

The Thermodynamics of Climate Change

Peter L. Ward, US Geological Survey, retired, Teton Tectonics, Jackson, WY

When you stand in sunlight, you feel hot, but when you stand outside at night, you feel cool, even on a warm night. Why? Because Sun emits ultraviolet radiation that is hot enough to burn your skin, while Earth emits infrared radiation that is, on average, 21°C cooler than your body. Computer models based on greenhouse-gas theory have this backward. They calculate that Earth is heated more by its own infrared radiation than by Sun's ultraviolet radiation. Your personal experience strongly suggests that these models are wrong. In this paper we show that thermal energy consists of the frequencies and amplitudes of oscillation of all the degrees of freedom of all the bonds that hold matter together. These frequencies and amplitudes of oscillation on the surface of matter transmit thermal energy through air and space as electromagnetic radiation. Climate models assume that electromagnetic radiation (EMR) travels as waves through space, but that assumption is unwarranted because the physical properties of EMR and mechanical waves in matter are very different. Observations of climate change can be explained quite clearly by ozone depletion. Ozone absorbs ultraviolet radiation from Sun, warming the ozone layer 20 to 30 km above Earth's surface. When there is less ozone, more of this hot ultraviolet radiation is observed to reach Earth's surface, warming Earth instead of the ozone layer.

1. Introduction

Earth's atmosphere and surface are warmed primarily by the flow of ultraviolet, visible, and infrared radiant thermal energy from Sun through the atmosphere to Earth's surface and are cooled primarily by the flow of infrared thermal energy from Earth's surface and atmosphere back into space. The purpose of this paper is to evaluate the thermodynamics of these two energy flows in order to determine the relative potential of changes in either to cause changes in climate. Climate change occurs when these two flows are not equal and opposite. The greenhouse-gas theory of climate change posits that infrared energy radiated from Earth and absorbed by greenhouse gases in the atmosphere slows the cooling of Earth and, according to currently accepted climate science, actively heats Earth with downwelling re-radiation. The ozone depletion theory of climate change, on the other hand, posits that when the ozone layer is depleted, it absorbs less of the very hot ultraviolet-B energy from Sun that would normally warm the lower stratosphere. This allows more ultraviolet-B radiation to reach Earth's surface than usual, warming the troposphere and Earth instead of warming the lower stratosphere.

There is some confusion in climate science over precisely how thermal radiation warms Earth. In order to understand the flow of energy, we need first to define clearly the difference between macroscopic temperature and microscopic thermal energy. Then we will need to understand how microscopic thermal energy flows through matter, how it is transmitted through air and space, and what happens when it is absorbed by gases, liquids, or solids.

2. Temperature is a macroscopic property

Temperature is a macroscopic, intensive, physical property of gases, liquids, and solids, something we can sense and measure, and something to which all living creatures must adapt in order to survive. Thermodynamics is the study of thermal energy in motion, i.e. the flow of heat (Knight, 2012). “From the zeroth law of thermodynamics, one can define temperature as that which is equal [i.e., uniform or homogeneous] when heat ceases to flow between systems in thermal contact” (Grossman, 2014, p. 49). Differences in temperature provide the thermodynamic force driving the flow of heat. The second law of thermodynamics and our personal experience tell us that thermal energy flows spontaneously in matter, air, or space only from higher temperature to lower temperature, i.e., from a heat source to a heat sink.

“By measuring temperature, we’re measuring how fast the atoms in the material are moving. The higher the average velocity of the atoms, the higher the temperature of the material” (Grossman, 2014, p. 52-53). Gas molecules are free to move in any direction until they collide with other molecules or with the walls of a container. According to the kinetic theory of gases, the absolute temperature of an ideal gas is directly proportional to the average kinetic energy of all the molecules making up the gas. Kinetic energy is defined as one half the mass of a molecule times its velocity squared ($E_k = \frac{1}{2}mv^2$). The average velocity for oxygen gas molecules at room temperature (296 K) is around 1600 km/hr (Halliday et al., 2013, p. 519), 1.7 times the cruise speed of a Boeing 747 jetliner. The velocity of atoms in matter is more complicated and requires more explanation.

