

12.335/12.835, FALL 2014
CO₂ & CLIMATE CHANGE, Lecture 1-1,

Shuhei Ono

Agenda of the day

- Observation since 1970
- Earth Energy Budget. Why is CO₂ a powerful green house gas?
- Global Carbon Cycles. Where all the CO₂ goes, and how.

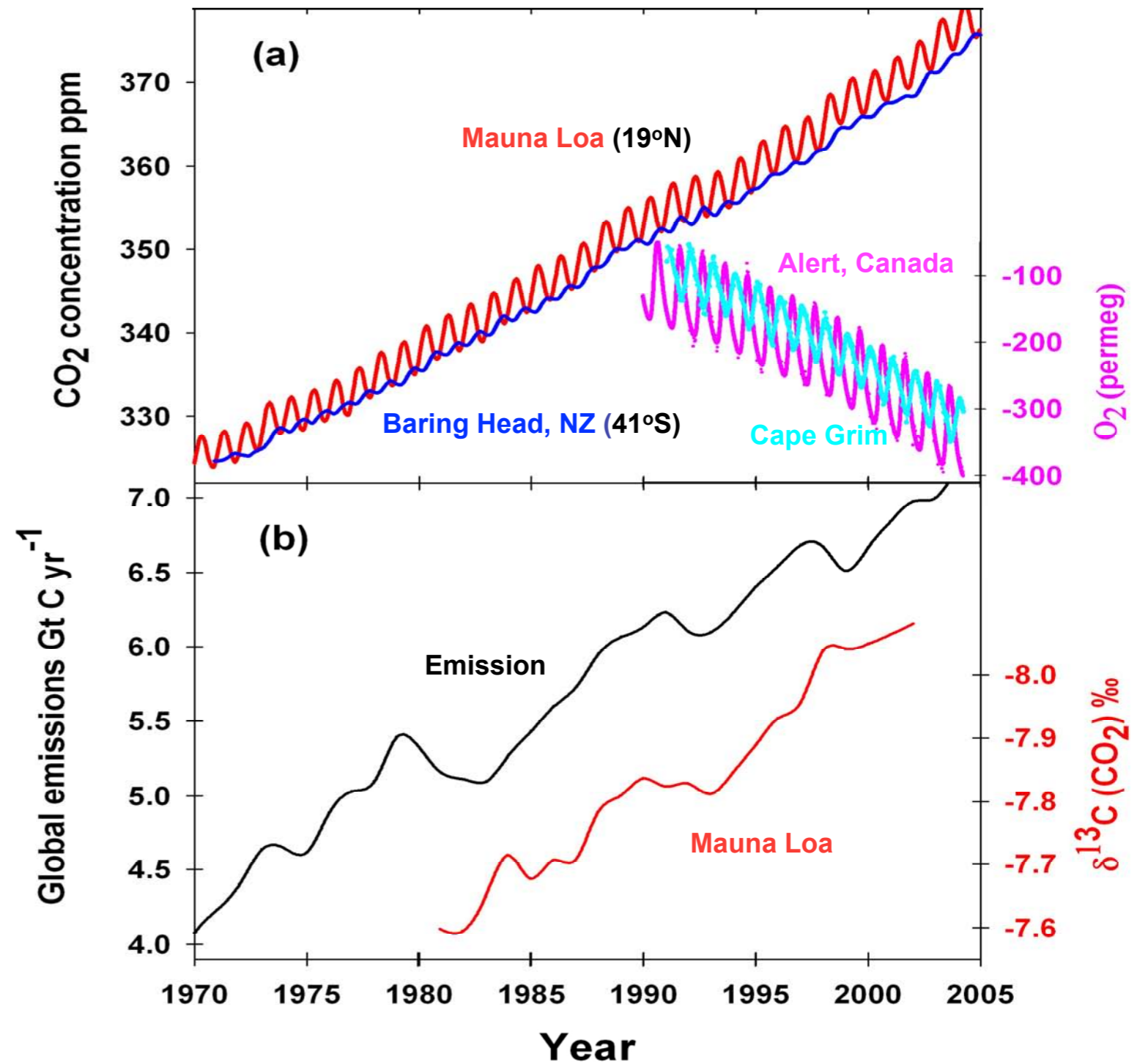
TOPIC 1 CO₂ & CLIMATE

CAUSES OF SEASONAL & INTERANNUAL VARIATIONS IN THE CO₂ CYCLE?

Ref: IPCC 4th
Assessment, WG1, 2007

$$\{ \text{Note} : \delta R = 10^x \left(\frac{R(\text{sample})}{R(\text{standard})} - 1 \right) \}$$

$$x = 2(\text{percent}); 3(\text{permil}); 6(\text{permeg}) \}$$

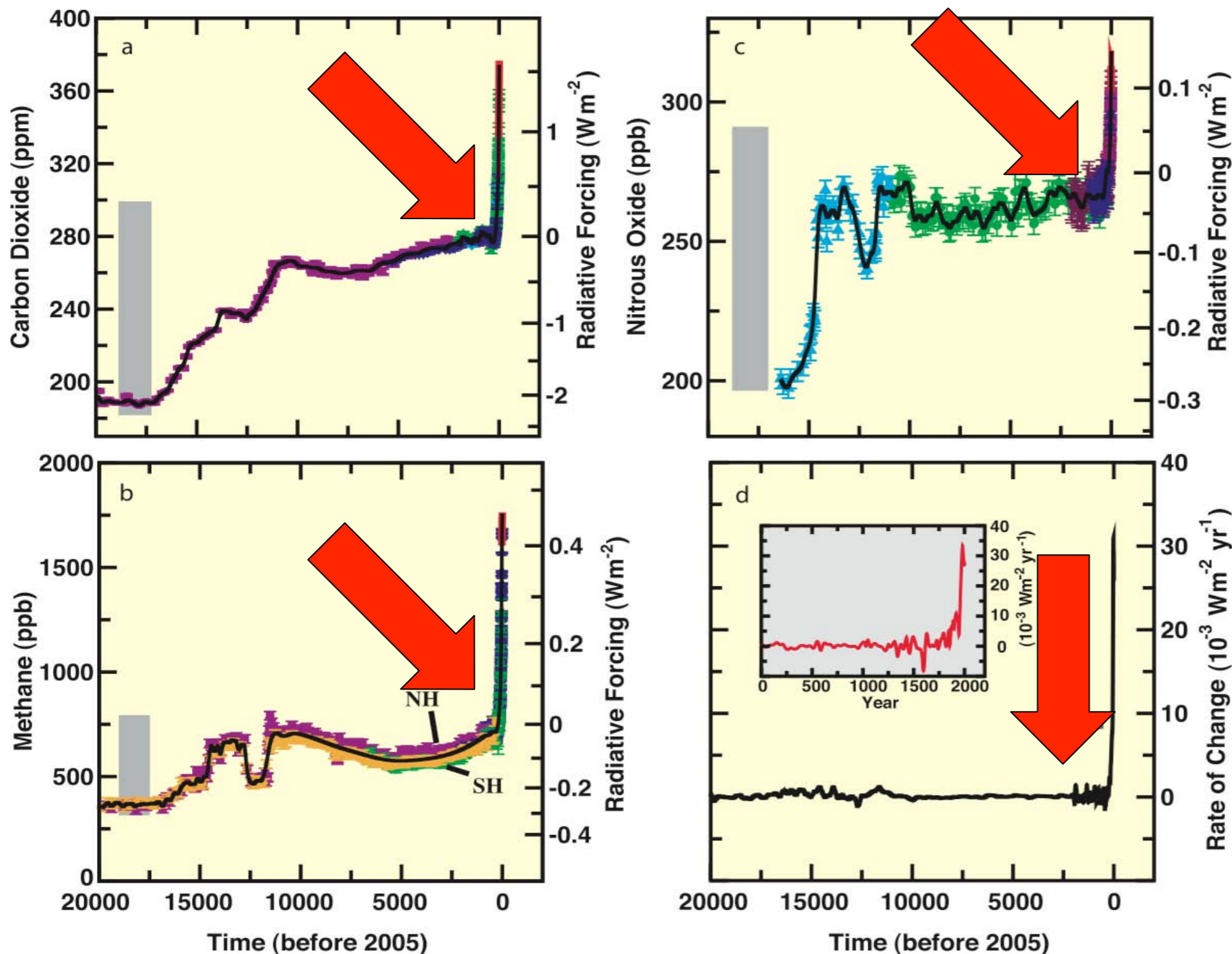


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Panel (a) shows CO₂ mole fractions (monthly averages) measured by continuous analyser over the period 1970 to 2004 for **Mauna Loa** (19°N red) and **Baring Head** (41°S blue). Due to the larger amount of terrestrial biosphere in the Northern hemisphere, seasonal cycles in CO₂ are larger there than in the Southern hemisphere. In the lower right of the panel, atmospheric oxygen measurements (permeg) are shown from **Alert, Canada** (pink) and **Cape Grim** (41°S cyan).

Panel (b) shows the annual global CO₂ emissions from fossil-fuel burning and cement manufacture Gt C yr⁻¹ (black) through to 2002. Data from the CDIAC website. Preliminary emissions data for 2003 and 2004 of 7.0 and 7.2 Gt C yr⁻¹ respectively are added derived from BP Statistical Review of World Energy 2005 website. Annual averages of ¹³C/¹²C (permil) measured in atmospheric CO₂ at **Mauna Loa** from 1981 to 2002 (red) are also shown.

ATMOSPHERIC COMPOSITION & RADIATIVE FORCING: TRENDS OVER THE LAST 20,000 YEARS



The concentrations and radiative forcing by (a) carbon dioxide (CO₂), (b) methane (CH₄), (c) nitrous oxide (N₂O) and (d) the rate of change in their combined radiative forcing over the last 20,000 years reconstructed from Antarctic and Greenland ice and firn data (symbols) and direct atmospheric measurements (panels a,b,c, red lines). The grey bars show the reconstructed ranges of natural variability for the past 650,000 years. The rate of change in radiative forcing (panel d, black line) has been computed from spline fits to the concentration data. The negative rate of change in forcing around 1600 shown in the higher-resolution inset in panel d results from a CO₂ decrease of about 10 ppm in the ice core record.

Climate Change 2007: The Physical Science Basis. Working Group I Contribution to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Figure 8 Cambridge University Press.

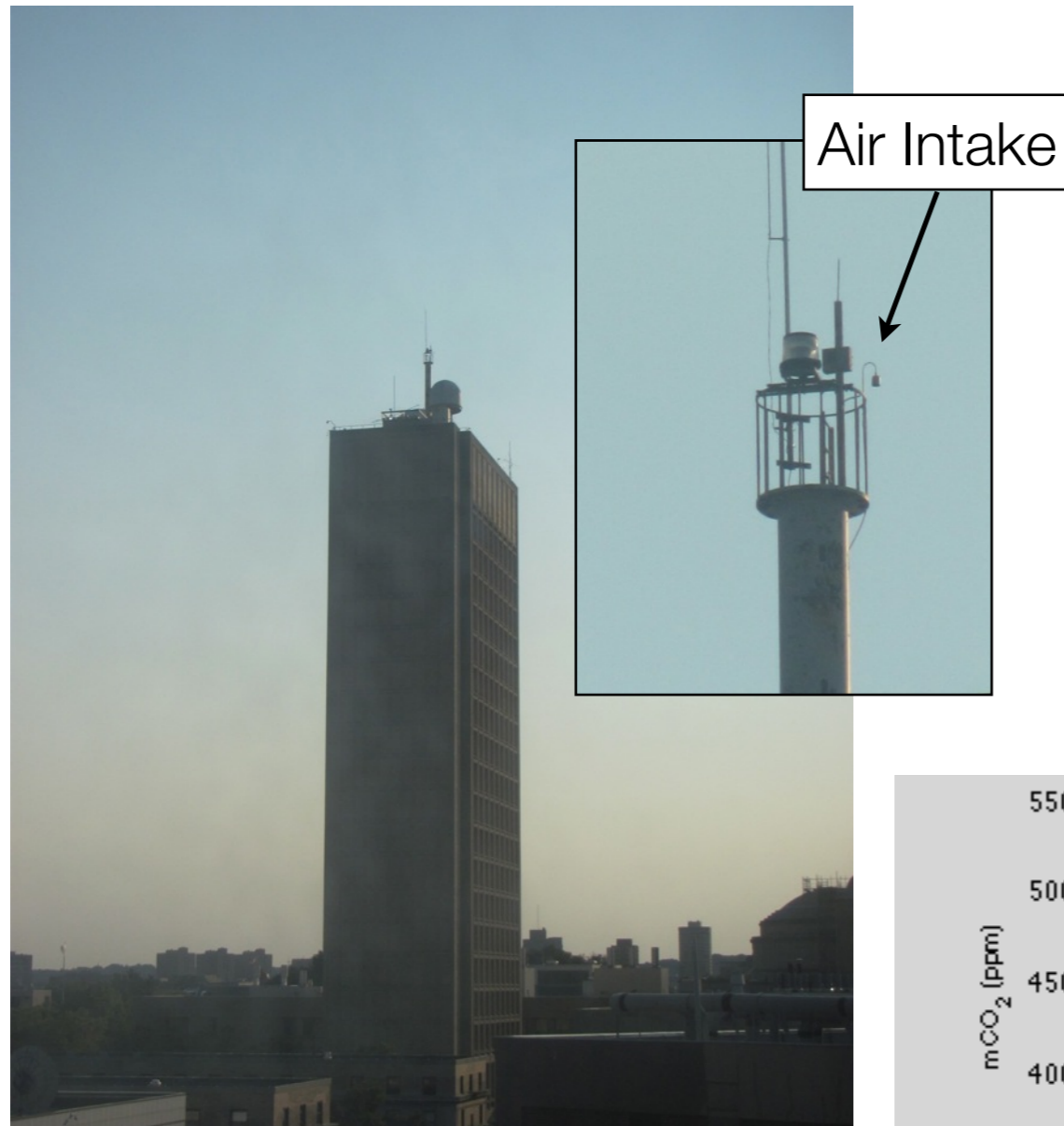
Ref: IPCC 4th Assessment, Summary for Policymakers, Feb. 2, 2007

Project 1

How do we monitor CO₂?

CO₂ & Climate Change

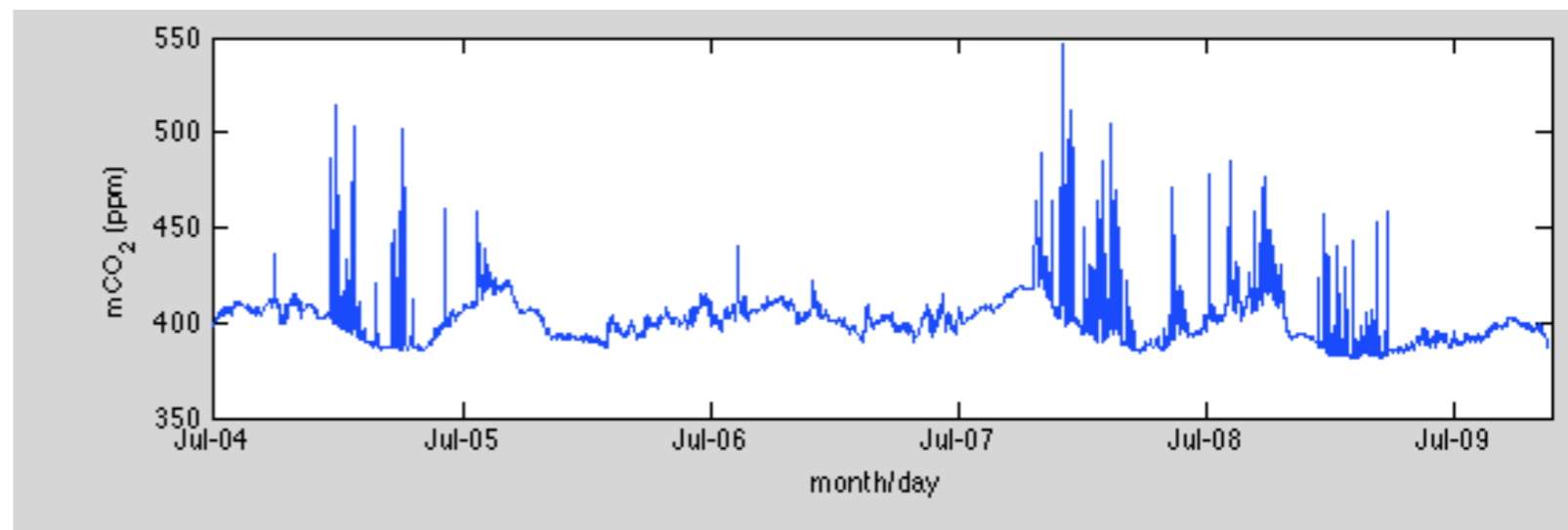
Part 2: CO₂ at the Green Building Roof



Air Intake

During the second part of the CO₂ session, we'll examine the main control of CO₂ in the urban environment using CO₂ data from air taken from the roof of the Green Building. e.g., diurnal cycles (amplitude, phase), pollution plume events. We will test a simple box model.

