

Lecture 6 - spectroscopy

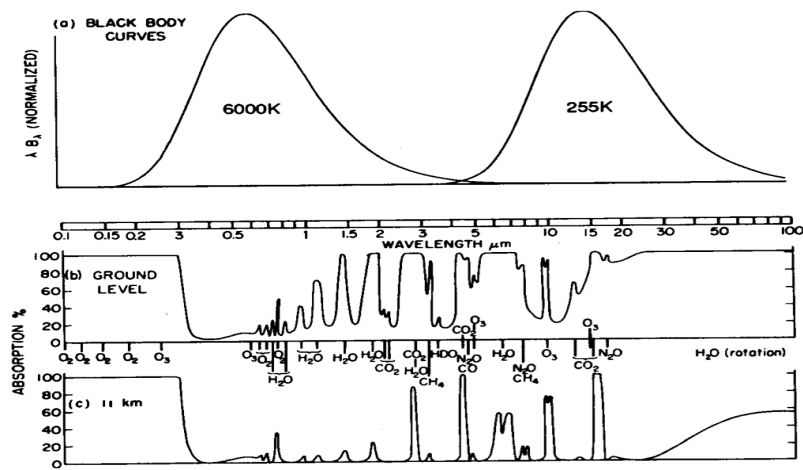


Fig. 3.2 The normalized blackbody emission spectra for the sun (6000 K) and Earth (255 K) as a function of wavelength (top). The fraction of radiation absorbed while passing from the surface to the top of the atmosphere as a function of wavelength (middle). The fraction of radiation absorbed from the tropopause to the top of the atmosphere as a function of wavelength (bottom). The atmospheric molecules contributing the important absorption features at each frequency are indicated. [Taken from Goody and Yung (1989). Reprinted with permission from Oxford University Press.]

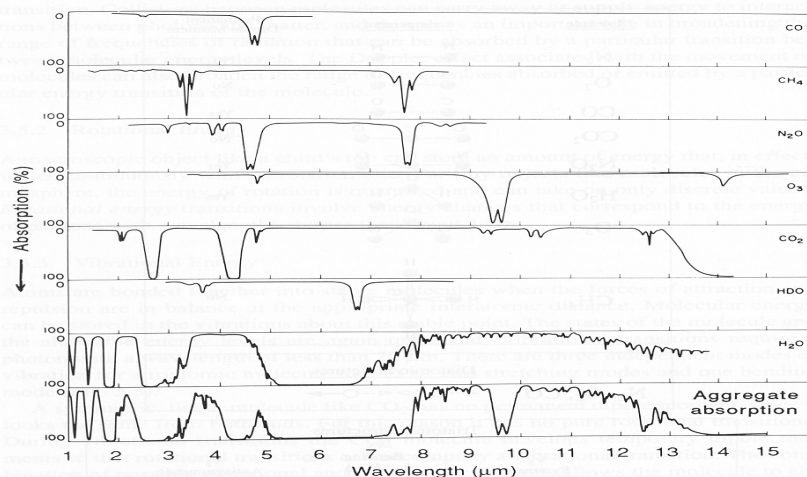


Fig. 3.4 Infrared absorption spectra for various atmospheric gases. [From Valley (1965). Used with permission from McGraw-Hill, Inc.]

Light

Electromagnetic radiation can be thought of as either a wave or as a 'particle' (particle/wave duality). For scattering of light by particles, air, and surfaces, wave theory is most useful; for absorption and emission of radiation, thinking of light as discrete parcels of energy (photons) is most useful. Any doubts about photons? We can count individual photons using a photomultiplier tube.

In vacuum, the speed of electromagnetic radiation is constant $c^* = 3 \times 10^8 \text{ m s}^{-1}$. Frequency, ν , and wavelength, λ , are thus related:

$$\nu = c^*/\lambda$$

The energy of a photon is proportional to its frequency:

$$E_\nu = h\nu$$

where h , Planck's constant, $= 6.625 \times 10^{-34} \text{ J s}$.

Most of the sun's energy is emitted between 100 nm and 4000 nm $= 4 \mu\text{m}$. 99% of this energy is in the visible (400-750nm) and near IR (750-5000 nm). UV is important for formation of atmospheric ozone and for driving the radical photochemistry of Earth's atmosphere (Ge/ESE/Ch 171 – spring). Thermal emission from Earth occurs between 4 and 200 μm (IR and FarIR).