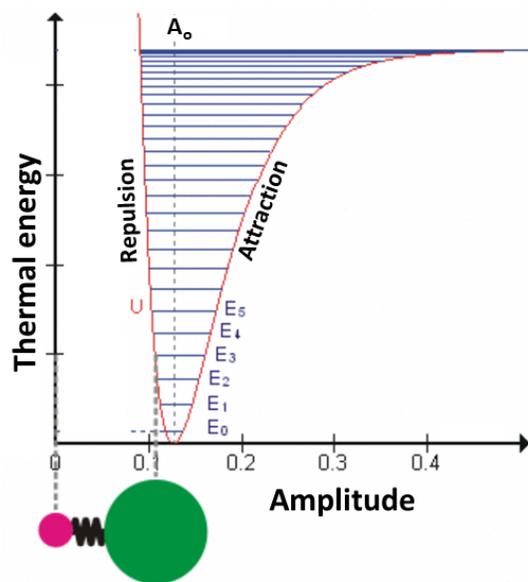


Figure 1. Each degree of freedom of each bond holding matter together oscillates around an amplitude A_0 , which is at a potential-energy minimum between electrostatic forces that attract atoms when they are close and other electrostatic forces that repel atoms when they are too close. When the temperature of matter is increased, i.e. the thermal energy is increased, both the amplitude and the energy of these oscillations increase. These oscillations can be thought of as similar to a mass (green circle) oscillating on a spring (black), shown schematically, except that the amplitudes are very small, there is no friction, and the amplitudes are not symmetric about A_0 , which means the bonds expand in length with increasing temperature, increasing the volume.

3. Microscopic thermal energy

The microscopic atomic and molecular bonds that hold matter together are not rigid. Each bond oscillates in a number of characteristic ways, called degrees of freedom, in each of which the bond oscillates around a potential-energy minimum between electrostatic forces that attract atoms when they are close and other electrostatic forces that repel atoms when they are too close (Fig. 1). The atomic dimensions of these oscillators are very small, so their natural frequencies of oscillation are very high, around 30.6 terahertz (30.6×10^{12} cycles per second) at room temperature (Table 1).

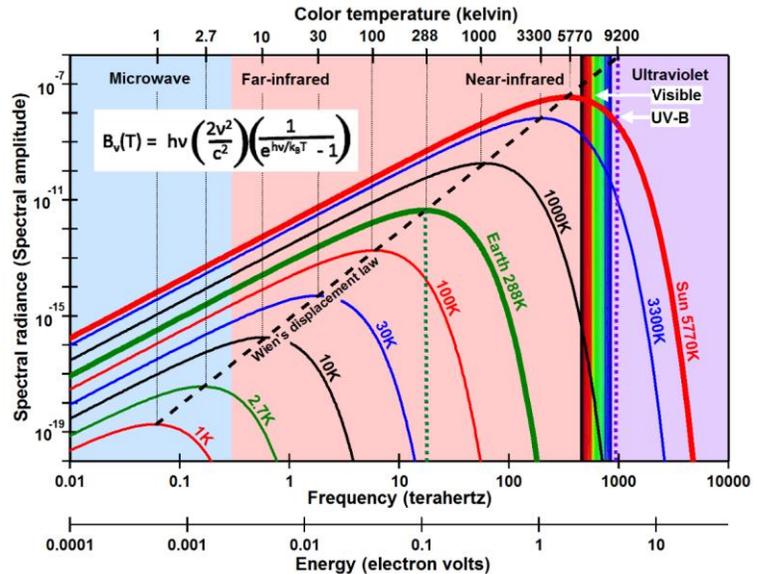
Radiation Band	Minimum Wavelength Nanometers	Maximum Frequency Terahertz	Maximum Energy Electronvolts	Color Temperature Kelvin	Effects
Gamma rays	0.001	3×10^8	1.24×10^6	2.9×10^9	Lethal even in small amounts
Extreme ultraviolet	10	30,000	124	290,000	Ionizes N ₂ , O ₂ , etc. Forms and heats ionosphere
Ultraviolet-C	100	2,998	12.4	29,000	Dissociates O ₂ , SO ₂ , etc. Heats stratosphere
Ultraviolet-B	280	1,071	4.43	10,300	Dissociates O ₃ , sunburn, vitamin D, skin cancer
Ultraviolet-A	315	952	3.94	9,200	Skin cancer, fading of materials
Visible light	380	789	3.26	7,630	Photosynthesis, dissociates NO ₂ , NO ₃ , HONO
Near infrared	750	400	1.65	3,860	Begin absorption by water vapor
Short wavelength infrared	1,400	214	0.886	2,070	Absorption by water vapor
Mid-wavelength infrared	3,000	99.9	0.413	966	Main absorption by greenhouse gases
Long-wavelength infrared	8,000	37.5	0.155	362	Main absorption by greenhouse gases
	9,804	30.6	0.127	296	Room temperature, 23 °C, 73 °F
Far-infrared	15,000	20	0.0827	193	
Microwave	100,000	3	0.0124	29	
Longwave AM radio	1.08×10^9	2.79×10^{-7}	1.15×10^{-6}	2.7×10^{-3}	

Table 1. Higher frequency radiation contains more energy than, and is much hotter than, lower frequency radiation. Values shown, except for room temperature, are for the top of the radiation band so that, for example, frequencies for extreme ultraviolet radiation range from 30,000 to 2,998 THz, etc. The red highlighting shows frequencies, energies, and temperatures involved when ozone is depleted; the green highlighting shows frequencies, energies, and temperatures involved when greenhouse gases absorb terrestrial infrared radiation.