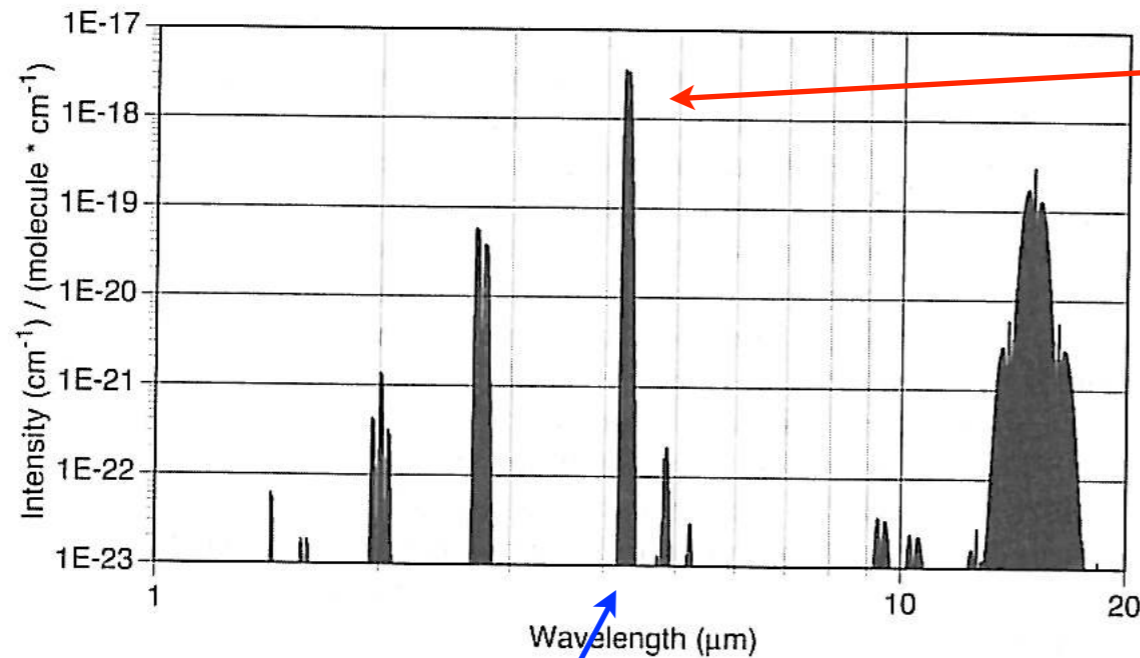
MIT Green Building (~95 m)



CO₂ mixing ratio data for July 4-9th

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Infrared Spectrum of CO₂



ω_3 : asymmetric stretch
2349.5 cm⁻¹ (4.26 μm)

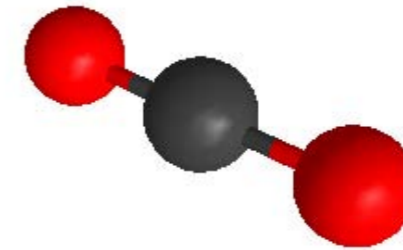
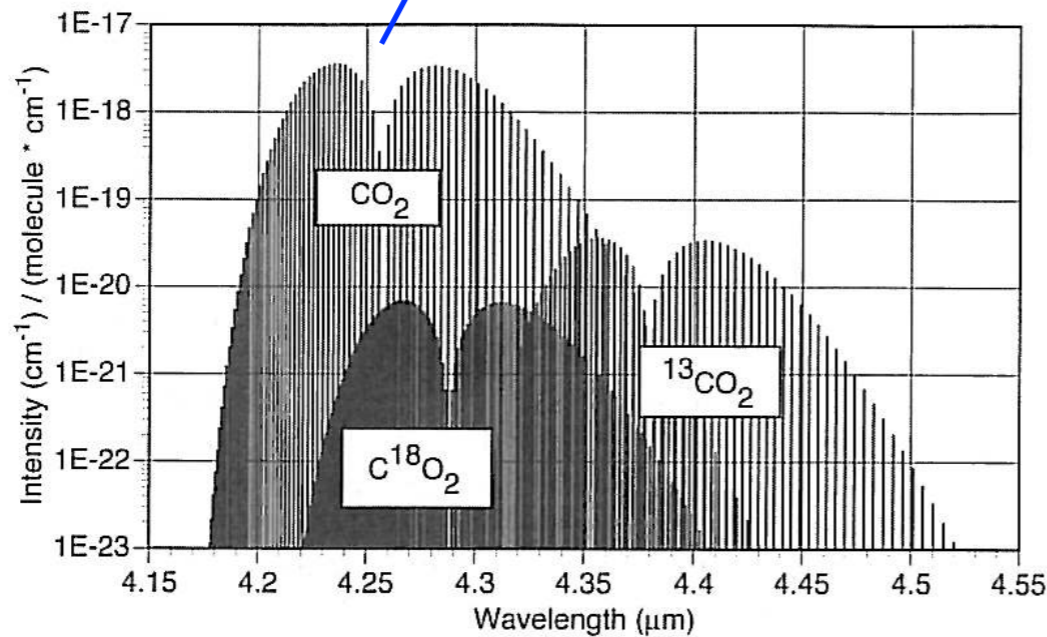


Fig. 13-1. CO₂ absorption spectrum. Source: HITRAN96 (Rothman et al., 1998).

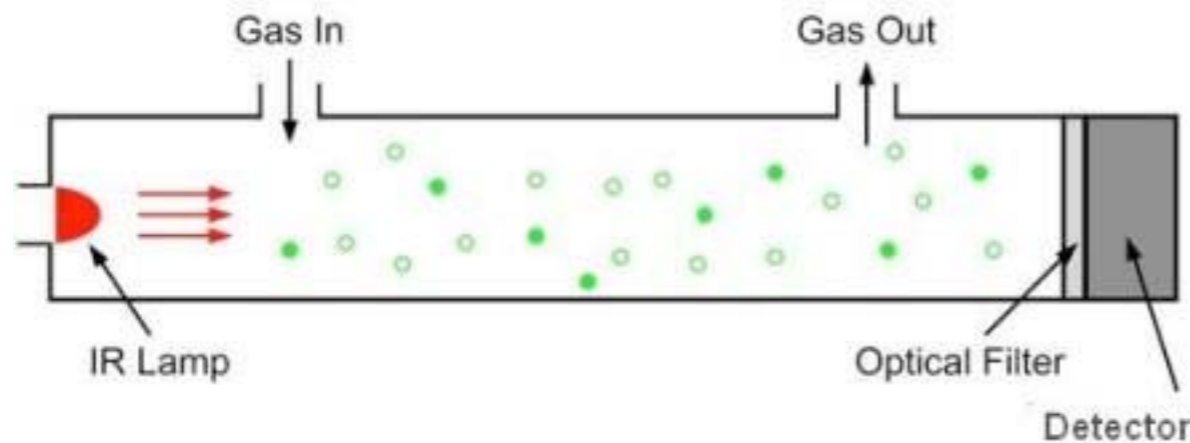


High resolution spectrum
showing individual rotation lines

Fig. 13-2. CO₂ absorption near 4.26 μm, including two major isotopes, adjusted for typical atmospheric abundance. Source HITRAN96 (Rothman et al., 1998).

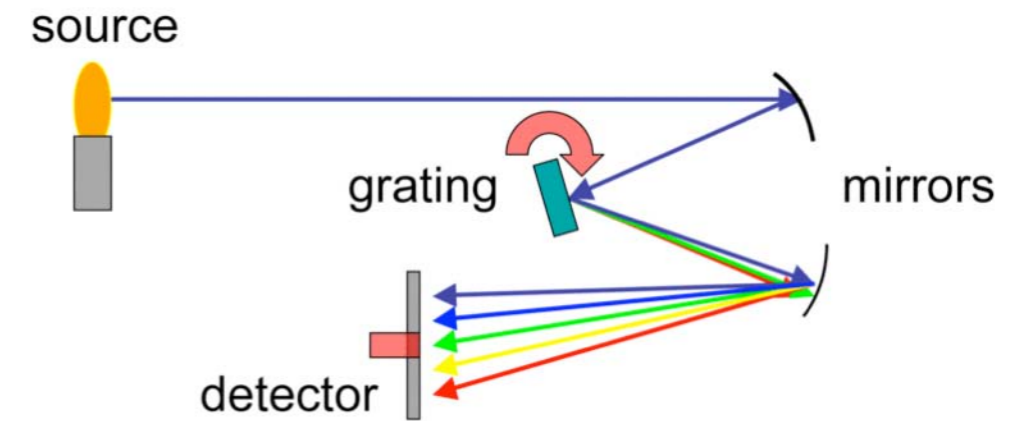
Instrument to measure IR absorption

1. Non-Dispersive Infrared Analyzer (NDIR)



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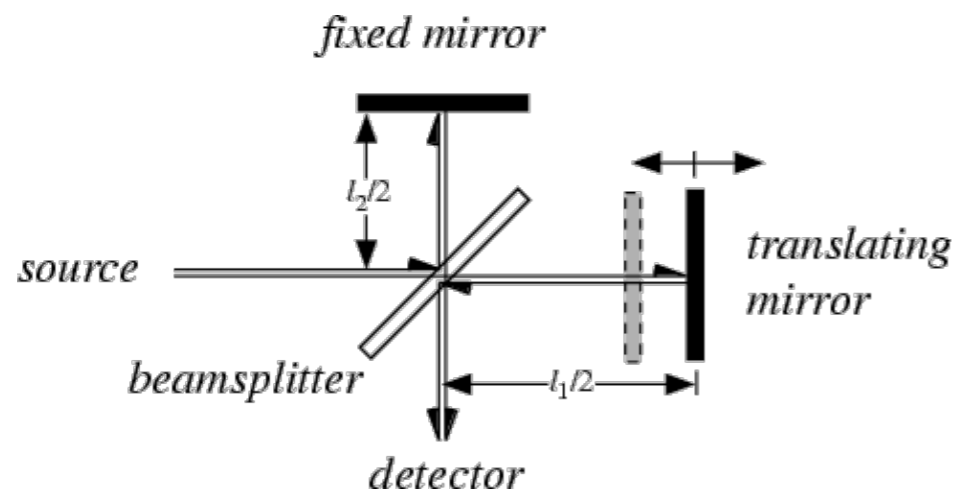
2. Dispersive Infrared Analyzer



Diffraction Grating Spectrometer

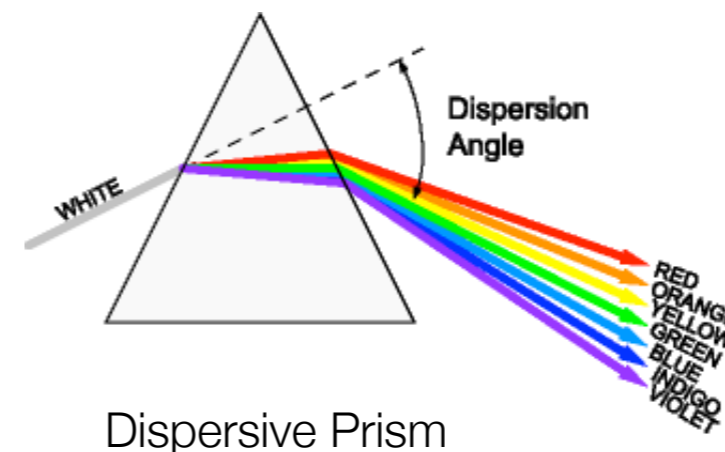
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3. Fourier Transform Infrared Spectroscopy

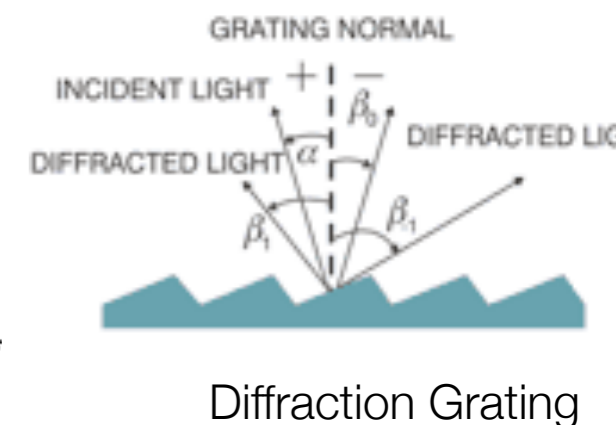


Michelson Interferometer used for FTIR

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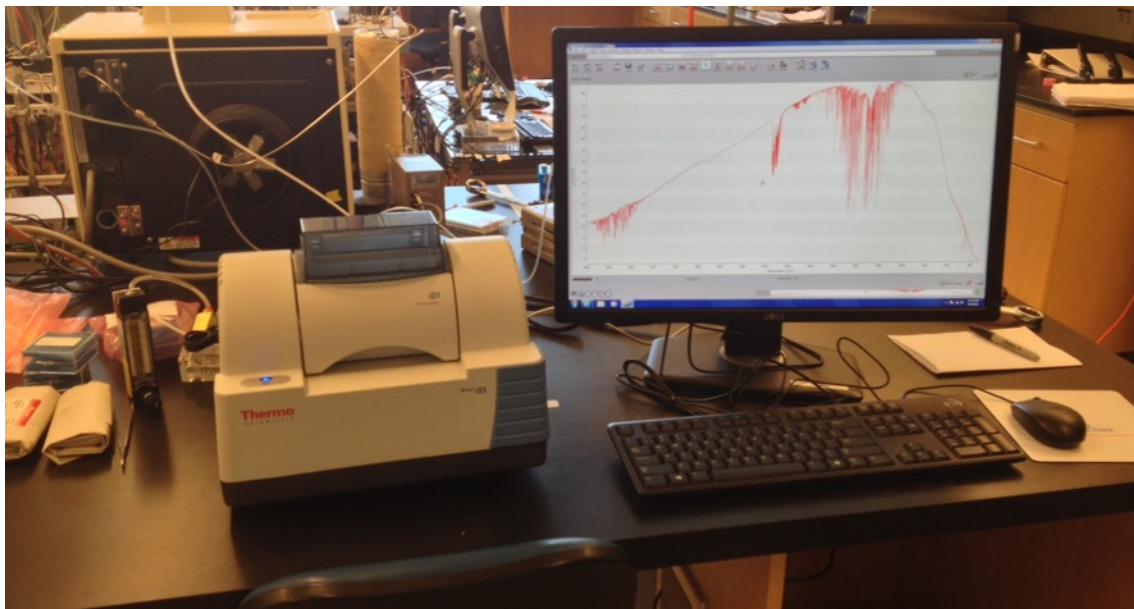