The Interaction of Light and Molecules

When a photon is absorbed by a molecule it ceases to exist and its energy is transferred to the molecule. This energy can be transferred to vibrational, rotational, electronic, or translational forms. In many cases, multiple modes are excited. The first law thermodynamics requires:

$$E_{\text{photon}} = h\nu = \Delta E_{\text{translational}} + \Delta E_{\text{rotational}} + \Delta E_{\text{vibrational}} + \Delta E_{\text{electronic}}$$

A molecule can absorb a photon of a given energy only if there exist two states of the molecule separated by this energy. In addition, this excitation must be quantum mechanically 'allowed'. These allowable transitions determine what radiation will be absorbed and emitted by atmospheric gases. In general, electronic transition occur in the UV while vibrational and rotational transitions occur in IR. The visible is largely devoid of absorbers.

Electronic and Translational Energy

Electronic transitions (those that move electrons into other orbitals) are typically the most energetic and UV (and a few in the visible) wavelengths are required. These transition are critical for breaking bonds and thereby driving atmospheric photochemistry. Rotational transitions on the other hand require weak photons in the far IR (20 μm and longer).

Translational Energy is not quantized. The kinetic energy of a molecule is typically small compared to the energy required for a vibrational transition (though there are important exceptions). Temperature is a measure of the translational energy of a body. For an ideal gas:

$$p \times V = 1/3 \rho \langle v^2 \rangle \times V = nRT$$

expresses the fact that the total translational kinetic energy per mole of molecules of an ideal gas is proportional to the temperature.

As we discuss below, collisions can also add (or subtract) energy during the interaction of a photon and a molecule and this is critical for determining the lineshapes of the optical transitions

Rotational Energy

Unlike large objects which have essentially infinite numbers of rotational states, the rotational states of molecules are quantized and only certain transitions are allowed. [For typical gas-phase molecules] Rotational transitions occur at wavelengths longer than $\sim 20\text{ }\mu\text{m}$. At temperatures characteristic of Earth's atmosphere, most molecules are rotationally excited. As a result, for molecules that have a handle with which to 'grab' a photon (a permanent dipole moment, μ) numerous spectrally-overlapping transitions occur and the far IR is nearly opaque at all wavelengths. H_2O is by far the most important molecule for blackening the spectral region longward of $20\text{ }\mu\text{m}$ (500 cm^{-1}). The larger the dipole moment, the more intense the transition will be.

The frequency of these transitions is proportional to the inverse of the moment of inertia \rightarrow only small molecules with a hydrogen will have transitions at high enough energy to interact with thermal radiation from Earth.

Vibrations of Molecules

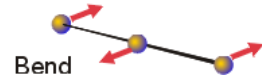
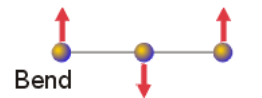
The bond in a molecule produces an equilibrium separation between the atoms. About this equilibrium separation, a molecule can vibrate. As with rotational states, vibrational states are also quantized. Excitation of vibrational modes in a molecule requires a photon with wavelength typically shorter than $20\text{ }\mu\text{m}$. In addition, quantum mechanical selection rules make transitions that in addition excite (or de-excite) a single quantum of rotation much more intense than those which change the rotational energy by more or less than this amount. In addition, excitation of a single mode of a molecule (a so-called fundamental) is in general much more intense than excitation of multiple modes (so-called combination or overtone bands, c.f. CO Figure 3.4). Finally, a handle is also required. In this case, the critical issue is whether upon excitation of a mode, the dipole moment changes, $\Delta\mu \neq 0$. Examination of the geometry of the molecule can tell us if a gas will be infrared active.

N_2 and O_2 , which possess neither a permanent, nor induced dipole do not absorb in the IR. The presence of N_2 and O_2 , however, strongly influence the absorption line shapes and thus radiative forcing, particularly for optically deep transitions.

CO₂

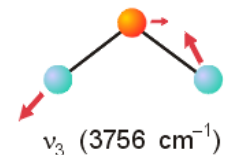
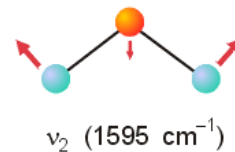
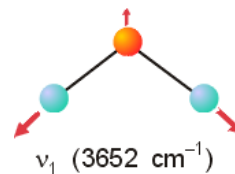
CO₂ is a linear molecule O=C=O. It has no permanent dipole moment (why?) and as a result, no significant rotational spectrum. As with all tri atomic systems, there are three modes of vibrational modes that can be excited:

1. Symmetric stretch ($\Delta p=0$) not infrared active.
2. Antisymmetric stretch ($\Delta p \neq 0$). (4.3 μm)
3. Bend ($\Delta p \neq 0$) – very strong transition near 15 μm .