What is unique about each of these simple, asymmetric, harmonic atomic oscillators, but is contrary to our everyday experience, is that there is no friction, and therefore no damping, since only electrostatic forces are involved. Thus, an individual atomic oscillator can only gain or lose amplitude of oscillation through resonance with surrounding oscillators. In solid matter, this resonance is aided by the interconnections of all the bonds that hold matter together. The effect of resonance is to equalize the amplitudes of oscillation among all nearby oscillators with the same frequency of oscillation so that the amplitude of oscillation can be thought of as flowing from higher amplitude to lower amplitude at each frequency. Thermal equilibrium is the physical state in which the amplitude of thermal oscillation is no longer flowing because all the amplitudes at each frequency have been equalized.

In solids, where all the atoms are held together by oscillating bonds, the higher the frequency of oscillation, the higher the velocity at which individual atoms must travel to have the same amplitude of oscillation. Since there is no net movement of mass, as there is in the case of the molecules in a gas, mass does not play a primary role in thermal energy in solids, but mass, together with material stiffness, does determine the specific normal frequency of oscillation of each degree of freedom of each bond. From the standpoint of thermal energy at the atomic level, the most important physical properties of each of these tiny oscillators are its frequency and its amplitude of oscillation. Thus, microscopic thermal energy in matter is quantified by the frequencies of oscillation of the bonds that hold matter together and by their amplitudes.

Thermodynamics describes heat in motion. Heat is not a physical thing, but it is the result of physical motion of frequency and amplitude of oscillation. The motion of atomic components produces electrical charge. Electrical charge in motion induces an electric field. The motion of an electric field at a given frequency induces a corresponding magnetic field. The motion of the magnetic field in turn induces an electric field, transmitting electromagnetic radiation.



In order to be able to write an empirical equation that describes observed thermal radiation from a black body at thermal equilibrium, Max Planck (1900) (Fig. 2), found it necessary to postulate that the energy (E) of a single atomic oscillator is simply equal to its frequency (ν , the Greek letter nu) times a constant (h), giving the expression $E=h\nu$. This constant of proportionality, now known as the Planck constant, is simply the energy contained in an oscillation of one cycle per second. Note that the exponent in the denominator of Planck's empirical equation in Fig. 2 is equal to $h\nu/k_b T$, the energy per atomic oscillator ($h\nu$) divided by the energy per degree of absolute temperature ($k_b T$). k_b is the Boltzmann constant, the energy per degree of absolute temperature, commonly thought of as the bridge between macroscopic and microscopic physics.

Figure 2. Planck's law shows that radiation from a warmer body has higher spectral amplitudes of oscillation at all frequencies than does radiation from a cooler body and exhibits its greatest amplitude at a higher frequency, following Wien's displacement law (black dashed line). Each solid line shows the spectral amplitude radiated from a body at thermal equilibrium for the temperature shown. Note that solar ultraviolet-B (UV-B) radiation (purple dotted line) has much higher energy and much hotter temperature on these log scales than infrared radiation from Earth (green dotted line). 3300K is the temperature of the filament of a typical incandescent light bulb. 2.7K is the approximate temperature of the cosmic microwave background (Fixsen, 2009).

This basic equation ($E=h\nu$), now known as the Planck-Einstein relation, is integral to quantum mechanics. Energy (E) is commonly thought of as the energy of a photon, a hypothetical, massless particle that theoretically accounts for the quantized nature of electromagnetic radiation. Note, however, that frequency of electromagnetic radiation, and therefore microscopic energy ($E=h\nu$), are *continuous* functions over much more than 12 orders of magnitude of frequency (Table 1). In the case of gases, frequency and energy are quantized only when a molecule of gas absorbs frequencies from an electromagnetic field that are the resonant normal modes of oscillation of the molecule, thereby forming spectral lines of absorption. It is the physical structure of the molecule that determines the quantization. From such absorption spectra, physicists can identify the atoms that make up molecules anywhere from close at hand to the far reaches of distant galaxies (Rothman et al., 2013). In the case of solid matter, on the other hand, conduction

smooths the amplitudes and frequencies out to approach the distribution approximated by Planck's equation in Fig. 2, now called Planck's law.

This spectrum of increasing energy with increasing frequency makes observational sense when we look at the chemical effects as a function of frequency (Table 1). It is well known that very high frequency gamma rays (nuclear radiation) have enough energy to be lethal if absorbed in small quantities. Lower frequency X-rays have enough energy to destroy cancer cells when focused at high dosages, but must be used at very low dosages to prevent damage when imaging the interiors of human bodies. It is common knowledge that lower frequency solar ultraviolet radiation has enough energy to burn human skin, that still lower frequency visible light has enough energy to power photosynthesis, and that much lower frequency infrared radiation does not have enough thermal (chemical) energy to do either, but that it can provide comforting warmth on cold days. Note that dosage is proportional to energy times the length of time of the exposure, the result of dynamic processes.

