

Carbon Dioxide

No other atmospheric constituent is better known to the general public as a “greenhouse gas” than carbon dioxide (CO_2). In actuality, water vapor has a larger overall impact on the radiative energy budget of the atmosphere. But CO_2 is of particular concern from a public policy point of view owing to its steadily increasing abundance in the atmosphere due to fossil fuel use (see Fig. 7.5).

CO_2 possesses two very strong rotation-vibration bands in the IR band, one centered on $4.3 \mu\text{m}$ (ν_3 fundamental), the other at $15 \mu\text{m}$ (ν_2 fundamental). The $4.3 \mu\text{m}$ band is actually the stronger of the two, but because it's located out on the edge of both the solar and longwave bands, it isn't terribly important for broadband radiative fluxes in either band.

The $15 \mu\text{m}$ band is very important for longwave radiative transfer in the atmosphere, because it is positioned near the peak of the Planck emission function for terrestrial temperatures and renders the atmosphere completely opaque between 14 and $16 \mu\text{m}$ (Fig. 9.12). Moreover, the atmosphere is at least partly absorbing for several micrometers more to either side of the above wavelengths.

Problem 9.6: The effect of the CO_2 $15 \mu\text{m}$ band on atmospheric transmission to space of surface emission can be crudely approximated by assuming total opacity between 13.5 and $17 \mu\text{m}$, and total transparency outside these limits. Use Fig. 6.4 to estimate the fraction of surface longwave emission that is reabsorbed by the CO_2 in the atmosphere (ignoring other absorbers). Assume a surface temperature of 288 K .

Examining the center of the $15 \mu\text{m}$ band closely (Fig. 9.13), we find that it looks much like the idealized vibration-rotation band associated with a diatomic molecule — that is, it exhibits a strong central Q branch associated with pure vibration transitions ($\Delta v = 1$; $\Delta J = 0$), as well as the usual P branch ($\Delta v = 1$; $\Delta J = -1$) and R branch ($\Delta v = 1$; $\Delta J = +1$). Unlike the random-appearing H_2O rotation spectrum, the P and R branches for CO_2 consist of very regularly spaced lines, again as predicted for a diatomic molecule (Fig. 9.3).

Why does CO₂, which is triatomic, yield a spectrum so unlike that of another triatomic molecule, H₂O? The reason is that CO₂ is a linear molecule with effectively only one rotation mode (similar to a diatomic molecule), as compared with three for H₂O, which is an asymmetric top. This seemingly minor difference eliminates the whole universe of lines that would arise from transitions involving J_2 or J_3 .

As noted also for water vapor, isotopic variations of the constituent atoms multiply the total number of lines found in the CO₂ absorption spectrum. Here we have not only the two most common oxygen isotopes ¹⁶O and ¹⁸O, but also two major carbon isotopes ¹²C and ¹³C, the latter comprising about 1% of total carbon in the atmosphere.

We conclude our discussion of CO₂ by noting that the central lines of the 15 μm band are really quite strong. Despite the diluteness of CO₂ in air (about 370 parts per million by volume), the strongest part of the central Q branch (Fig. 9.13b) absorbs all but 5% of radiation over just a 1-meter path in air at 1000 mb pressure! Also, we see that, at reduced pressure (Fig. 9.13c), the Q branch resolves into a series of very closely spaced but separate lines. Each of these is associated with a ($\Delta v = 1$; $\Delta J = 0$) transition, but depending on the rate of rotation of the molecule (i.e., value of J), there are slight differences in the energy associated with a pure $\Delta v = 1$ transition.

Ozone

Ozone (O₃), which (except in urban pollution) is confined primarily to the stratosphere, is another nonlinear triatomic molecule, like water vapor. Therefore, it possesses many of the same general absorption features as water vapor, such as a relatively strong rotation spectrum consisting of numerous quasi-randomly spaced lines, as well as three fundamental vibrational bands ν_1 , ν_2 , and ν_3 . These bands, respectively, are found at 9.066, 14.27, and 9.597 μm. In the atmosphere, the 14.3 μm band is essentially masked by CO₂'s 15 μm band — that is, the presence or absence of ozone doesn't change much in this band, because absorption by CO₂ is already overwhelmingly strong.

The moderately strong ν_1 and very strong ν_3 bands are close

enough to each other that they are commonly viewed as a single entity known as the $9.6 \mu\text{m}$ band of ozone. Note that this band sits squarely in the middle of the $8\text{--}12 \mu\text{m}$ “window” of H_2O as well as falling not far from the peak of the Planck function for terrestrial emission. For both reasons, ozone is an important player in the atmospheric radiation budget, especially in the stratosphere.

Ozone also has a strong band at $4.7 \mu\text{m}$, but this is at the edge of the Planck functions for both solar and terrestrial emission (as was also the case for the CO_2 $4.3 \mu\text{m}$ band) and therefore is of very limited relevance for broadband radiative fluxes. Additional vibration-rotation absorption bands can be found in the near-IR regions of the spectrum down to about $2.5 \mu\text{m}$ (see Fig. 9.10c), but these are weak and therefore of only minor importance.

Also, as is well-known to the many specialists and laypeople alike concerned about recent observed declines in stratospheric ozone concentrations, ozone exhibits very strong absorption in the UV band below $0.28 \mu\text{m}$ due to electronic rather than vibrational excitations. As was discussed in Section 3.4.1, this absorption is exceedingly important for life on earth, because of the biologically damaging effects of UV-B radiation. A near-steady-state balance between absorption of solar UV-B and re-emission of longwave IR in the $9.6 \mu\text{m}$ band is largely responsible for the temperature structure of the stratosphere and lower mesosphere.

Methane

Methane (CH_4) is a spherical top molecule with five atoms and therefore $3(5) - 6 = 9$ fundamental modes of vibration. However, because of the symmetry of the molecule (four hydrogen atoms all bound to one central carbon atom), five of the modes are equivalent, leaving only four distinct modes v_1 , v_2 , v_3 , and v_4 . The most important of these are the v_3 and v_4 fundamentals at approximately $3.3 \mu\text{m}$ and $7.6 \mu\text{m}$, respectively. In addition, there are a few weak overtone ($\Delta v_i > 1$) and combination bands scattered through the near-IR.

Although methane is present in the atmosphere in relatively low concentrations, its $7.6 \mu\text{m}$ absorption band is strong enough, and is placed in an otherwise relatively transparent part of the atmo-