H₂O

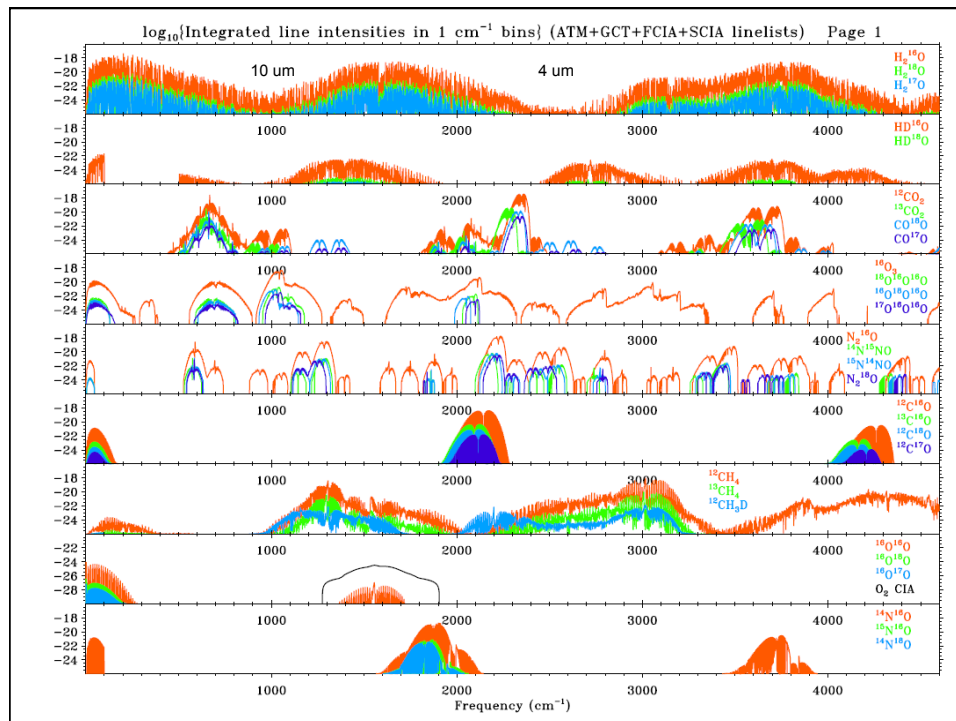
Because water is a bent, it possesses a permanent dipole moment (and is thus active in rotation). As with CO₂, there are three normal modes, but unlike CO₂, all are infrared active. The 1595 cm⁻¹ (6 μm) band of H₂O is particularly important in radiative forcing. In addition, overtones of the OH stretching frequency (e.g. 2 ν_1 (1.8 μm), 3 ν_1 (1.5 μm), etc.) are quite strong and absorb significant amounts of solar radiation.



O₃, N₂O, and CH₄

Ozone, O₃, is bent molecule and possesses a permanent dipole moment (like H₂O). Ozone is an important greenhouse gas due to its strong absorption at 9.6 μm (ν_3). Because ozone is present in the (relatively) warm upper stratosphere, strong emission from ozone can be observed at the surface.

N₂O (nitrous oxide) and CH₄ (permanent dipole?) round out the stable of important greenhouse gases on Earth. Both are increasing rapidly and strongly influence atmospheric photochemistry. The oxidation of methane is an important sink of the hydroxyl radical in the lower troposphere. The oxidation of N₂O in the stratosphere is responsible for most of the NO_x gases at these altitudes, which in turn strongly influence the amount of ozone.