Clearly, then, the effectiveness of electromagnetic radiation in bringing about certain changes in matter is governed by a threshold effect. Radiation having a frequency that is higher than the threshold will produce the effect, whereas radiation having a lower frequency will not. A good example of this is the photoelectric effect, which occurs only when incident light has a certain minimum frequency. The photoelectric effect is not dependent, however, on the amplitude (intensity) of the light (Lenard, 1902; Einstein, 1905a). In photochemistry, $E=h\nu$ is widely used to signify the minimum radiant energy (frequency) required at the microscopic level to cause a chemical reaction such as the dissociation of oxygen. Typically, such thresholds are expressed as a function of wavelength (λ), the velocity divided by the frequency:



This can, of course, also be written in terms of frequency (ν):



In summary, radiant energy is clearly observed to be solely a function of frequency as stated in the Planck-Einstein relation, and not a function of amount, amplitude, or bandwidth. Some minimum frequency determines whether there is enough thermal energy for a chemical reaction to take place. The amount, brightness, intensity, or amplitude of incident radiation do, however, determine the rate at which these microscopic reactions can take place by determining how much amplitude of oscillation is transferred by resonance. We are not burned by starlight, for example, because its amplitude is so low.

It is the "thermal motions of the molecules, their bonds, vibrations, rotations, and excitations" (Grossman, 2014, p. 74) that store microscopic thermal energy within matter. Indeed, the heat capacity of a material is observed to increase with increasing number of degrees of freedom of oscillations within the material (Grossman, 2014). In thermodynamics, thermal energy stored in the bonds that hold matter together is referred to as internal energy. A body of matter has a macroscopic potential energy (the potential to move), a macroscopic kinetic energy (actual net movement), and a microscopic internal thermal energy (due to internal oscillations at the molecular level) that gives rise to macroscopic temperature.

4. Spectral radiance

The relationship between microscopic thermal energy and macroscopic temperature is plotted in Fig. 2, showing spectral radiance, or the radiant flux, as a function of frequency emitted by a black body at thermal equilibrium, whose surface is at some specific absolute temperature. These curves, each representing a discrete macroscopic temperature, are based on detailed laboratory measurements made by many physicists in the late 19th century, with infrared radiation finally measured most reliably by Lummer and Pringsheim (1899). By the next year, Planck (1900) was able to find, by trial and error, the mathematical expression shown in Fig. 2 that reproduces these observed curves (Kuhn, 1987; Gearhart, 2008). This mathematical equation became known as Planck's law, and it is still used today as the basis for all observations and calculations of radiant flux in climate science. These curves show that the relationship between macroscopic temperature and frequencies of microscopic oscillations is fairly complicated.

We observe in Fig. 2 that, for a given temperature, a black body, which is defined as a perfect emitter and absorber of radiation, emits a very broad range of frequencies. We also observe that the curves do not intersect. When the temperature of the body is raised, the spectral radiance at each and every frequency is raised and the frequency that has the greatest spectral radiance is also raised. At the microscopic level, the oscillations throughout a body of mass share amplitudes and frequencies of oscillation via conduction, approaching the spectral distribution shown by these curves as the body approaches thermal equilibrium at any given temperature. It is the process of conduction, which is basically resonance in a mechanically interconnected environment that integrates the microscopic oscillations over the whole body to form the macroscopic distribution of spectral radiance observed to change as a function of macroscopic temperature.

According to Planck's empirical formula, spectral radiance is defined on the y-axis as the number of watts (joules of energy per second) at each frequency that passes through a square meter of surface area perpendicular to the direction from the emitter per unit solid angle. This exercise in empirical curve fitting, however, introduces a serious problem, of which Planck himself appears to have been unaware. As formulated, the formula assumes, in contradiction of the Planck-Einstein relation $E=h\nu$, that energy is the same at every frequency, that the amount of energy at a given frequency is a function of its amplitude, and that the total amount of energy is equal to the area under the curve. In reality, however, the empirically fitted curve does not physically describe the actual energy distribution in the spectrum. Energy does not remain constant across the spectral bandwidth; it increases to the right with increasing frequency, as the Planck-Einstein relation states. The spectrum, in other words, is actually a histogram of energy with values increasing to the right with higher frequency. Therefore, an area beneath the curve measured on the right side of the distribution will contain a much greater energy than the same area on the left side of the distribution. Unfortunately, all climate models assume areal homogeneity under the curve, as a result of which energy calculations in the infrared portion of the spectrum have been greatly overvalued while those in the ultraviolet portion have been greatly undervalued. It is unsurprising, therefore, that climate scientists have had such difficulty in balancing Earth's energy budget.

