very specific frequencies
- Lasers with extremely precise frequency control are used to match the pass band of the cavity and fill it with light.
- Once filled to a preset intensity, the laser is switched off.
- Because the mirrors are so highly reflective, the light leaks out of the cavity through them relatively slowly, on the order of microseconds.
  This is easily accomplished with modern electronic methods.
- With this technique, the absorption response has been turned into a measurement of two times, that with the cavity filled with the absorber and that with it empty or non-absorbing.
- Noise and drift in the detector no longer are sources of noise in the instrument.
- Precision, accuracy, and temporal stability are improved considerable over NDIR methods.
- Instruments using these methodologies are seeing widespread usage in the atmospheric monitoring community worldwide.

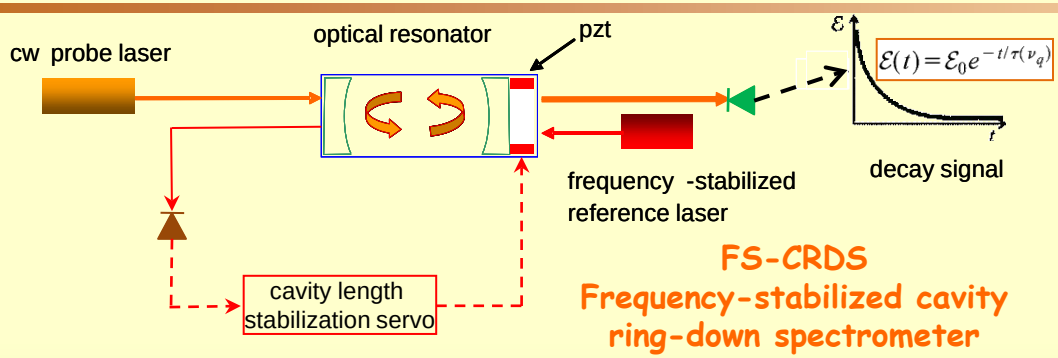


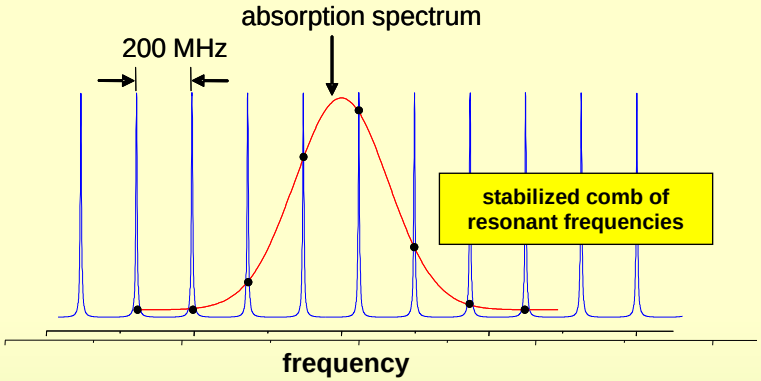
$$A = (1 - R)\left(\frac{\tau_o - \tau}{\tau}\right)$$



High Accuracy Spectroscopic Reference Data

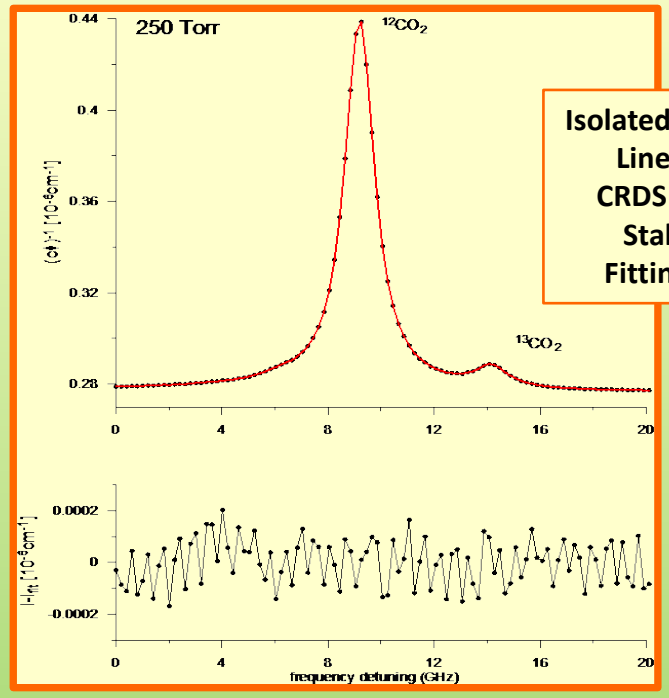
Visible and Infrared (1.45 – 1.6 µm Atm. water window)