Dispersive Prism

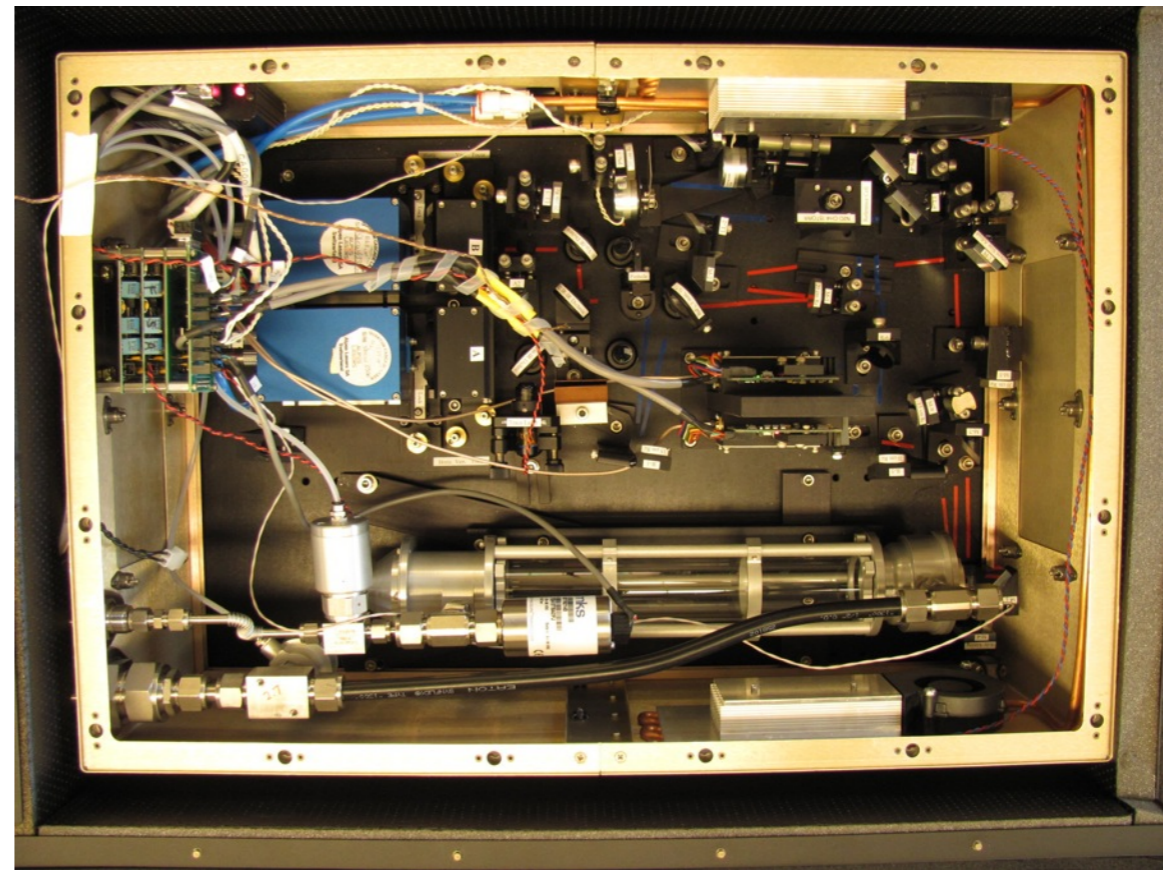


Diffraction Grating

Explore different ways to measure CO₂



FTIR (Thermo is5)



Aerodyne Research
Tunable Infrared Laser Direct Absorption Spectroscopy

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Gas Chromatography
Shimadzu GC-2014

Teledyne 360E



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K033 from CO2meter.com

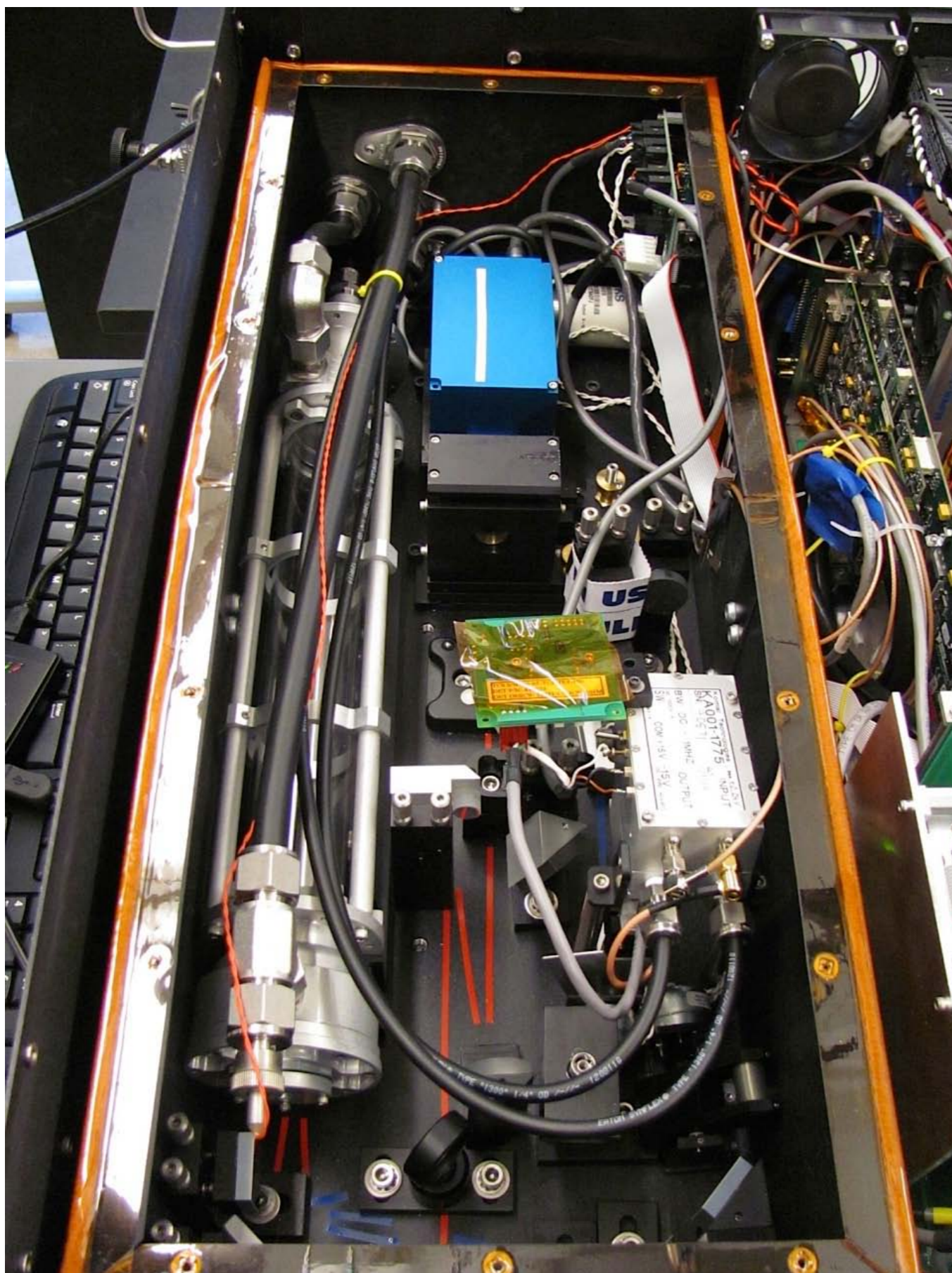


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NDIR CO₂ meter; we will use this to set up 2nd observatory

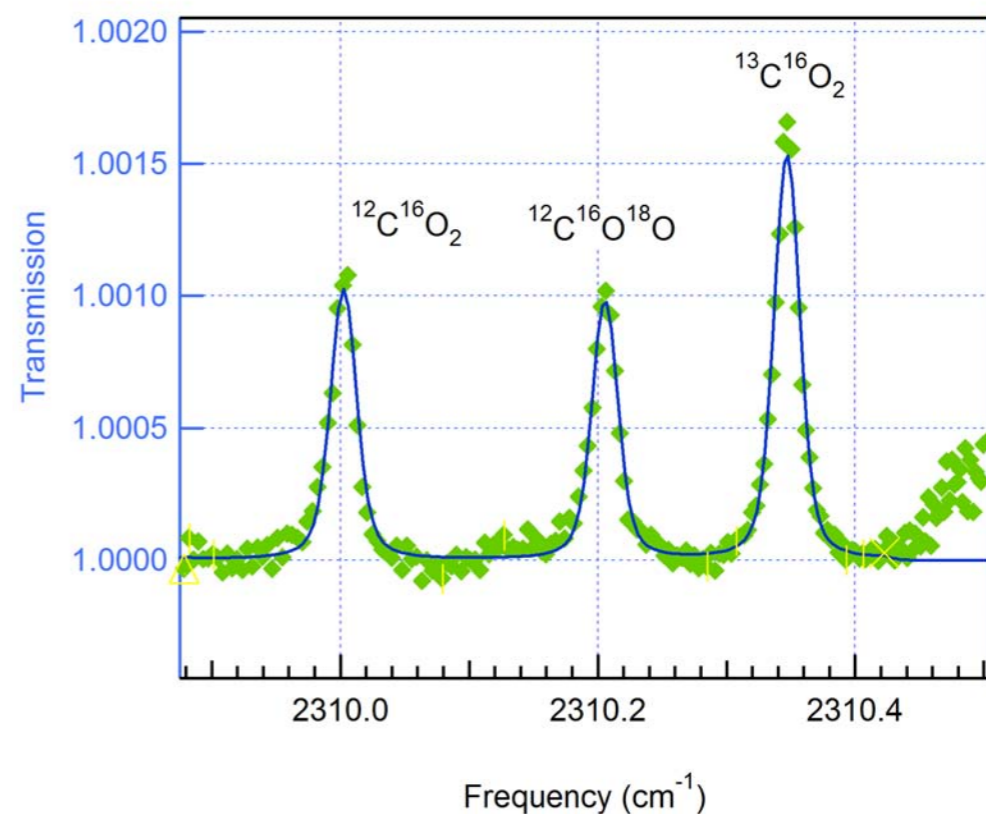


Portable CO₂ meter/data logger in a bird house



Aerodyne Tunable QC Laser Spectroscopy

Path Length, 76 m
Cell Volume, 500 mL
Precision ± 0.05 ppm
Quantum Cascade Laser at 4.2 μm (4.6 μm for N_2O)
Pressure at <30 mbar



Teledyne CO2 Carbon Dioxide Analyzer (NDIR)

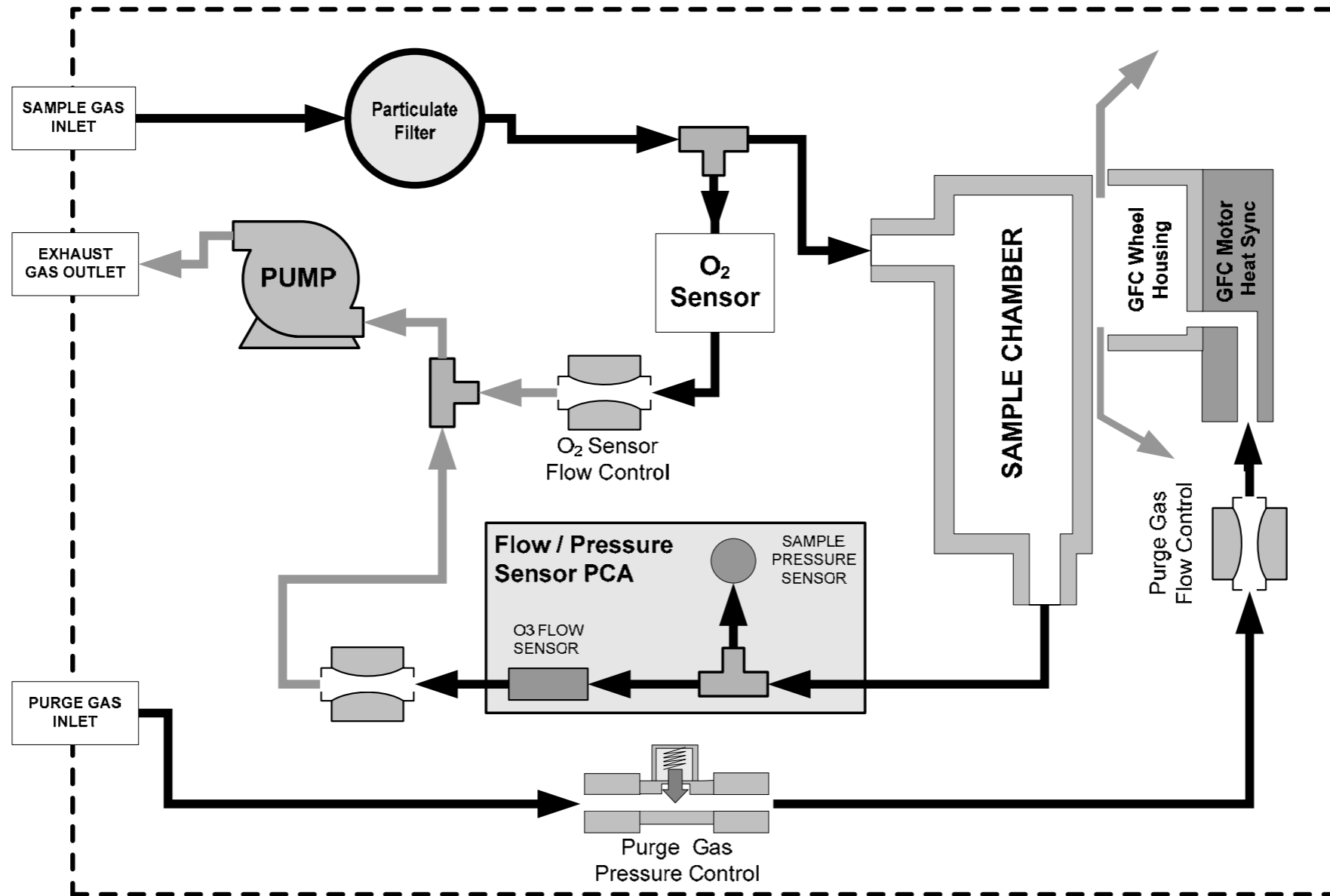
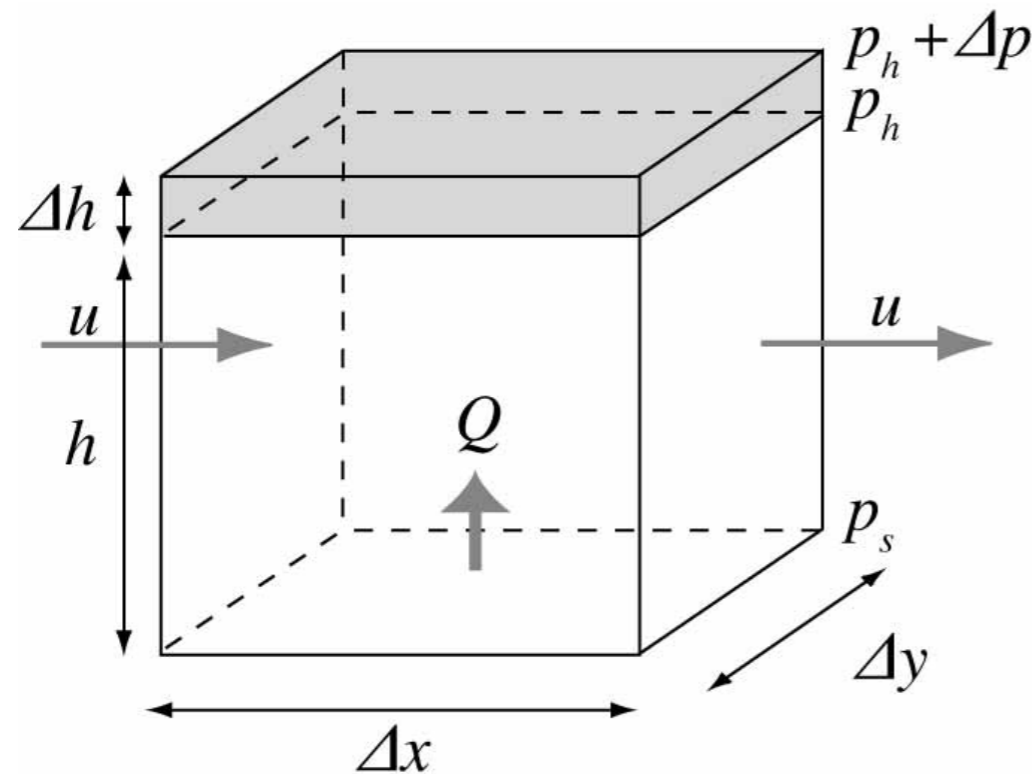