These curves of Planck's law were measured, and are still measured today, by determining how much the temperature of a small body of matter, typically contained in a thermocouple, thermopile, or resistor, is raised when illuminated by a narrow bandwidth of radiation. Thus we are measuring the *thermal effect* of radiation, not an actual physical property of radiation. Electromagnetic radiation, or more narrowly, the visible light for which we have an intuitive feel, has two observable physical properties: color (frequency of oscillation) and brightness (amplitude of oscillation). Fig. 2 should be plotted showing microscopic amplitude of oscillation (brightness or amplitude) on the y-axis as a function of the microscopic frequency of oscillation (energy) on the x-axis. Temperature in the macroscopic world is then related to these microscopic oscillations via the Planck curves, which were plotted on the basis of the conduction of thermal energy within matter leading to thermal equilibrium. Measuring microscopic amplitude of oscillation would have been very difficult in 1900, and it is still much more difficult than measuring thermal effect. But to clearly understand the physics of microscopic energy and macroscopic temperature, these measurements need to be made. In anticipation of this important step being taken, I will refer to the Planck's law curves as if they plotted microscopic amplitude as a function of microscopic frequency, fully recognizing that the precise shape of the curves may vary to some extent when measured according to the aforementioned criterion.

The Planck curves in Fig. 2 result from the facts that each degree of freedom of each bond holding matter together has a specific frequency of oscillation and a normal maximum amplitude of oscillation at a given temperature. In other words, if you specify the temperature, these curves predict the normal amplitudes of oscillations at each frequency for oscillators in matter whose energies are given by the Planck-Einstein relation. The smooth, continuous appearance of the curves is due to equilibration by conductive transfer of both frequencies and amplitudes within matter. In constructing a laser, we add energy to pump up the amplitude of oscillation, which makes laser light brighter than normal light at the same frequency. Referring to Fig. 1, increased amplitude of oscillation will ultimately cause atoms to separate, resulting in melting of the material. Therefore a red laser, for example, can be more physically destructive of matter than ordinary red light.

5. Electromagnetic waves?

The foregoing discussion of electromagnetic radiation is all in terms of frequency and amplitude. There is no mention of wavelength, and it is not clear physically how wavelength could be involved in the processes described. Yet light, when interacting with matter, displays wave-like properties such as reflection, refraction, dispersion, diffraction, birefringence, and interference. Also, we are accustomed to calculating wavelength by dividing velocity by frequency. We tend to think about electromagnetic waves based on our experience with mechanical waves in matter, such as compressional sound waves, water waves, and seismic waves, as well as seismic shear waves and surface waves. Mechanical waves, however, have very different physical properties from electromagnetic radiation.

A mechanical wave, whether transverse (shear) or longitudinal (compression), is a physical disturbance of matter that propagates through a solid, liquid, or gas, in which each molecule is displaced by the wave's kinetic energy and is then normally restored to its original position by

the bonds or pressure holding the matter together. The energy of the wave is the kinetic energy required to deform the matter, allowing the wave to propagate, and it is typically proportional to the square of the amount of displacement (wave amplitude). The wave does work against the bonds or pressure holding the matter together, and it is therefore attenuated with distance. The stiffer the material, the more work is necessary, and the faster the attenuation. High frequencies are typically attenuated more rapidly than low frequencies. We feel and/or observe with our eyes and instruments seismic and water waves as they deform matter with frequencies most commonly in the range of 0.005 to 100 cycles per second, and we hear sound waves with frequencies primarily in the range of 20 to 20,000 cycles per second. Transverse waves can only propagate through solid matter, whereas longitudinal waves can propagate through all media. Neither can propagate in space. The motion of each molecule in matter is connected by its bonds or by pressure to the motion of all surrounding molecules so that waves from different sources are observed to interact and interfere. A specific waveform at a specific location can be approximated by a Fourier series, the sum of a large, if not infinite, series of terms consisting of an amplitude times the sine and/or cosine of different wavelengths or frequencies. It is the bonds or pressure holding solid matter together that provide the physical basis for the plus signs, or “addability,” in the Fourier series. Everything involved with mechanical waves is interconnected.

We observe that the physical properties of electromagnetic radiation (EMR; e.g., light) are distinctly different from the physical properties of mechanical waves. Light radiated by a black body at thermal equilibrium contains a broad spectrum of frequencies (colors) with different amplitudes (brightnesses) at each frequency described by Planck’s law (Fig. 2). The frequencies and amplitudes of light originate from the frequencies and amplitudes of the atomic oscillators on the surface of the radiating body. In air and space, these frequencies are observed to exist totally independently, maintaining their individual integrities. They do not interact, except in the immediate presence of solid matter. They do not change over distance, even galactic distance, except for Doppler effects and gravitational redshift. EMR in air and space can be thought of as a Fourier series without plus signs. There is some red light, some blue light, some yellow light, etc., that do not interact until the full spectrum interacts with matter, as in a rainbow or prism (Fig. 3). Amplitude (brightness), on the other hand, decreases in