- Accurate absorption line shape measurements augmented with high accuracy absorber number density determination reduced absorption line intensity uncertainties from 2% to <0.03%
- Update HYTRAN Database
- Quantified corrections required to accurately describe line intensities in the O_2 A-band (~765 nm)

- Recent work appears to improve S/N by ~100x with fast probe laser scanning (~200 kHz)



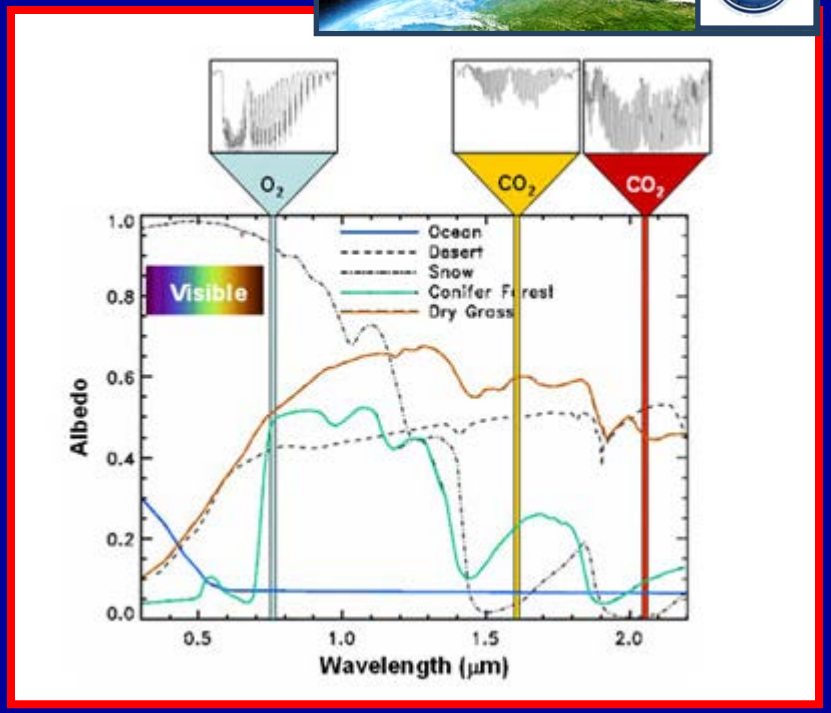
Isolated CO_2 Absorption Line Region - Air CRDS Data for Both Stable Isotopes Fitting RSD ~ 0.1%

Reference Data Utilization:

NIST/NASA-JPL Collaboration:

The Orbiting Carbon Observatory 2

Improving CO_2 Measurement in the Atmospheric Column

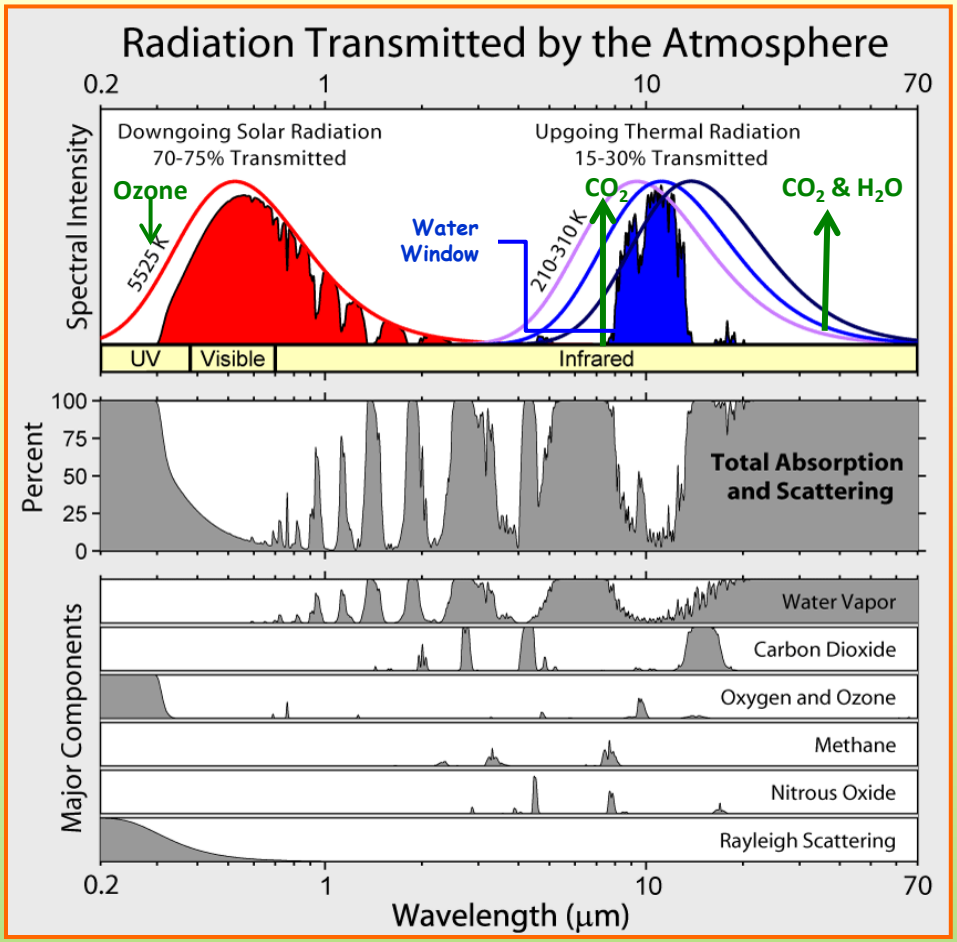


- *Observes total column CO_2 Concentration*
- *Accuracy target : <0.5% (2 ppm)*
- *Has ~3 km² (1 x 3 km) spot size for dense local observations in target mode*
- *A new class of observing platforms with the potential for emission inventory diagnosis and verification by independent means*
- *Well-recognized, ground-based calibration methodologies are critical*
- *NIST provides spectroscopic reference data at the required accuracy levels or better for:*
  - *the O_2 A-band (~765 nm),*
  - *the pertinent CO_2 bands (~ 1.61 and 2.06 μm), and*
  - *radiometric references*

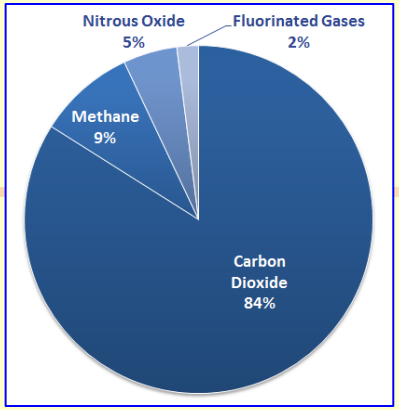
Program Components

Greenhouse Gas and Climate Science Measurements

- **GHG Measurements Tools, Standards, and Reference Data**
  - GHG Concentration Standards
  - Spectroscopic Reference Data
  - Surface Air Temperature Assessment
- **Climate Science Measurements - Advanced Satellite Calibration Standards**
  - Optical and Microwave
  - Top of Atmosphere and Surface Solar Radiance
- **Aerosol Measurement Science**
  - Black Carbon Optical Properties
  - Black Carbon Reference Materials and Measurements
- **Stationary/Point Source Metrology**
  - Test Beds for Continuous Emission Monitoring Technologies
- **Distributed GHG Source Metrology**
  - GHG Flux Measurement Tools
    - Differential Absorption Lidar Developments
  - Measurement Approaches in Urban Settings
    - Dense GHG Observing Networks – Measurements to Independently Verify GHG Emission Inventories
    - Indianapolis Flux Experiment - INFLUX
    - Los Angeles Megacity Carbon Project
    - Extension to Megacities and Development of an International Metrology Framework for MRV



What is NIST Doing in Greenhouse Gas and Climate Science Measurements



2011 U.S. Emissions
6,702 M Metric Tons CO_{2e}

Program Objectives:

- **Develop advanced measurement tools and standards:**
  - Improve the accuracy capability for:
    - Greenhouse gas inventory data, and
    - Remote observations, both satellite and surface-based

      with an emphasis on cities and metropolitan areas.
  - Independently verify greenhouse gas emissions inventories both nationally and internationally, and
  - Extend measurement science to better understand and describe the Earth's climate and its change drivers.
- **Enable international measurement standards and protocol developments that ensures accuracy, confidence, and reliability of local and global assessments of GHG emissions.**

GHG Emissions Data, the basis for:
- National GHG inventories
- Basic data/information utilized by future market-based and/or regulatory-based mitigation policy mechanisms
- Primary atmospheric radiative forcing agents

Remote Observations:
- A Mainstay for Climate Observations
- Accuracy and continuity of climate data records
- Potential applications in GHG mitigation policy verification

Thanks' for your Attention

Questions or Discussion