Figure 5-3: M360E – Internal Pneumatics with O₂ Sensor Option 65

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Box Model for Flux Chamber Experiments and Green Building data



Q : source (mol/hour)
 $\Delta x \Delta y h$: volume of a box (m^3)
 u : wind velocity (m/hour)

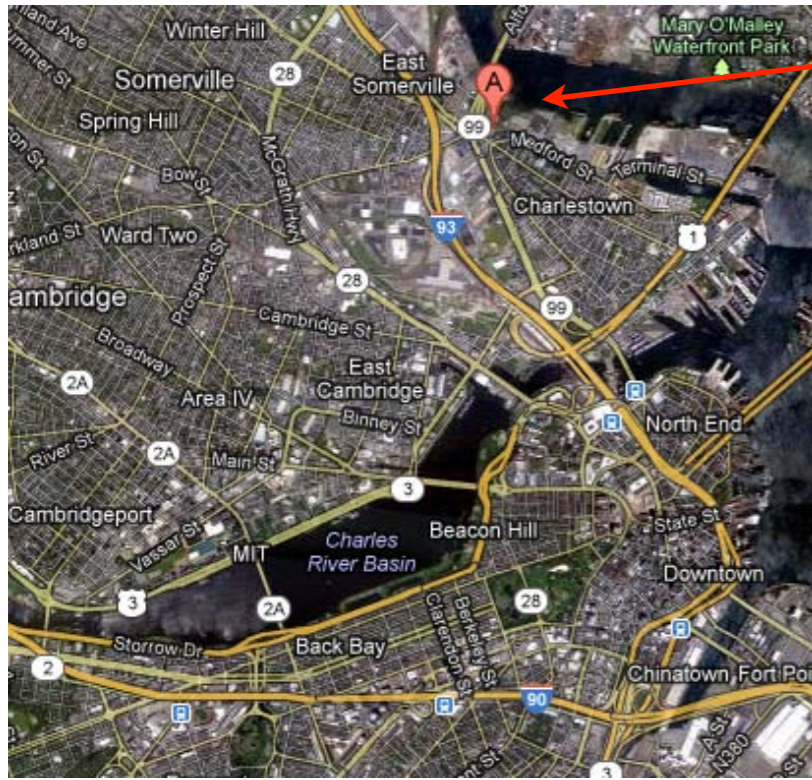
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Figure 1: Dimensions and parameters for the box model

See Seinfeld and Pandis, Chapter 25

BLmodel2.m

CO₂ source



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Boston Generating Station

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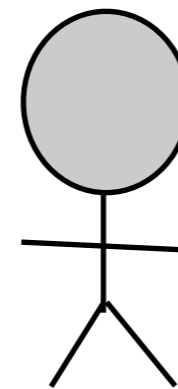


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Photograph by [IFCAR](#); in the public domain.

Car: 9 kg CO₂/gallon, I drive 14 miles per day making 2.5 kg CO₂/day @ 50mpg



People: 2k food cal diet per day
Free Energy Gain from Glucose =
2870 kJ/mol glucose (makes 6
CO₂), I get 770 g CO₂ per day
how many people are in the box?

Meteorology data 1

Weather Underground

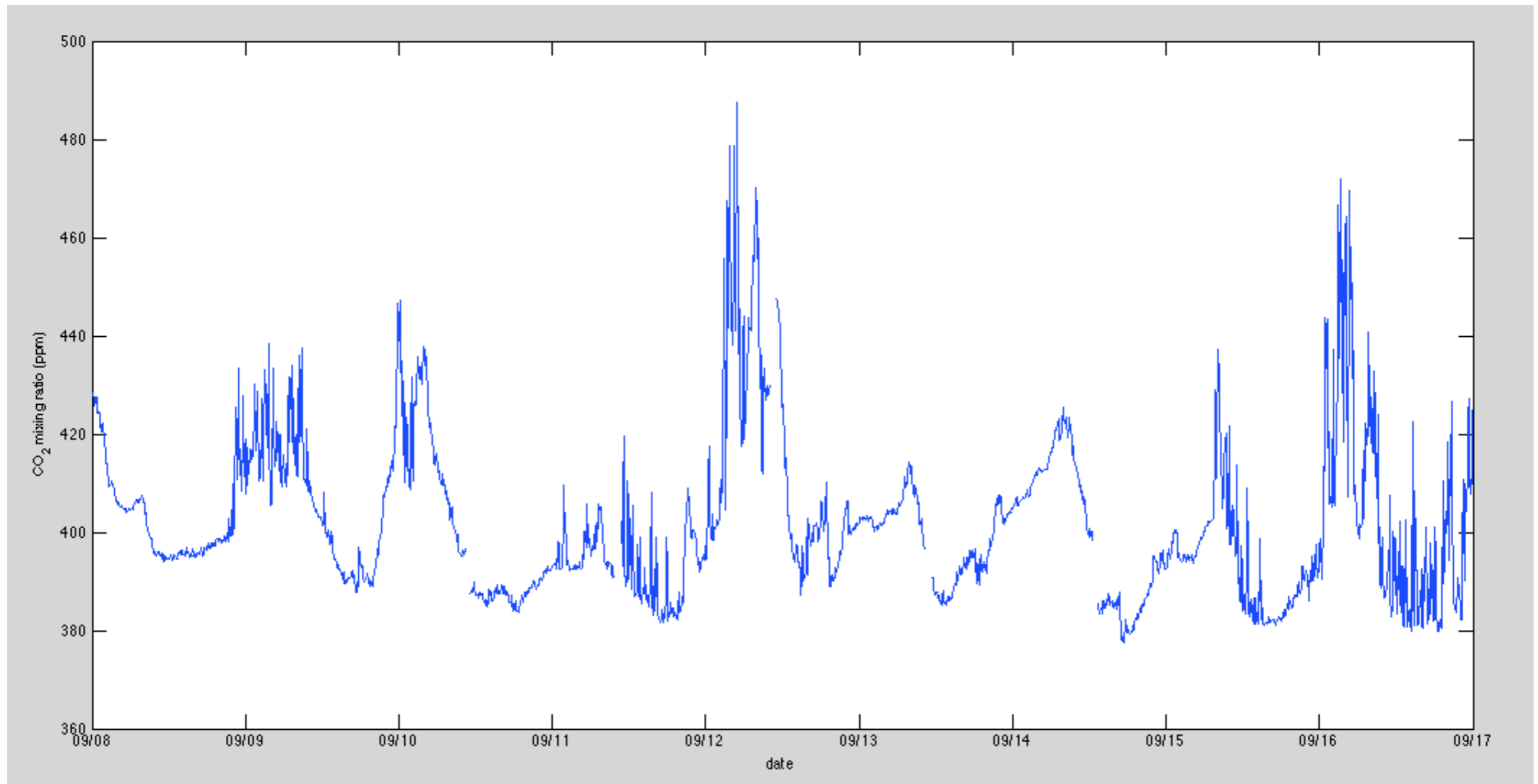
<http://www.wunderground.com>

For Green Building Roof

<http://www.wunderground.com/weatherstation/WXDailyHistory.asp?ID=KMACAMBR9>

You can download comma delimited file for each day

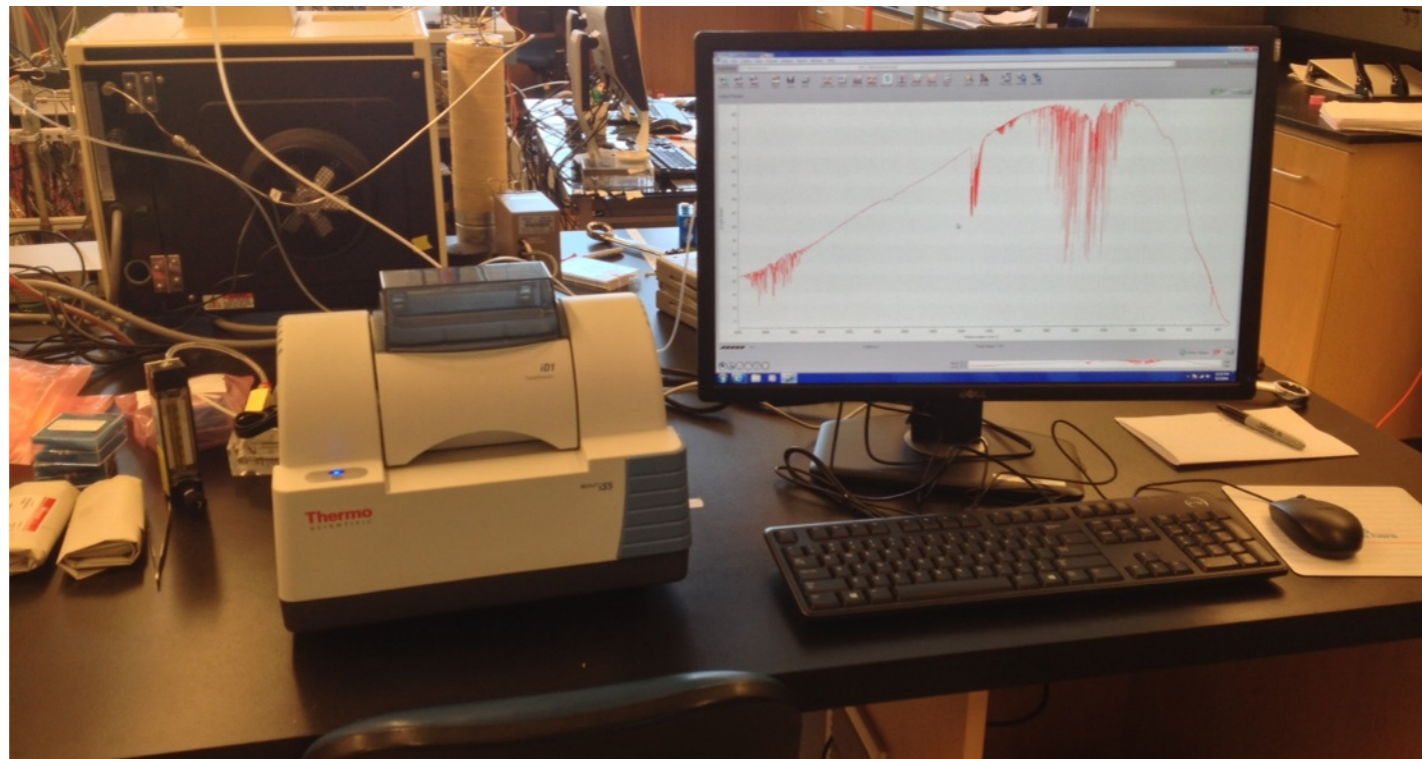
Lab-2: Green Building CO₂ data



data "co2_full_record.mat"

Project 2

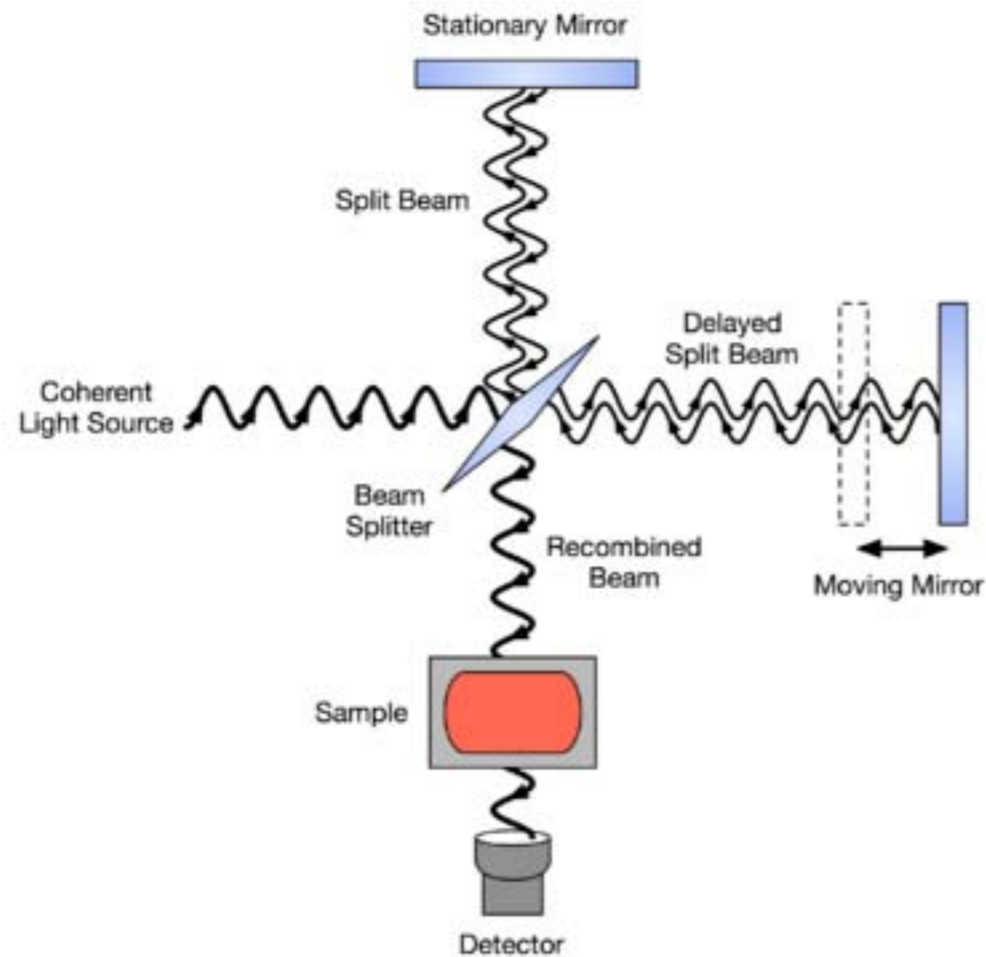
Why is CO₂ a Powerful Green House Gas?



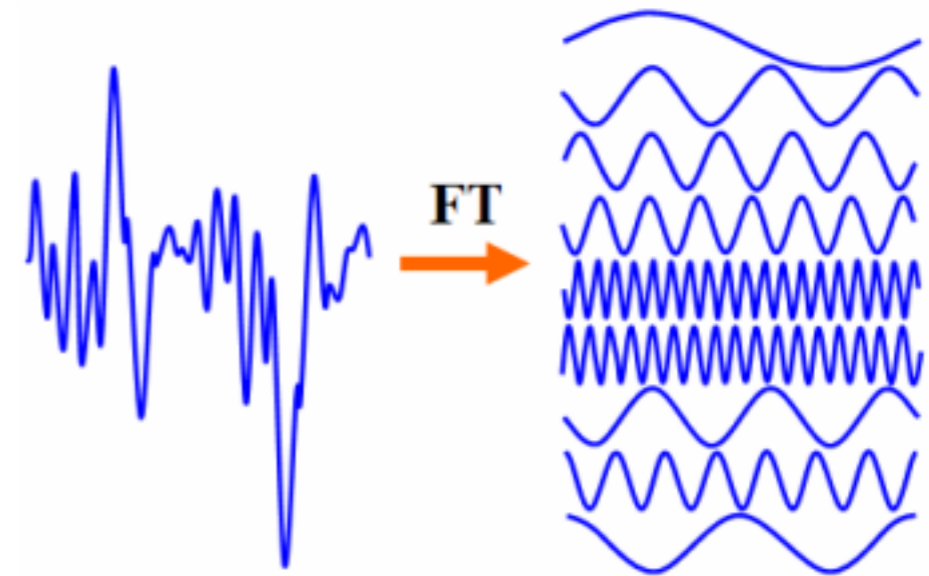
FTIR (Thermo iS5)

Fourier transform infrared spectroscopy (FTIR)

Michelson interferometer



Fourier transform



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Image is in the public domain.

