Atoms and Molecules

By Howard “Cork” Hayden, The Energy Advocate, January 2025

To understand both the bites taken out of the IR spectrum by atmospheric gases and the radiative forcing due to changes in concentrations of those gases, it is necessary to understand a little bit about spectra. Figure 3 shows the spectra of visible light for hydrogen and helium atoms in the usual way: vertical lines as they are seen in a spectroscope. At the left of Figure 3 is a schematic energy level diagram for hydrogen showing the transitions between levels as colored arrows representing the colors of light emitted. The intensity of the lines in the spectroscope manifests itself in the brightness of the lines.

More broadly, spectra such as those in the Guam graph [see What “Climate Science is Not About (Figure 1)] are graphs showing intensity on the vertical axis versus the “color” (wavelength, frequency, or wavenumber) on the horizontal axis.



Figure 3: Left: Energy levels (black lines) and transitions (arrows); Right: spectral lines of hydrogen and helium

During the 1800s, scientists used Bunsen burners—and later, electric arcs—to heat materials and then used spectroscopes to look at the light emitted. They learned that chemicals could be identified by their spectra. In 1885, Johann Balmer found a formula that fit the very simple hydrogen spectrum. In 1913 Niels Bohr found a theoretical way to fit Balmer’s formula and extended it to fit lines in both the infrared and ultraviolet that had yet to be observed. His simple orbital model had been supplanted by a quantum-mechanical formulation, but two insights remain to this day.

Bohr had found that electrons in atoms have certain energy levels that they can occupy—steps upon which they can reside—and that electrons cannot have energies between those steps.

The other insight is that when an electron transits between a higher energy level to a lower one, it emits a photon which carries away the energy that is lost as the electron goes to the lower state. The higher the energy, the shorter the wavelength of the photon. It is common to refer to wavenumbers—the number of wavelengths per centimeter) rather than to wavelengths, because photon energy is proportional to the wavenumber.

Molecules have far more energy states than atoms because their vibrational and rotational modes are also quantized—in discreet steps. Also, the energies and step sizes are much smaller than those of atoms. Whereas hydrogen has only four (or possibly five) visible spectral lines, CO2 has tens of thousands of lines (see Figure 4) in a broad band between 500 and 850 wavenumbers.





Figure 4: The IR absorption spectrum for CO2, expressed as a cross-section, which (for this discussion) is simply related to the probability that the molecule will absorb IR. In the upper graph, the vertical scale is linear and the horizontal scale is the IR wavelength. In the lower high-resolution graph, the vertical scale is logarithmic (covering 8 factors of 10), and the horizontal axis is in wavenumbers (number of wavelengths per centimeter)

All of this can become a little confusing: energy levels expressed in electron-volts (eV); “colors” expressed in nanometers or microns, or in inverse centimeters; temperatures expressed in ºC, ºF, or kelvins (K). What can we make of it all?

What matters for climate and/or the greenhouse effect is that for earthly temperatures, the kinetic energies of atmospheric molecules, the energies associated with vibrational and rotational modes, and the energies of IR photons are all in the same range, so they can all interact.

Molecules in the atmosphere are a tiny fraction of a millimeter apart, and they travel at about the speed of sound (ca. 1,000 feet per second; 330 meters per second). Not surprisingly, they undergo collisions extremely frequently. While climate alarmists like to focus attention on CO2, it is unwise to forget the other 99.96% of the atmosphere.

Now, picture a CO2 molecule colliding with (say) a nitrogen (N2) molecule. The collision can impart energy to the CO2 molecule such that it becomes excited to a state that can radiate IR. Maybe the CO2 emits an IR photon, or maybe another collision removes that energy. With the enormous number of collisions that are occurring, there are always a small percentage of CO2 molecules in excited states. The percentage is temperature-dependent, increasing with higher temperature. At any temperature, all the way from the surface to the stratosphere, there is constant interplay between excitation and de-excitation, including IR absorption and IR emission.

Start with the blackbody spectrum emitted by the surface, consider all the molecular dynamics involving energy exchange by collisions and IR emission and absorption, and you can account for the loss of IR and the jagged spectrum of IR that goes to space.

We mentioned the one and only reference in IPCC’s *Assessment Reports* to IR spectra, saying that it was laughably incorrect. That graph, shown below, was published in 1990 in the *First Assessment Report*, fully 20 years after the Guam data were published. Notice that the intensity goes to zero at about 650 wavenumbers, whereas the Guam spectrum of actual data does not.