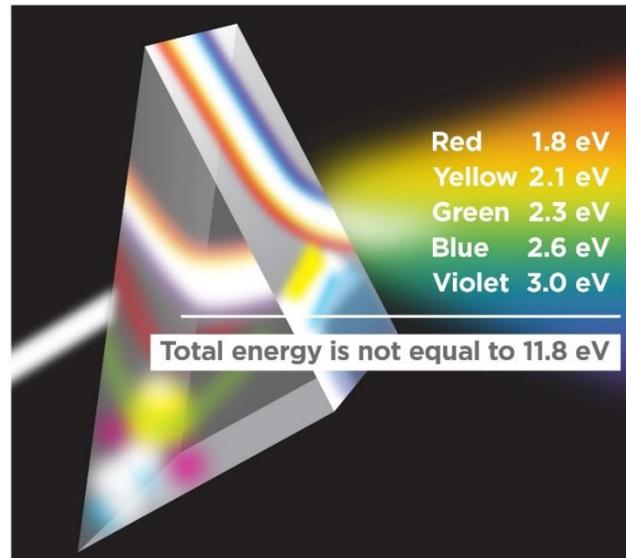


Figure 3. White light entering from the left is spatially separated by a prism into its component colors. The total energy contained in white light is not the sum of the energies of the colors (frequencies) that it contains. White light contains visible energies ranging from 1.65 to 3.26 electronvolts (eV) (Table 1). Summing the component energies yields 11.8 electronvolts, an energy level that is characteristic of ultraviolet-C radiation, which is well outside the actual distribution of energies. Computer models that calculate the energy absorbed by greenhouse gases mistakenly integrate energy across all frequencies (wavelengths) involved, leading to erroneous results.

inverse proportion to the square of the propagation distance as the signal spreads out over the surface of an expanding hemisphere due to its radiating from a point on a surface. There is no evidence of attenuation of amplitude by friction.

The co-existence in electromagnetic radiation of numerous frequencies that do not interact is shown quite clearly by radio signals transmitted and received at millions of very precise frequencies. These signals do not interfere with each other except when receivers are too close to two or more transmitters at the same or very similar central frequencies. Similarly colors that we observed do not interact with each other in air and space. Otherwise everything we see would be blurry.

Fresnel (1818) noticed that light (electromagnetic radiation) could be polarized, concluding that light must therefore travel as transverse waves. He understood, however, that transverse waves can only propagate in solid matter, where the bonds holding the matter together provide the restoring forces that allow the waves to propagate. He therefore proposed that there must be some form of "luminiferous aether" in space that somehow provides those restoring forces. Faraday (1849) introduced the concept of an electromagnetic field in air and space consisting of coupled transverse electric and magnetic waves vibrating in mutually perpendicular planes. Maxwell (1865) formulated a set of partial differential equations showing that electric and magnetic fields in space satisfy the wave equation when you think of EMR as transverse waves traveling at some velocity. He showed that this velocity was equal to one divided by the square root of the product of two constants: the vacuum permittivity (the resistance to forming an electric field) times the magnetic permeability (the ability to form a magnetic field) (Maxwell, 1873). Thus, the velocity of light is proportional to the maximum rate at which an electric field can induce a magnetic field, which in turn can induce an electric field, ad infinitum.

For decades, physicists sought to discover what Fresnel's luminiferous aether was or to prove that it could not exist. A famous experiment by Michelson and Morley (1887) convinced most physicists that an aether does not exist and therefore waves could not propagate through space. The need to explain how waves could travel through space became less focused, however, with the introduction of light quanta (Einstein, 1905a), which ultimately also became known as photons (Lewis, 1926), special relativity (Einstein, 1905b), and wave-particle duality. Experiments searching for the luminiferous aether have continued into the 21st century, nevertheless, as explained quite cogently by the Wikipedia definition for "Timeline of luminiferous aether."

Richard Feynman et al. (1963) wrote on page 4-2 of the famous Feynman Lectures on Physics: "It is important to realize that in physics today, we have no knowledge what energy is. We do not have a picture that energy comes in little blobs of a definite amount." Jennifer Coopersmith (2010) builds on Feynman's work describing the evolution of our ideas about energy and how energy is a subtle concept. This paper shows that internal and radiant thermal energy are frequency that exists with certain amplitudes of oscillation, but not as "little blobs of a definite amount." Physicists that I talk to about this have trouble thinking of frequency as a thing. It is not the way we have been trained to think. It is much easier to think of wavelength as a thing, something we can visualize. After all, we have debated for 2500 years whether light, something

we cannot see until it interacts with matter, travels through space as either a wave or a particle, things we can see. There is a logical disconnect here. Electromagnetic radiation, light, thermal radiation is a broad band of frequencies, the energy at each frequency is equal to the frequency times the Planck constant, and the frequencies form a continuum, they are not discrete. They do not interact or interfere in air or space. Visualizing this continuum is not easy. And visualizing how amplitude spreads physically over the surface of an expanding sphere as the energy propagates is not easy. But both are happening. Maybe that is why understanding energy in radiation has eluded us for so long.