“Extremely brief” overview of rotational-vibrational spectroscopy

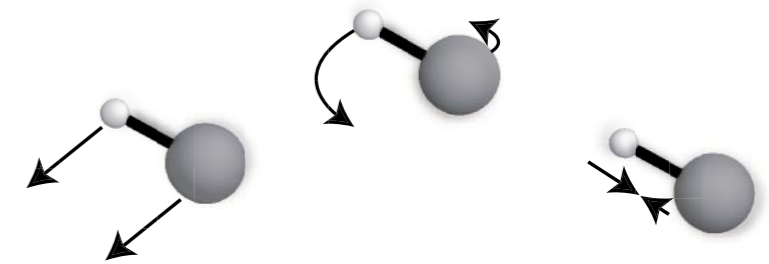
Neglecting centrifugal distortion, vibration-rotation coupling and anharmonicity (i.e., no change in bond length), the rotation-vibration energy of diatomic molecules (e.g., CO) is:

$$E \approx \omega_v(n + 1/2) + B_e J(J + 1)$$

n is the vibrational quantum number, can be 0, 1, 2, ...

J is the rotational quantum number, can be 0, 1, 2,

ω_v is the fundamental vibration frequency.



B_e is the rotation constant:

$$B_e = \frac{h^2}{8\pi^2 c \mu R_e^2}$$

μ is the reduced mass, for $^{12}\text{C}^{16}\text{O}$ it will be $12 \times 16 / (12 + 16)$.

R_e is the equilibrium bond length

c is the speed of light

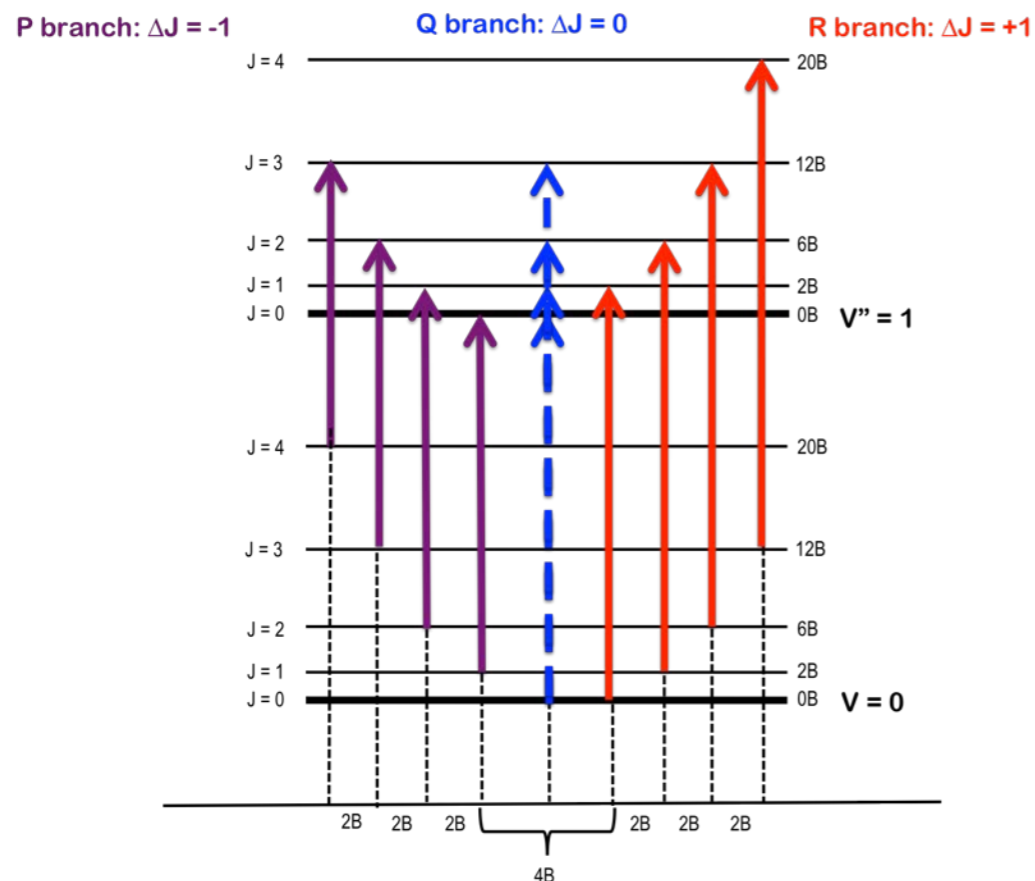
For diatomic molecule like CO, selection rule tells that transitions for $n = 0$ to $n = 1$, rotational level of $\Delta J = \pm 1$ is infrared active. For transition, $J'' \leftarrow J'$, where lower energy state is J' , The absorption band occur at the wavenumber at

$$\omega \approx \omega_v + B_e(J'(J' + 1) - J''(J'' + 1)) \quad (3)$$

then,

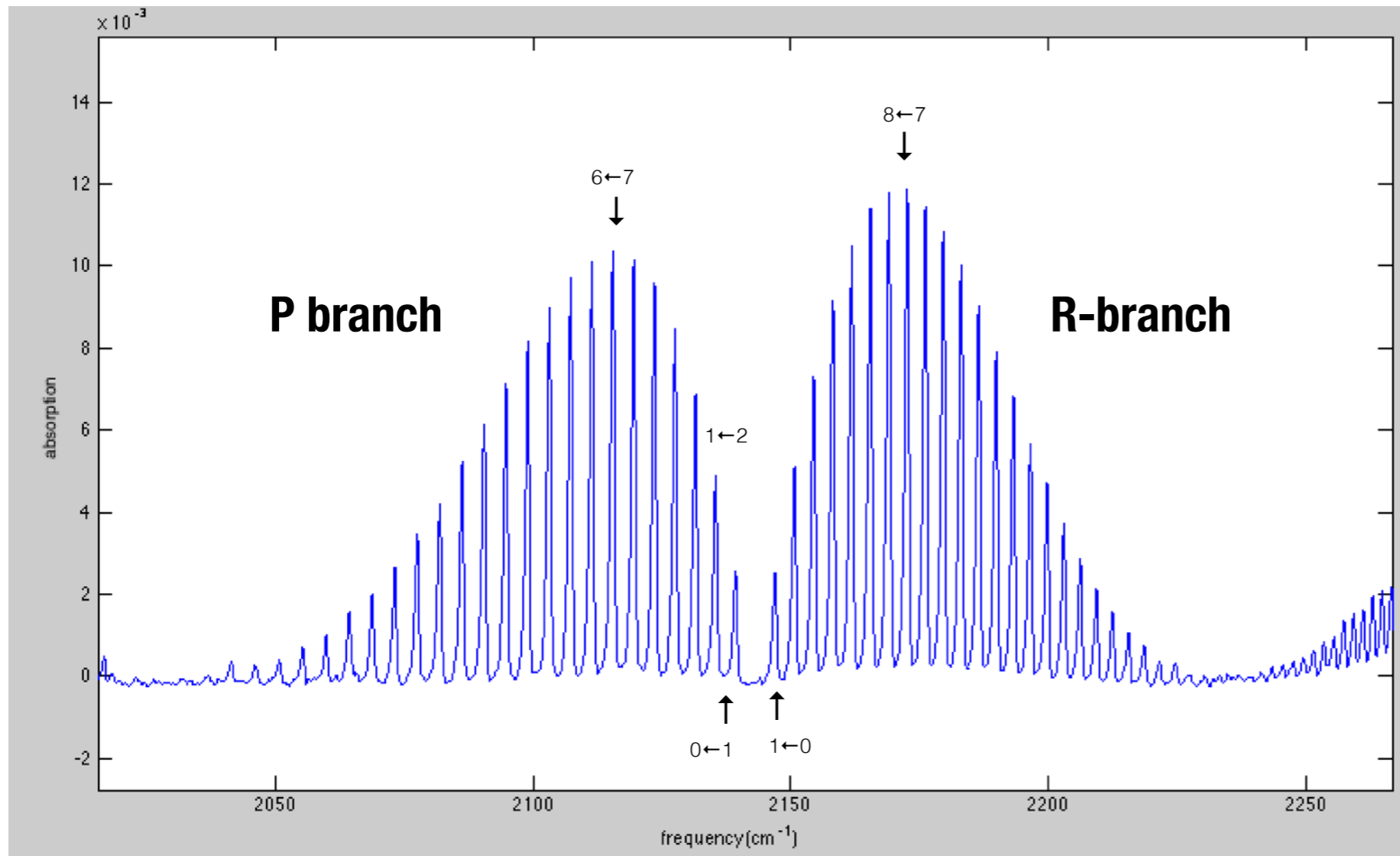
$$\omega_P(J'') \approx \omega_v - 2B_e J'' \quad (4)$$

$$\omega_R(J'') \approx \omega_v + 2B_e(J'' + 1) \quad (5)$$



http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Rotational_Spectroscopy/Rovibrational_Spectroscopy

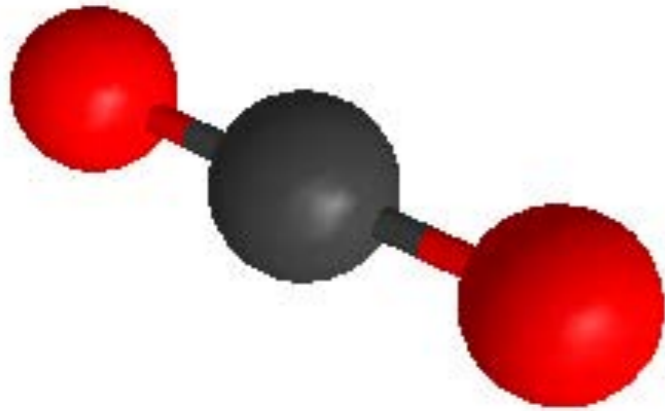
Basic of Infrared spectrum (diatomic molecule)



* Each molecule (and each vibrational mode) has characteristic absorption pattern because the center of the band corresponds to vibrational frequency, which depends upon force constant (strong bond) has high frequency and reduced mass (proportional to $\sqrt{k/\mu}$) and spacing between lines goes with rotation constant (bond length and reduced mass).

Molecular vibration

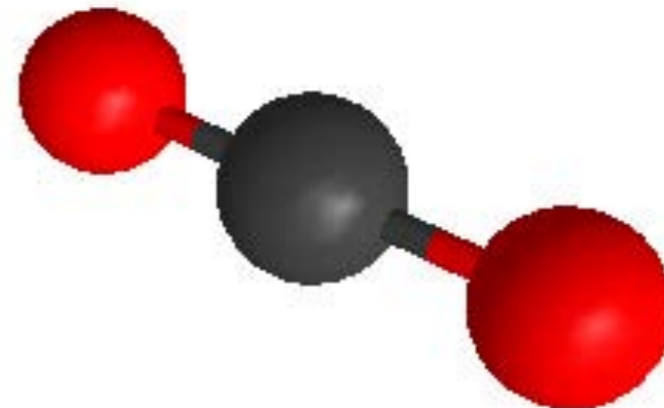
Three Fundamental Vibrational Frequency of CO₂



ω_3 : asymmetric stretch
2349.5 cm⁻¹ (4.26 μm)

