CHAPTER 9

Absorption by Atmospheric Gases†

In the previous chapter, we developed the mathematical tools for describing monochromatic radiative transfer, including both absorption and thermal emission, in a nonscattering atmosphere. Specifically, given the absorption profile $\beta_a(z)$ and temperature profile $T(z)$ in a plane parallel atmosphere, we can use (8.27) through (8.30) to compute the atmospheric contribution to the radiant intensity, as seen from the surface looking up or from a satellite looking down. With only slight modifications, they may be used to compute monochromatic intensities at *any* level z between the surface and the top of the atmosphere.

In these equations, it is the absorption coefficient β_a that directly links absorption and emission at any specific wavelength to the material composition of the atmosphere. In Section 7.4.1, we saw that a relatively small number of constituents, such as water vapor, carbon dioxide, and a few other trace gases, are responsible for almost all of the important features in the observed absorption/emission spectrum of the atmosphere. However, we have not yet examined *why* certain gases strongly absorb radiation at certain wavelengths nor *how* their absorption properties are influenced by temperature and pressure.

Is it really necessary, you ask, for the nonspecialist to know

the whys and hows of atmospheric absorption? Even without that insight, does anything prevent you from computing broadband fluxes (for example), simply by integrating monochromatic intensities over both solid angle and wavelength? No, of course not. All you need is a reasonably accurate specification of $\beta_a(\lambda, p, T, \ldots)$ for each relevant constituent. Such models are already available "off the shelf."

But while it is technically possible to learn to fly and land an airplane by rote without ever actually mastering the physical principles of flight, most of us would prefer to entrust our lives to a pilot with a deeper understanding of his/her job. When it comes to atmospheric radiation, the consequences of ignorance are less grave, but the argument is basically the same: the more you know, the less likely you are to do something embarrassing, even when working with someone else's well-tested models.

Note, by the way, that even though I conceded the possibility of blindly applying the equations cited above to the problem of computing broadband fluxes (as required for general circulation models, weather forecast models and the like), this "brute force" approach is rarely attractive for routine calculations. Quite often, we need to obtain fluxes of modest accuracy *with the least possible expenditure of computational effort.* That requires us to take advantage of highly simplified *parameterizations* of radiative absorption and emission. If you're going to stake your reputation on the results of such methods (as many atmospheric scientists do without even realizing it!), it's certainly in your interest to know where they come from and how far they can be trusted.

Atmospheric remote sensing methods typically rely on calculations of quasi-monochromatic radiant intensity. This is admittedly a far simpler computational problem than that of broadband fluxes. Nevertheless, it is the detailed absorption behavior of various atmospheric molecules that largely determine optimal channel wavelengths, spectral widths, and other instrument characteristics. Those who work with remote sensing data and/or instrumentation, as many of us can expect to do at some point in our careers, should have at least a basic understanding of these issues.

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9.1 Basis for Molecular Absorption/Emission

In Chapter 2, I pointed out that EM radiation has both wavelike and particle-like properties. Recall that there are times when radiation must be viewed as waves, times when it must be viewed as a shower of quantized particles having energy $E = h\nu$, and, finally, times when it doesn't matter which view you take.

The absorption of radiation by gases turns out to be one of those cases in which the quantized (particle) nature of radiation comes to the forefront. Simply stated, interactions between radiation and individual gas molecules — whether absorption or emission — are possible only for photons having energies satisfying certain criteria. Those criteria are largely determined by the arcane, and sometimes counterintuitive, laws of quantum mechanics. But don't despair: the *consequences* of those laws aren't difficult to grasp at the level targeted by this book.

When a photon is absorbed by a system, the energy originally carried by that photon must contribute to a corresponding increase in the internal energy of the system. Likewise, when a photon is emitted, the system must give up an equivalent amount of its internal energy. There are many different ways in which internal energy may increase or decrease. Examples include:

- Changes in the translational kinetic energy of molecules (i.e., temperature).
- Changes in the rotational kinetic energy of polyatomic molecules.
- Changes in the vibrational energy of polyatomic molecules.
- Changes in the distribution of electric charge within a molecule, possibly including the complete separation (or reunification) of two components previously bound by electrostatic forces.

Collisions between molecules tend to equalize the distribution of the total internal energy in a gas among the various "storage" mechanisms listed above. Imagine, for example, that you were able to put a diatomic gas like oxygen into a unusual state in which