6. Thermal energy flows as frequency

At the microscopic level, thermal energy flows when a degree of freedom of a bond with a higher amplitude of oscillation at a specific frequency gives up to an adjoining degree of freedom via resonance one half the difference in amplitude between the two at the same frequency. Thus both degrees of freedom end up with the same amplitude at the same frequency. In matter, it appears that higher frequencies can also share amplitudes with lower frequencies by conduction (mechanical contact). In air, the normal modes of oscillations of the bonds holding a molecule of gas together are caused to resonate at their particular frequencies by higher amplitudes of oscillation in the electromagnetic radiation, extracting half the difference in amplitude at those frequencies from the radiation. Each resonant frequency causes one of the well-observed spectral lines of absorption that are characteristically different for each chemical species (Rothman et al., 2013) and are used to determine the chemical content of things from near at hand to the far reaches of the Universe. Greenhouse gases contain three or more atoms, providing many degrees of freedom, and are therefore able to absorb more thermal energy than diatomic molecules or atoms (e.g., argon, a monatomic noble gas). Thermal energy can only move physically in this way from higher amplitude to lower amplitude at a given frequency and, through mechanical content in matter, from higher frequency to lower frequency, thus explaining the second law of thermodynamics. Note that the rate of exchange of thermal energy by this process increases with increasing difference in temperature, something well observed in Nature.

Simply put, thermal energy is the oscillation of bonds that hold matter together. Planck's empirical law describes the observed spectral radiance (although as we argued above, it should actually be spectral amplitude) as a function of the frequency of oscillation for the radiating body at a specific temperature. Fundamentally, it is a description of the spectrum of oscillations on the surface of the radiating body. It is the frequencies and amplitudes of these oscillations that induce, through the motion of charge, electromagnetic radiation. It is these frequencies and amplitudes of these oscillations on the surface of the radiating body that are transmitted through air and space by electromagnetic radiation. It is these frequencies and amplitudes of these radiating oscillations from which a molecule of CO₂ gas extracts spectral lines of absorption that are the resonant normal modes of oscillation of the CO₂ molecule. It is these frequencies and amplitudes of these radiating oscillations that, when absorbed by cooler matter, increase the amplitudes and frequencies of the internal oscillations of the absorbing matter, thereby increasing the absorbing matter's temperature. It is these frequencies and amplitudes that appear to be reflected, rather than absorbed, by warmer matter (Evans and Popp, 1985). When radiation has lower amplitudes at each frequency than the prevailing amplitudes of oscillation

within receiving matter, heat can only flow away from the matter. There is no physical way for warmer matter to absorb colder radiation. Resonance does not work in that direction. The flow of thermal energy is all about the propagation of a broad spectrum of oscillations in matter, in space, and in gas molecules from higher temperature to lower temperature.

EMR is transmitted through air and space without interactions among its frequencies and its amplitudes, just as a radio station transmits its unique frequency by the motion of charge on the surface of its antenna. The higher the temperature of the body, the higher the frequency (energy) and the higher the amplitude (brightness) of transmission. In matter, on the other hand, frequencies and amplitudes of waves do interact, do interfere, and are attenuated with propagation distance. EMR in space does not behave in the same way that waves in matter behave. Waves are not physically possible in space.

It was soon postulated in quantum mechanics that EMR must be the result of wave-particle duality. Spectral physicists document in great detail, however, that the specifics of the packet of energy extracted by a gas molecule from electromagnetic radiation – what we tend to think of broadly as a photon – are determined by the resonant frequencies of the receiving molecule. While the photon is a very useful mathematical concept, it is actually created at the molecule, by the molecule's normal modes of oscillation. Photons do not actually travel as physical entities from Sun or from any other radiating body.

We can divide the velocity of light by frequency to calculate wavelength, and we have become accustomed to describing radiation as a function of wavelength, but wavelength of EMR in space is a mathematical concept, not a physical property. As we have seen, thermal energy in matter is simply frequency of oscillation of chemical bonds ($E=h\nu$) and an amplitude of oscillation at each frequency. Thermal energy transmitted through space is simply a manifestation of the frequencies and amplitudes of these oscillations on the surface of the radiating matter. There are no waves involved. When EMR interacts with solid matter, wavelike properties such as reflection, refraction, birefringence, and interference are observed, but these are caused by the bonds in the matter involved, not by the properties of EMR in air or space. Thinking of EMR in terms of transverse waves where the electric field is perpendicular to the magnetic field is a mental construct that limits our thoughts about what EMR actually is physically.

7. Radiant energy is not additive

Where most people have trouble intuitively visualizing electromagnetic energy and understanding $E=h\nu$ is in recognizing that electromagnetic energy cannot be summed over frequency or wavelength, as is done today by virtually all climate models. It makes no physical sense to sum frequencies. For example, red light at 400 THz plus violet light at 700 THz does not equal ultraviolet-B radiation at 1100 THz. Similarly the total energy of the rainbow is not the sum of the energies of individual colors (Fig. 3). The rainbow simply contains some red light with energies from 1.6 to 2.0 electronvolts (eV), some orange light with energies from 2.0 to 2.1 eV, some yellow light with energies from 2.1 to 2.17 eV, and so on to some violet light with energies from 2.75 to 3.26 eV. The total energy contained in electromagnetic radiation cannot be summarized as a single number. Radiation is most accurately thought of as a basket of fruit where

each frequency is a distinct fruit with a distinct size (amplitude), containing an energy equal to its frequency times the Planck constant. Wave energy in matter can be thought of as a Fourier series of frequencies and amplitudes where the bonds holding matter together allow summing (interaction) across all frequencies. Electromagnetic energy in space, however, where there are no bonds, is best thought of as a Fourier series without the plus signs – a basket of fruit.