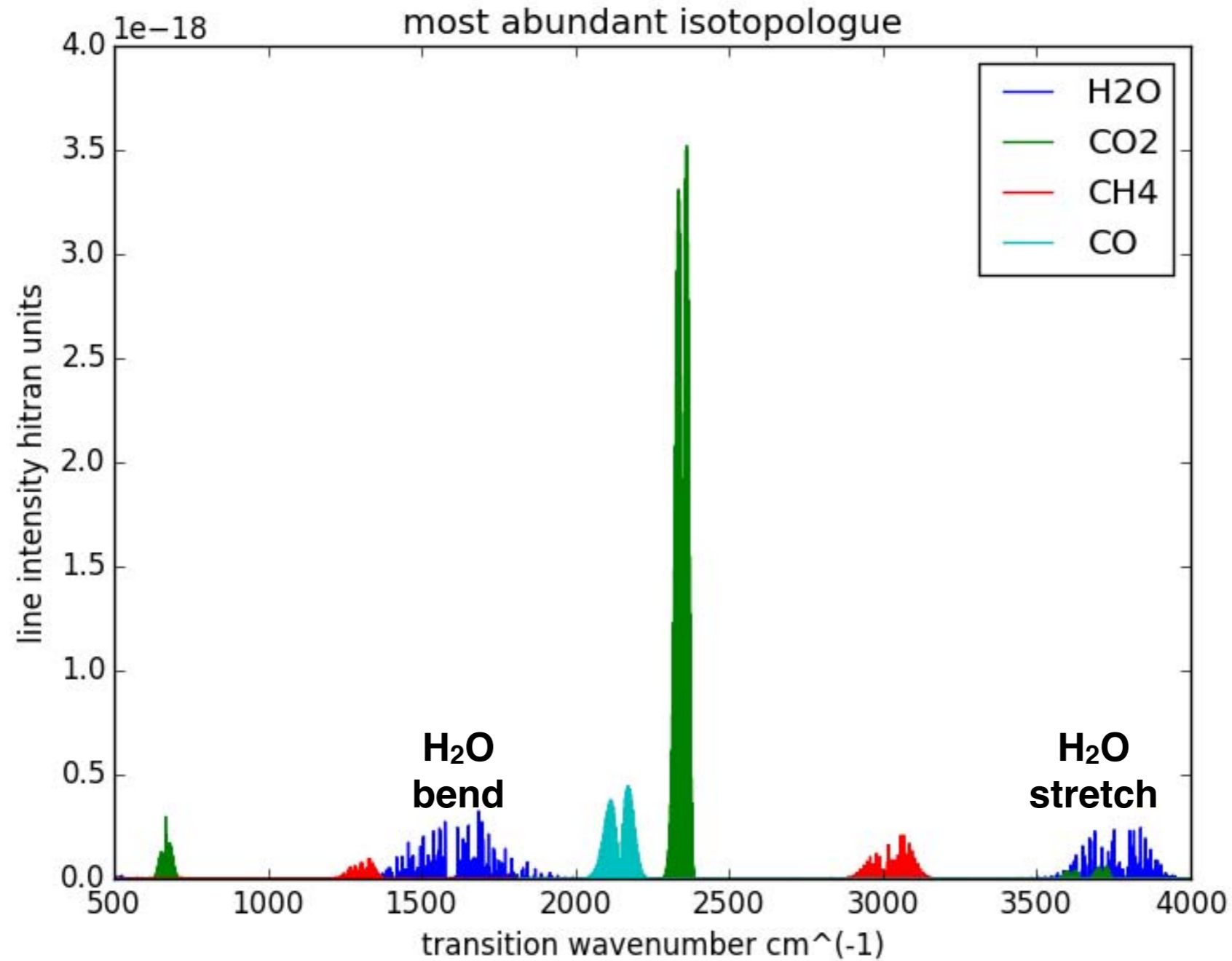


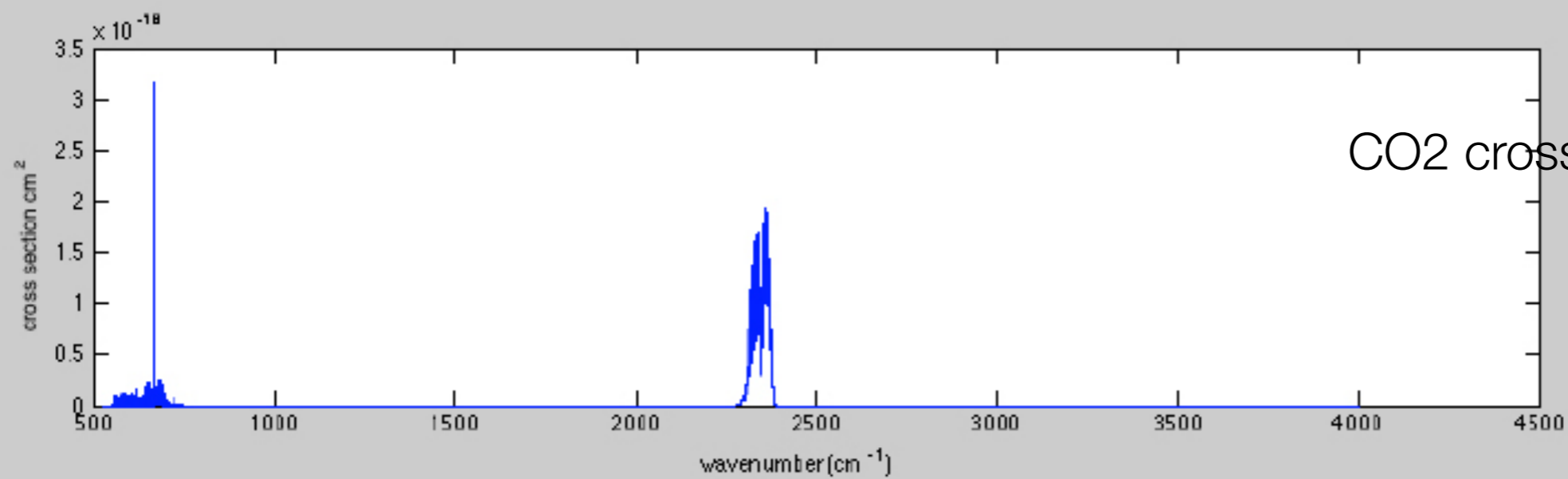
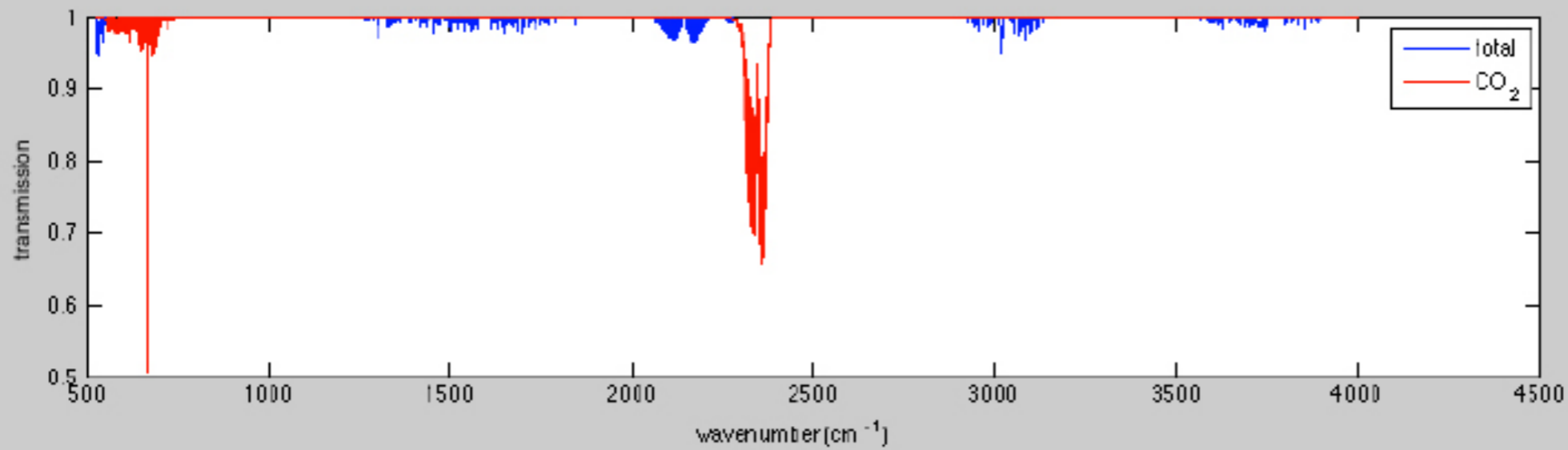
ω_1 : symmetric stretch
1345.4 cm⁻¹ (7.43 μm)



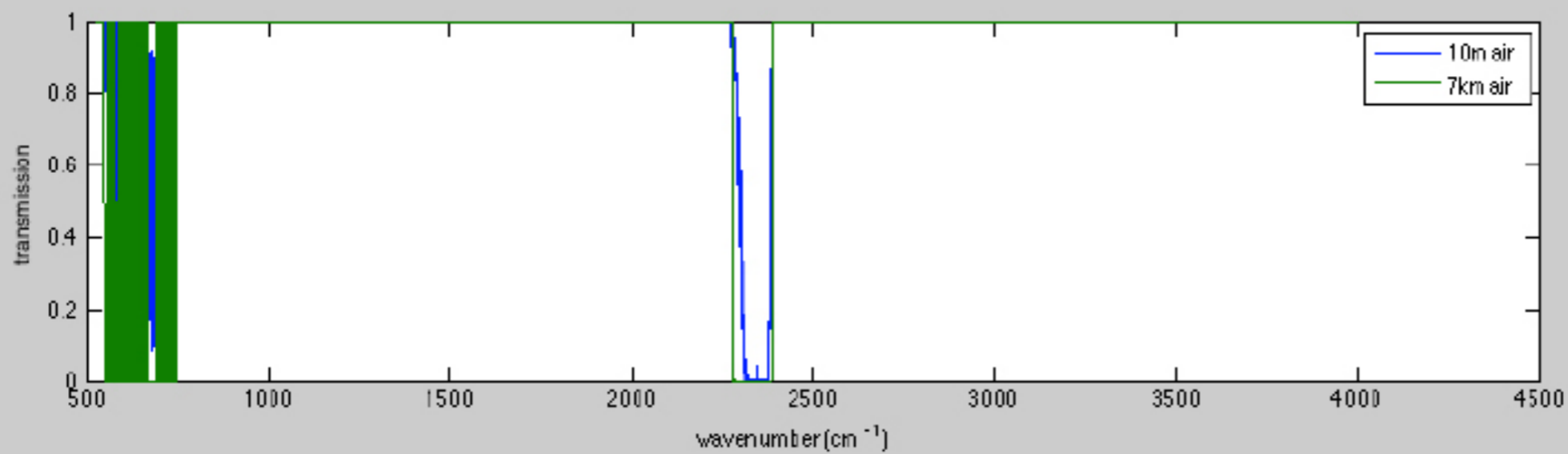
ω_2 : bending
661.7 cm⁻¹ (15.1 μm)

Infrared spectra for H₂O, CO₂, CH₄ and CO

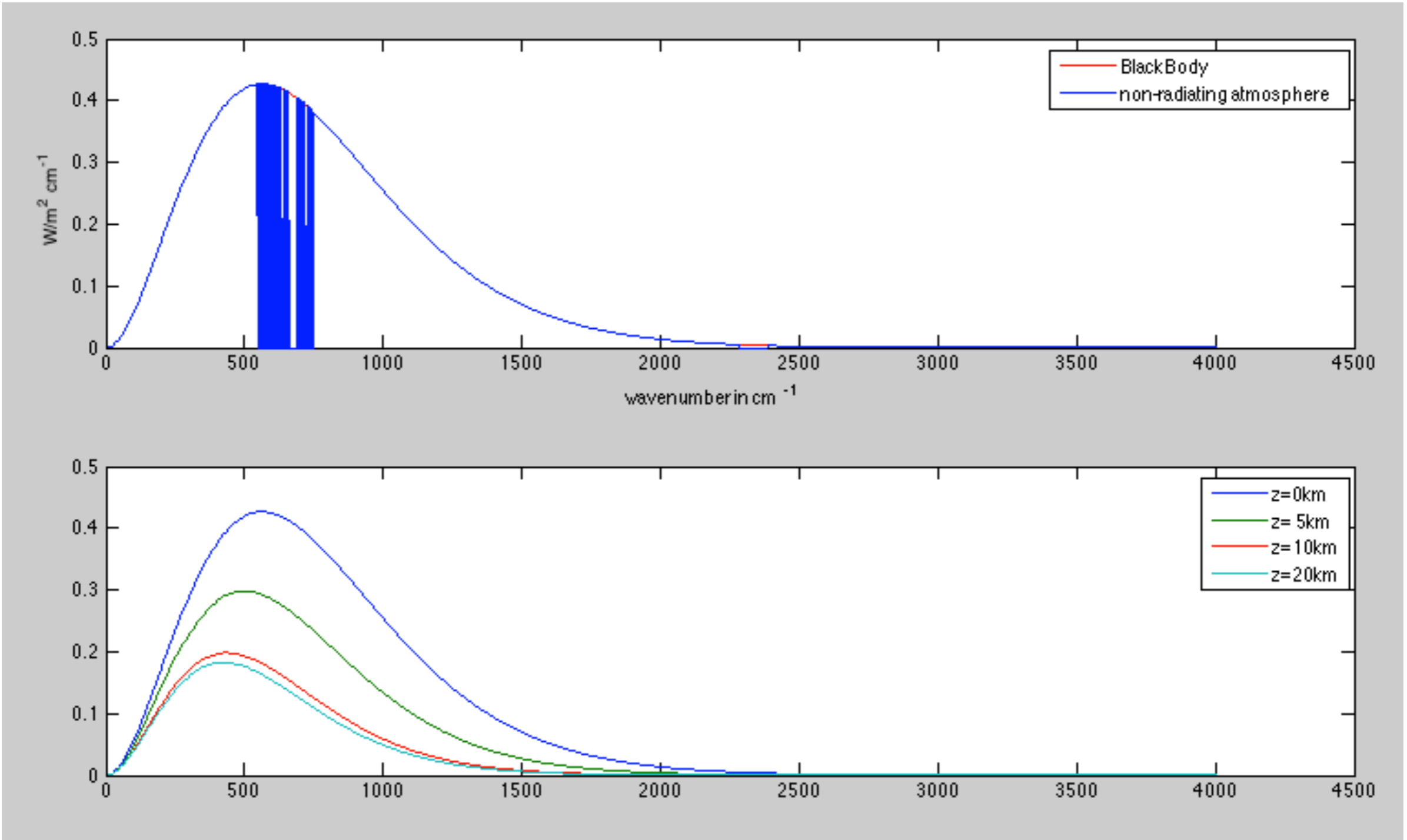




CO₂ cross section from FTIR

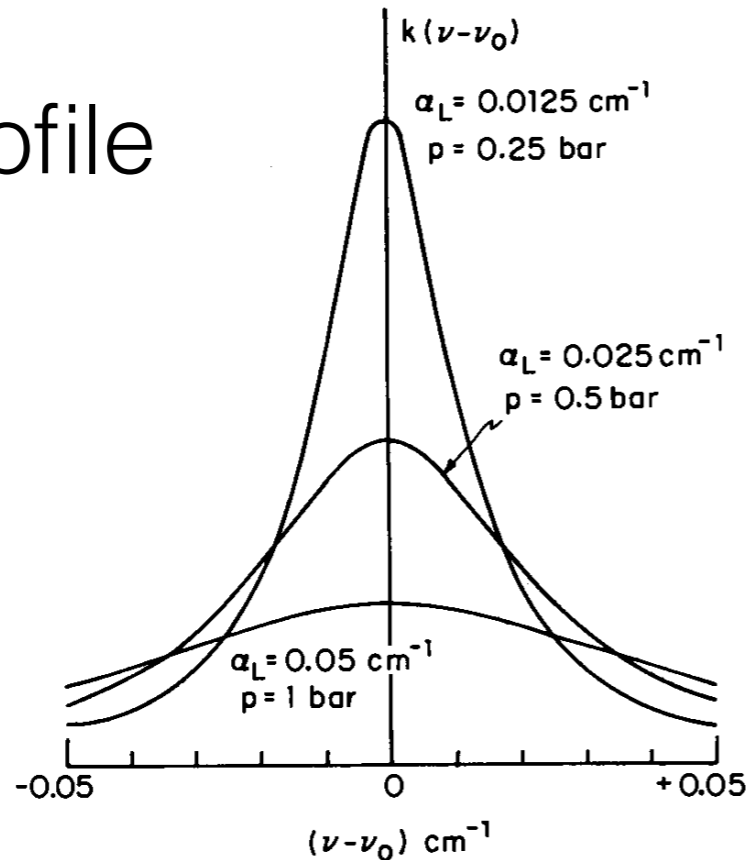


Exercise last week



Pressure and Temperature Effects of Absorption Line width

Voigt Profile



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Lorentz line shape profiles for three pressures. A line width of 0.05 cm^{-1} at a pressure of 1 bar is typical for vibration-rotation bands. [Goody & Yung, Fig. 3.18]