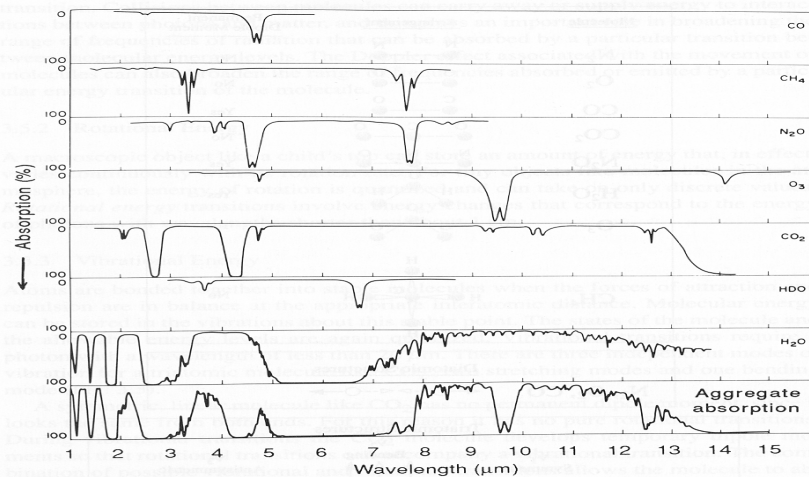
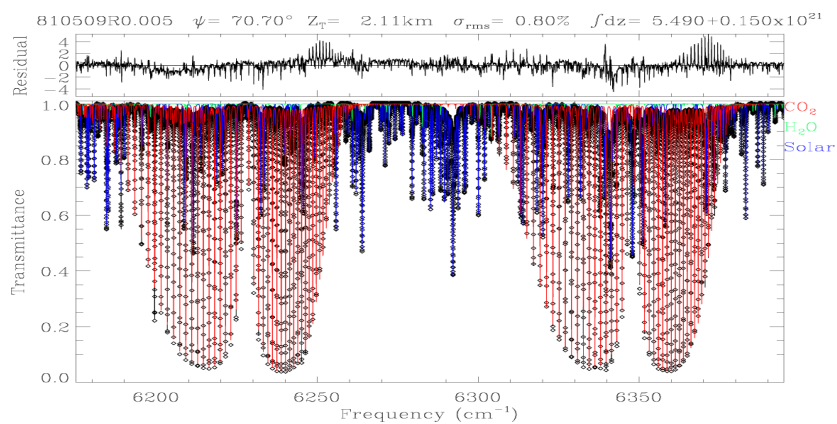


Fig. 3.4 Infrared absorption spectra for various atmospheric gases. [From Valley (1965). Used with permission from McGraw-Hill, Inc.]

Absorption Line Broadening

Figure 3.4 shows the individual and composite absorption for the important greenhouse gases. Figure 3.4 is the transmission spectrum at low spectral resolution, at high resolution, the individual rotational features within each vibrational absorption band can be seen. (CO_2 spectrum). Of critical interest for radiative transfer is the width of the individual absorption features.



Doppler Broadening

For climate science, two types of broadening are important, Doppler and Pressure Broadening. Doppler broadening can be understood by listening to a car passing. The frequency of engine noise you hear (standing still) is shifted from the frequency emitted by the engine by the velocity of the car. As the car is approaching you, the frequency is shifted higher by the speed of the source, after it passes, the frequency is shifted down by the speed:

$$\nu' = \nu (1 - u/\nu)$$

where u is the speed of the source relative to the observer and ν is the speed of sound. Because of relativity, the doppler effect is different for light (it is impossible to distinguish source receding from observer from observer receding from source). The Doppler effect for light is:

$$\nu' = \nu ((1-u/c)/\sqrt{1+u/c})$$

where u is the speed of separation between the source and the observer. Note, however that for small value of u/c (always the case for molecules in our atmosphere and light produced by in the solar system), the binomial theorem can be used to expand this equation and we recover:

$$\nu' = \nu (1 - u/c)$$

The rms speed of molecules depends on their molecular weight and the temperature of the bath:

$$V_{\text{rms}} = \sqrt{3RT/M}.$$

Note that this speed is independent of the pressure and thus Doppler broadening is independent of pressure of the bath gas. For CO_2 , $M=44$ g/mole and thus V_{rms} is about 400 m/s at 0 °C. **Doppler broadening is thus about 1×10^{-6} of the frequency of the transition.** Because the distribution of molecular speeds is maxwellian, the Doppler line shape is gaussian and the width is of order a few parts in 10^{-6} .

$$\phi_D(\nu) \propto \exp(-\delta\nu^2/\Delta\nu_D^2)$$

where $\Delta\nu_D$ is the Doppler width, and $\delta\nu$ is the distance from line center.

Pressure Broadening

A second type of broadening occurs due to the interaction of collisions with the absorbing medium. The broadening, known as pressure or collisional broadening increases linearly with the collision rate (and thus to first order pressure). The line shape is quite different from the Doppler shape (Lorentzian):

$$\phi_L(\nu) \propto (\Delta\nu_L / [\delta\nu^2 + \Delta\nu_L^2])$$

where $\Delta\nu_L$ is the pressure broadened width, and $\delta\nu$ is the distance from line center.

The Lorentzian line shape is much broader producing significant absorption far from line center.

Note that the strength of a given transition is intrinsic to the molecule and so the integrated intensity is conserved.