[Observed Infrared Radiation near Guam (1970) on top; IPCC version (1990) below it.]

What was IPCC’s error? They thought of IR absorption as a one-and-done process. That huge peak in the spectrum should be adequate to block all IR of that wavelength from going to space. No account was taken of collisional excitation and the presence at all altitudes of molecules in excited states that can radiate. Look again at the Guam data and you’ll see just the opposite of total absorption. In that bite of IR absorption, there is a sharp peak right where the absorption has its peak near 650 wavenumbers. On a wavelength-by-wavelength basis, a good absorber is a good radiator. That peak in the Guam spectrum shows that many molecules at high altitude are in excited states that can—and do—radiate. The point was entirely missed by IPCC in its *First Assessment Report*, the only spectrum they ever published.

Now we return to the absence [see Radiative Forcing (Fig. 2)] of any reference to the most important GHG: H2O. Much is said about increasing CO2 (much reference to doubling) and the radiative forcing therefrom. How do we assess increases in H2O, and what is the forcing? Figure 5 shows the radiative forcing from CO2 and H2O plotted against the fraction *f* of atmospheric concentration compared to reference concentration, adapted from van Wijngaarden and Happer [1]. Note that H2O, which is responsible for about 75% of the greenhouse effect, would have a radiative forcing of 7.9 W/m2 if its quantity were doubled.

We understand variations in CO2 because we have graphs showing concentration from 200 ppmv to 7,000 ppmv, and we are putting CO2 into the air by burning fossil fuels. But what variations do we expect for atmospheric H2O? We know that hot jungles are very humid, and that frigid air is pretty dry, so it is reasonable to ask how much the H2O concentration would increase if the temperature went up by 1ºC.

 

Figure 5: Radiative forcing for CO2 and H2O versus the ratio f of atmospheric concentration to present concentration. (0.5 = half; 2 = doubling) adapted from [1].

Fortunately, NASA has an answer for us [2]:

For every degree Celsius that Earth’s atmospheric temperature rises, the amount of water vapor in the atmosphere can increase by about 7%, according to the laws of thermodynamics.

A 7-percent increase is quite a bit short of a doubling. To get the corresponding forcing, we would find where the blue H2O line crosses 1.07. The H2O forcing closely follows 11.4\*ln(C/C0), so the forcing would be 0.77 W/m2.

NASA has a dramatic picture [2] to emphasize the positive feedback presumption: Step 1: CO2 increase causes warming. Step 2: That warming causes increased water vapor. Step 3: Increased water vapor causes greenhouse warming. Step 4: That warming causes increased water vapor. Step 5: That increased water vapor causes greenhouse warming. On and on it goes.



Let us have a look at that H2O feedback cycle. We will discuss the CO2 contribution and some subtleties later, but for now we’ll simply assume (for simplicity) a 1ºC rise in worldwide temperature. And, according to NASA, this would cause a 7% increase in H2O concentration. Figure 5 tells us that the radiative forcing would be 0.77 W/m2. The surface would then warm up until the additional IR from the surface matched the radiative forcing, specifically by 0.14ºC. That is, the water feedback adds 0.14ºC (14%) to the original 1ºC rise.

Ah, but that 0.14ºC rise causes more evaporation, the result of which is an additional rise of 14% of 0.14ºC, and there will be an additional 14% of that tiny rise, namely 14% of 14% of 0.14ºC. So, the temperature rise after many iterations and increases in atmospheric H2O content is

1°C\*(1+0.14+0.142+0.143+…) = 1.163°C

A similar calculation will be used later when we consider the fact that presently only 60% of the IR that is emitted from the surface goes into space.

Water molecules are responsible for about 75% of the entire greenhouse effect, but this calculation shows that the additional effect of H2O on small changes in temperature is nothing to get excited about.

[1] W. A. van Wijngaarden and W. Happer, “Dependence of Earth's Thermal Radiation on Five Most Abundant Greenhouse Gases,” arXiv:2006.03098v1 4 June 2020

[2] <https://science.nasa.gov/earth/climate-change/steamyrelationships-how-atmospheric-water-vapor-amplifies-earthsgreenhouse-effect/> [link now (Feb 8) states: “The cosmic object you were looking for has disappeared beyond the event horizon.”]