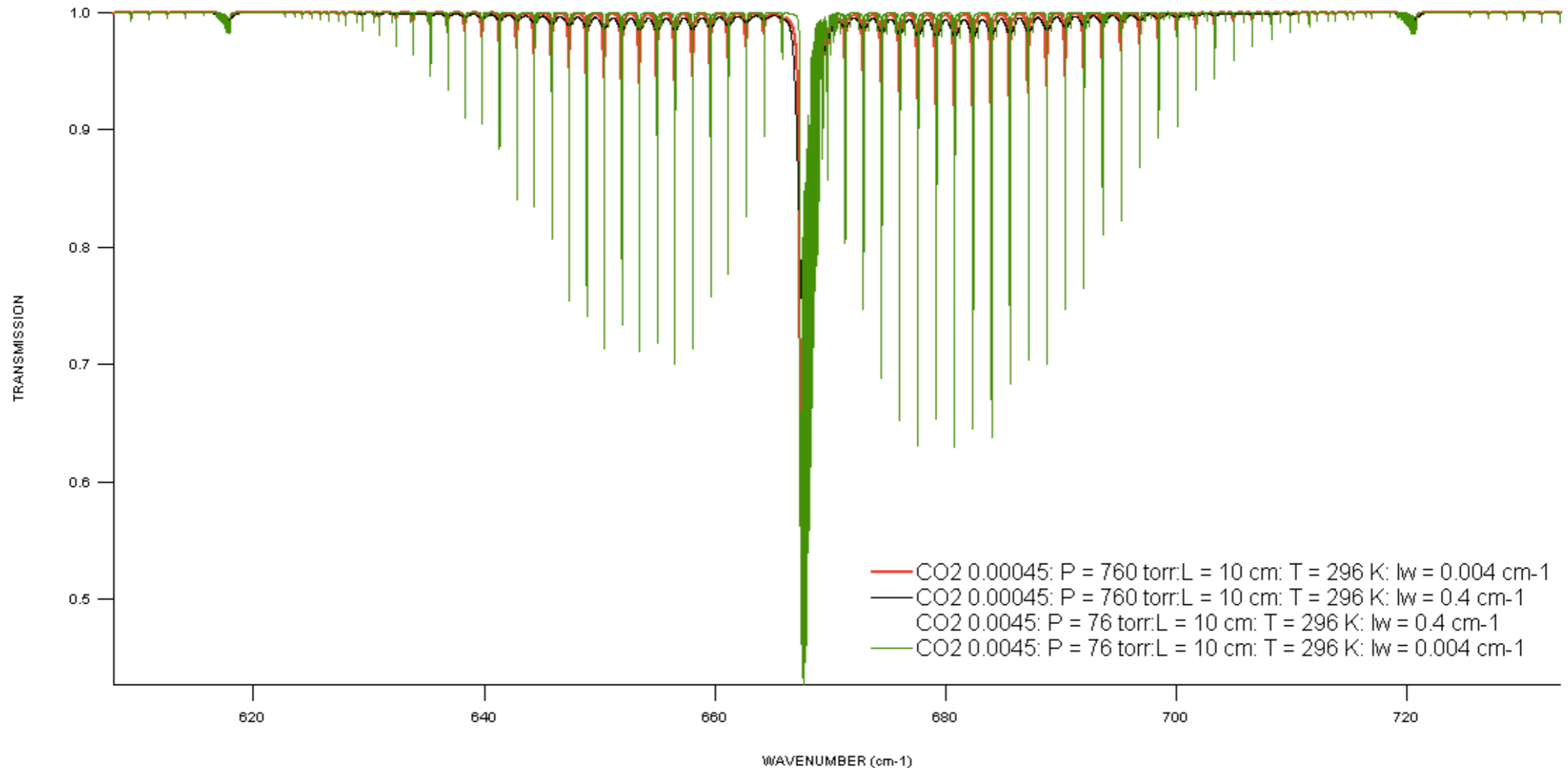
σ : doppler line width

$$\alpha_D = \nu_0 \sqrt{\frac{2k_B T}{mc^2}}$$

γ : Lorentzian line width

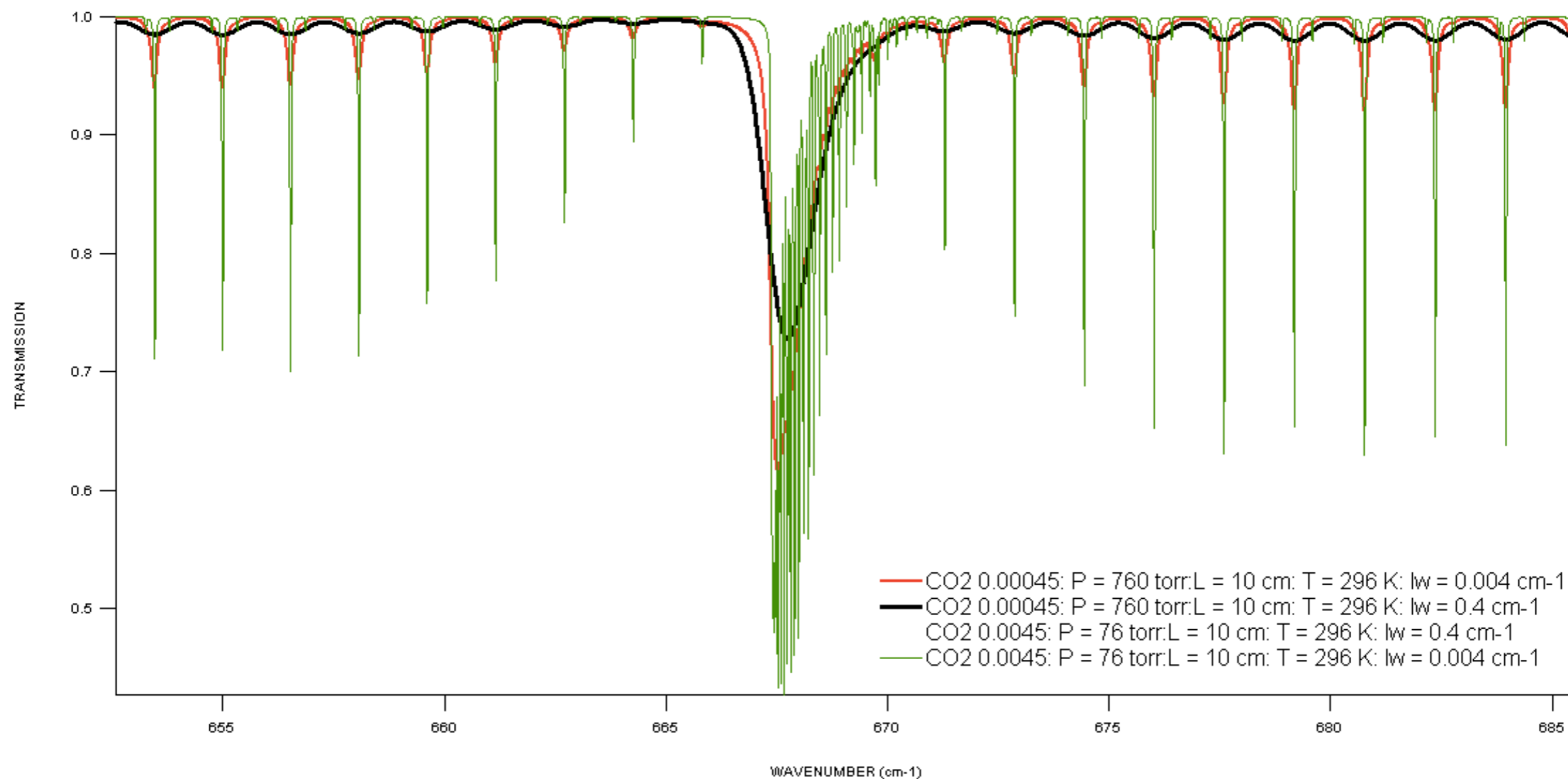
$$\alpha = \alpha_0 \left(\frac{p}{p_0} \right) \left(\frac{T_0}{T} \right)^n$$

Ro-vibrational transition of 15 μm CO_2 bending band



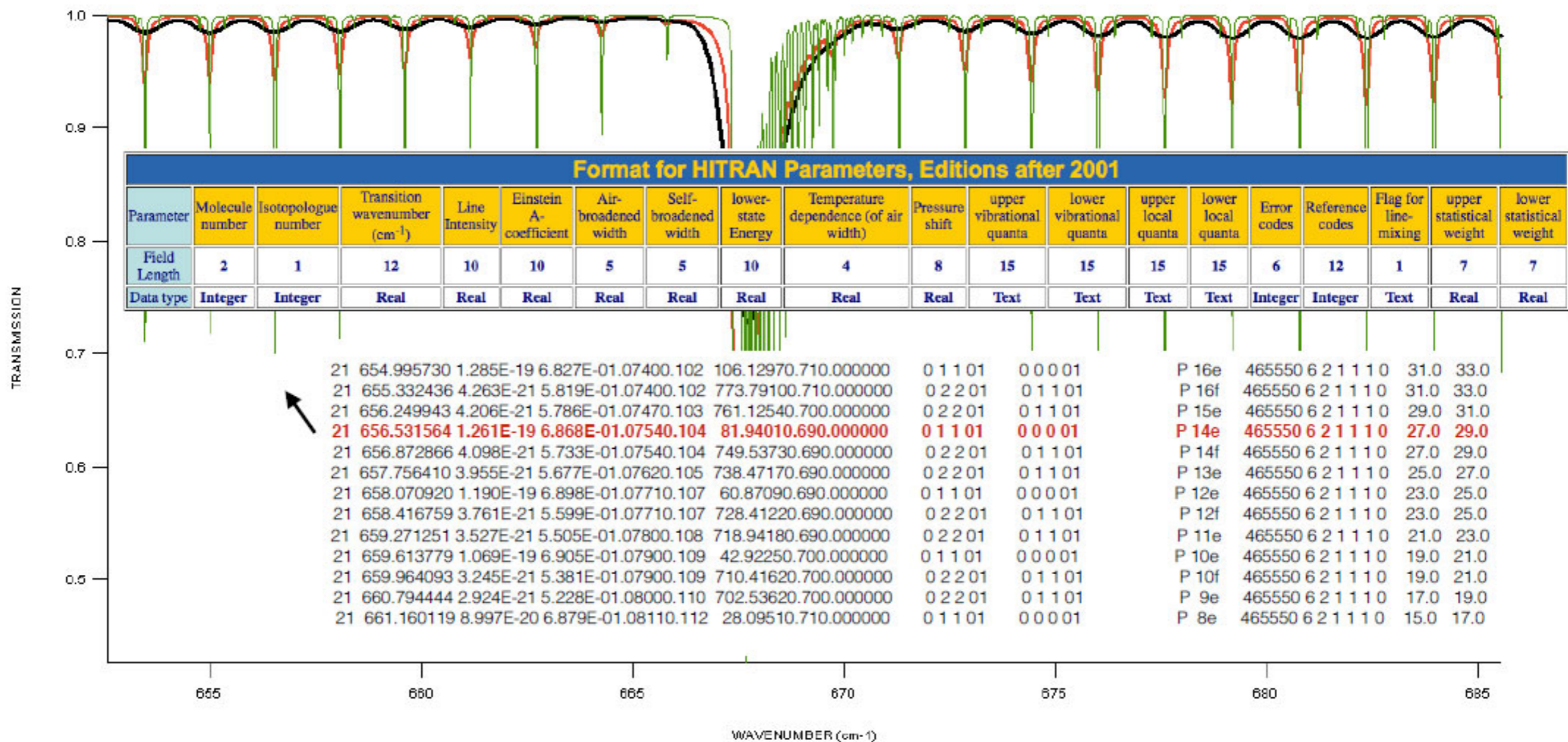
Low spectral resolution (0.4 cm^{-1}) high P (760 torr)
High spectral resolution (0.004 cm^{-1}), high P (760 torr)
High spectral resolution (0.004 cm^{-1}), low P (76 torr)

Instrument resolution, and pressure broadening



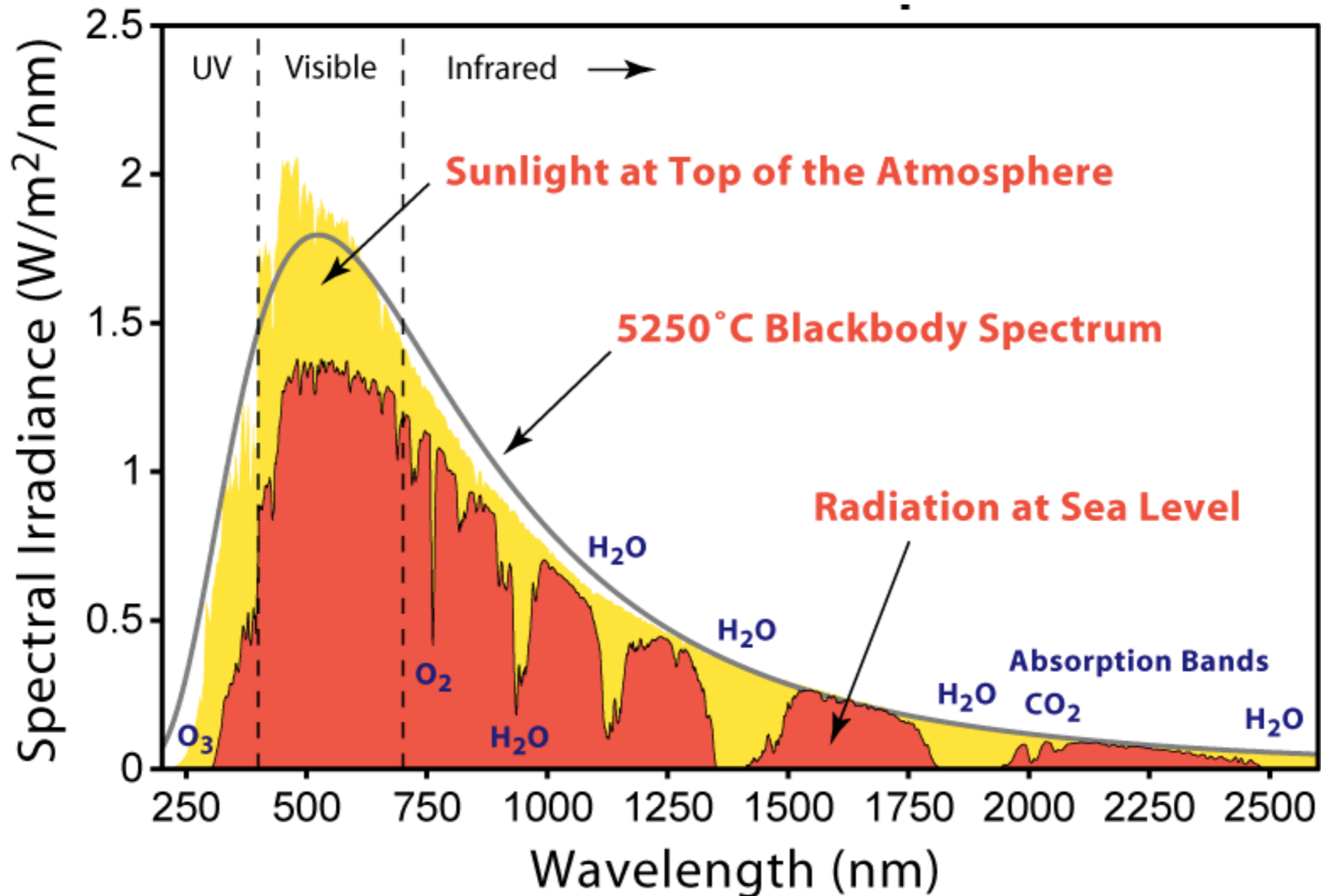
Low spectral resolution (0.4 cm^{-1}) high P (760 torr)
High spectral resolution (0.004 cm^{-1}), high P (760 torr)
High spectral resolution (0.004 cm^{-1}), low P (76 torr)

Quick overview of the HITRAN database



Low spectral resolution (0.4 cm⁻¹) high P (760 torr)
High spectral resolution (0.004 cm⁻¹), high P (760 torr)
High spectral resolution (0.004 cm⁻¹), low P (76 torr)

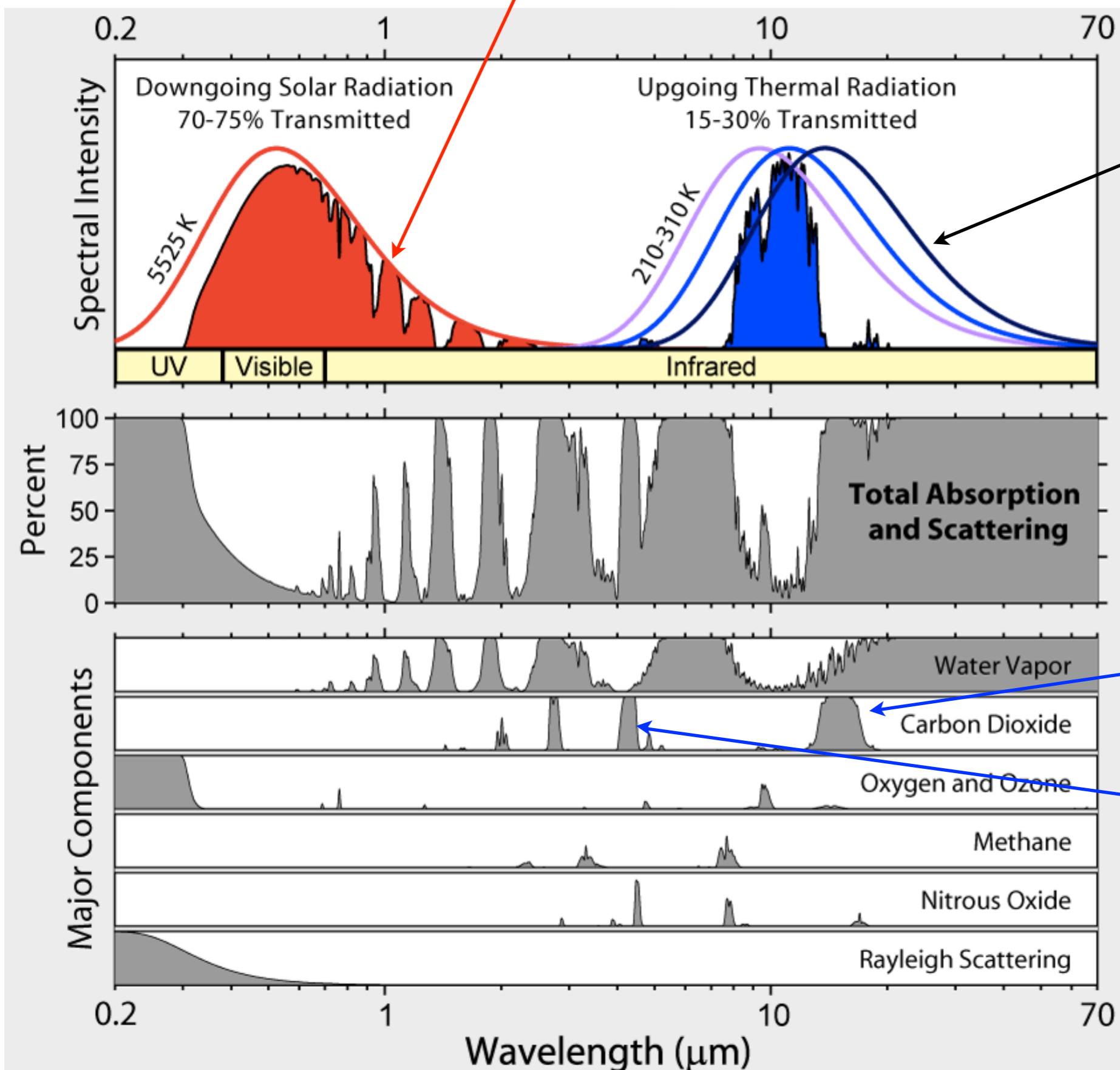
Incoming Solar Radiation and Absorption by the Atmospheric Constituents



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Solar irradiance spectrum above atmosphere and at surface

Incoming Solar Radiation



Radiation from Earth Surface

bending

asyn. stretch

Why isn't atmosphere totally black at 15 μm ?

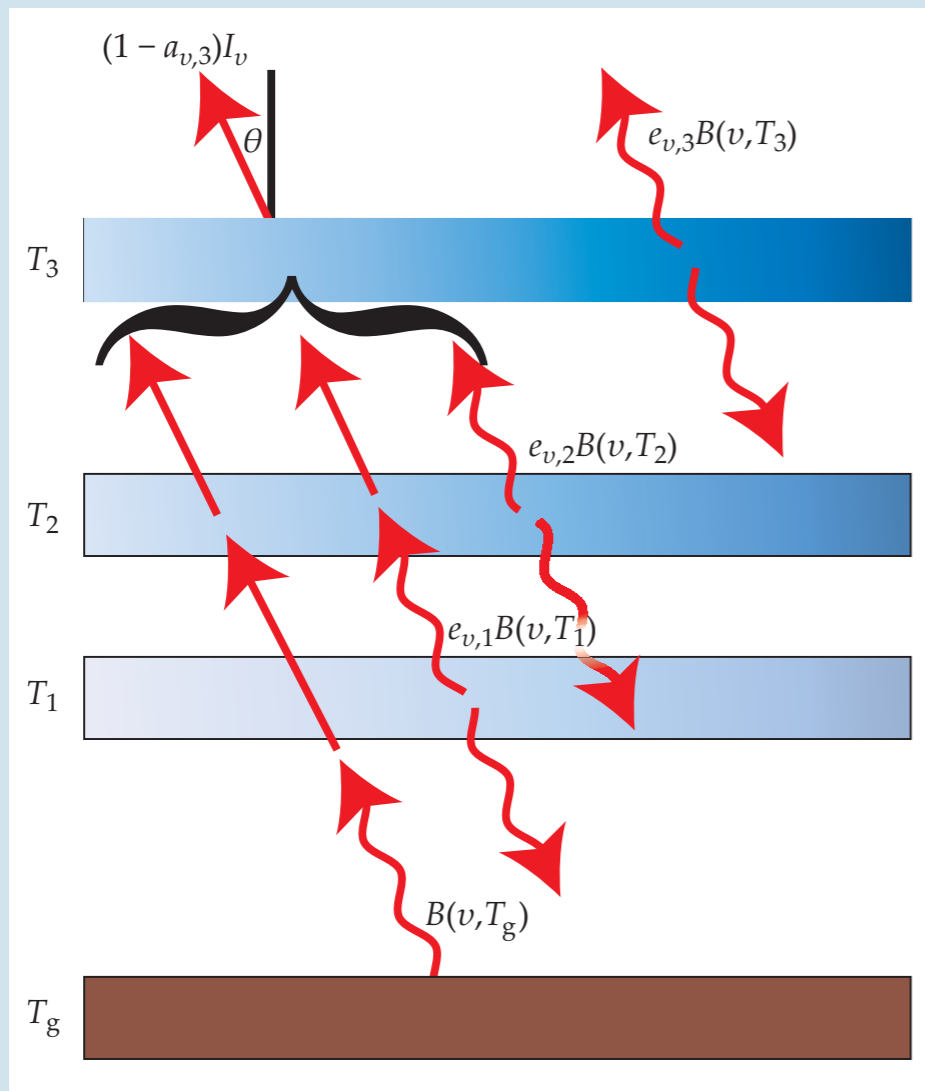
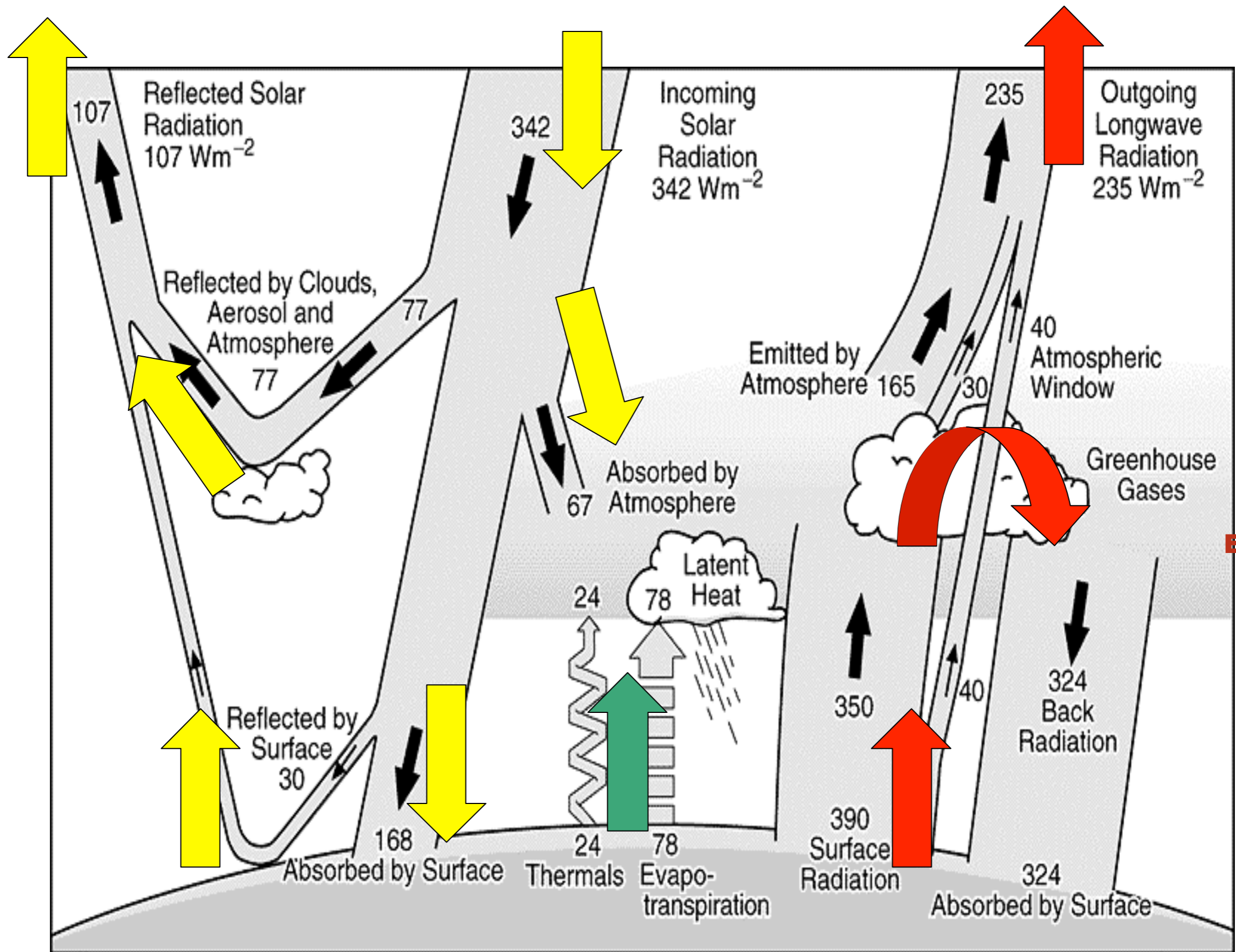


Figure 1. Three isothermal layers model the atmosphere in this illustration of upward-moving electromagnetic radiation with frequency ν . The radiation, assumed not to scatter, propagates at an angle θ with respect to the vertical and emerges from layer 3, the topmost atmospheric slice. The ground below the atmosphere emits as an ideal blackbody, characterized by the Planck function B . Each layer, at its own temperature T , emits with its own emissivity e_ν and, by Kirchhoff's law, absorbs a proportion $a_\nu = e_\nu$ of the incident radiation. The radiation flux distribution incident on layer 3 is I_ν . It is the sum of the thermal emission from the ground, layer 1, and layer 2, attenuated by absorption in the intervening layers 1 and 2. Squiggly arrows indicate thermal emission; straight arrows indicate transmitted radiation.

ENERGY BALANCE IN THE CLIMATE SYSTEM



**ESSENCE
OF THE
GREEN-
HOUSE
EFFECT**

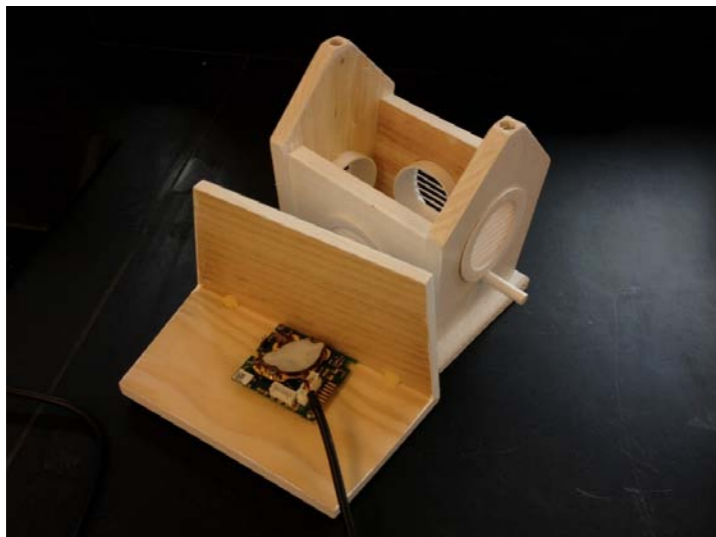
Compact/inexpensive NDIR detector



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Cost: \$ 60-200
Light source: Incandescent Lamp
Detector: Thermopile
4.25 $\mu\text{m} \pm 0.1\mu\text{m}$ (HW) IR filter
15 cm pathlength (gold coated cell)
hydrophobic filter to avoid liquid H₂O

Repeatability ± 20 ppm
Accuracy ± 30 ppm



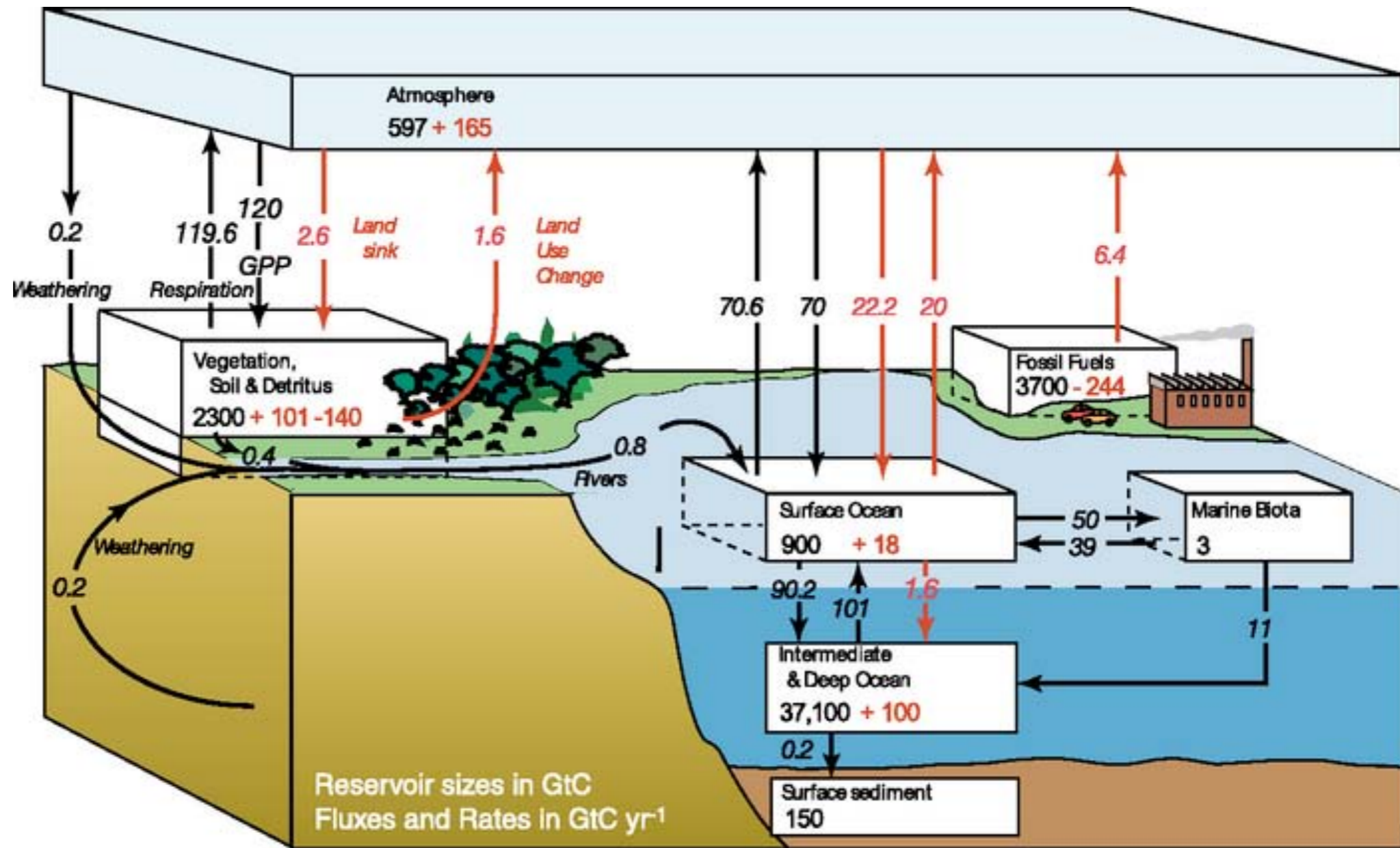
Portable CO₂ meter/data logger in a bird house

<http://www.co2meter.com/collections/co2-sensors>

Project 3

What is the fate of CO₂?

The Global Carbon Cycle for the 1990s



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Source: Sarmiento, Jorge L., and Nicolas Gruber. "Sinks for Anthropogenic Carbon." 2002.

Figure 7.3. The global carbon cycle for the 1990s, showing the main annual fluxes in GtC yr⁻¹: pre-industrial 'natural' fluxes in black and 'anthropogenic' fluxes in red (modified from Sarmiento and Gruber, 2006, with changes in pool sizes from Sabine et al., 2004a). The net terrestrial loss of -39 GtC is inferred from cumulative fossil fuel emissions minus atmospheric increase minus ocean storage. The loss of -140 GtC from the 'vegetation, soil and detritus' compartment represents the cumulative emissions from land use change (Houghton, 2003), and requires a terrestrial biosphere sink of 101 GtC (in Sabine et al., given only as ranges of -140 to -80 GtC and 61 to 141 GtC, respectively; other uncertainties given in their Table 1). Net anthropogenic exchanges with the atmosphere are from Column 5 'AR4' in Table 7.1. Gross fluxes generally have uncertainties of more than ±20% but fractional amounts have been retained to achieve overall balance when including estimates in fractions of GtC yr⁻¹ for riverine transport, weathering, deep ocean burial, etc. 'GPP' is annual gross (terrestrial) primary production. Atmospheric carbon content and all cumulative fluxes since 1750 are as of end 1994.

This image has been removed due to copyright restrictions.

Please see Figure 10.2.3. Time series figures of carbon dioxide from book: Sarmiento, J. L., and N. Gruber. *Ocean Biogeochemical Cycles*. Princeton University, 2006.

Fate of CO₂ in different time scales

Sarmiento&Gruber(2006)

Earth Simulator 2



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12.335 / 12.835 Experimental Atmospheric Chemistry
Fall 2014

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