8. A frequency (energy) gradient through the atmosphere

The highest frequency, highest energy, hottest, most chemically active radiation from Sun is absorbed in the atmosphere and never reaches Earth (Fig. 4b). Extreme ultraviolet radiation (Table 1) contains enough energy to ionize nitrogen, oxygen, and other chemical species, forming and warming the ionosphere and thermosphere 75 to 1000 km above Earth's surface. Most frequencies >1650 THz (energies >6.7 eV) are absorbed above 50 km in the ionosphere (Fig. 4b). Ultraviolet-C radiation dissociates oxygen and other species, forming and warming the stratosphere 10 to 50 km above Earth. There is more than enough nitrogen and oxygen to absorb all the extreme ultraviolet and ultraviolet-C energy available. Ultraviolet-B radiation dissociates ozone, warming the lower stratosphere and playing a major role in the Chapman cycle, a sequence of five catalytic chemical reactions that continually create and dissociate the ozone layer 20 to 30 km above Earth's surface. Most frequencies >1050 THz (>4.3 eV) are absorbed above 20 km where they dissociate O₂ and many other chemical species, warming the stratosphere. Most frequencies >950 THz with energies (>3.9 eV) sufficient to dissociate ozone, are absorbed by the ozone layer. When the ozone layer is depleted, more of this ultraviolet-B energy is observed to reach Earth's surface (Moore et al., 2007; Herman, 2010; McKenzie et al., 2011; Bais et al., 2015). This observed decrease in available photochemical energy with decreasing altitude demonstrates how solar radiation consists of many independent frequencies (energies) with the highest, most chemically active being absorbed first in the highest reaches of the atmosphere.

Photoionization and photodissociation are particularly effective ways to convert internal thermal energy in molecular bonds to temperature, because the molecular pieces fly apart at high velocity, directly converting all of the internal thermal energy in the bond to increased average kinetic energy of the molecules of the gas and of their atomic fragments. Photodissociation of

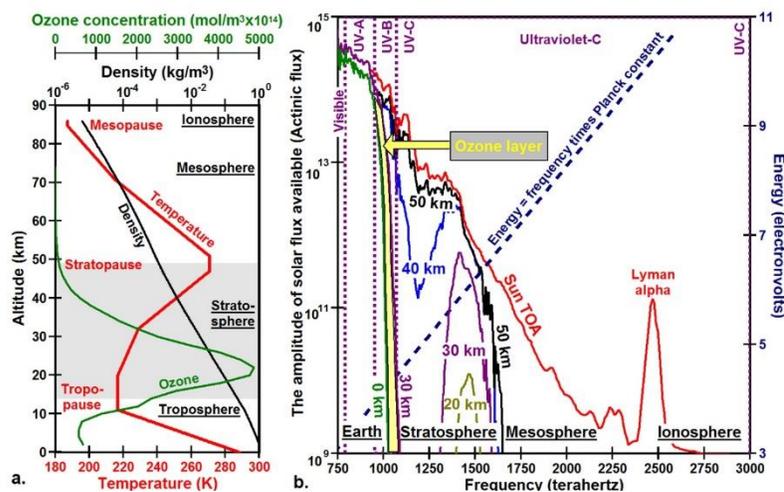


Figure 4. High-frequency solar radiation does not penetrate all the way through Earth's atmosphere. Atmospheric structure, density, and temperature on the left is based on the US Standard Atmosphere (Committee on Extension to the Standard Atmosphere, 1976) with ozone concentrations from Krueger and Minzner (1976). Actinic flux on the right is in units of photons per square centimeter per second per nanometer from Figure 7 of DeMore et al. (1997). Purple dotted lines and labels show the frequency ranges of visible light and ultraviolet A, B, and C radiation.

oxygen and ozone are particularly effective because they make up key parts of the Chapman cycle that continually creates and destroys ozone in the lower stratosphere in a catalytic cycle that increases the temperature of the gas with every dissociation. Note that the ozone layer is not a layer of stable gas. It is a range of altitudes in the atmosphere where there is sufficient ultraviolet radiation and other physical/chemical conditions to maximize the net production and lifetime of ozone molecules via the Chapman cycle. From Fig. 4b, it is clear that the primary chemical action occurs at the high-frequency, high-energy end of the Planck curves (Fig. 2).

9. What warms Earth?

A planet without an atmosphere at Earth's distance from Sun should have a mean surface temperature of around $-18\text{ }^{\circ}\text{C}$, but Earth's mean surface temperature is closer to $+15\text{ }^{\circ}\text{C}$. Many scientists suggest this $33\text{ }^{\circ}\text{C}$ difference is caused by the "blanket" effect of greenhouse gases, but the major warming observed in Earth's atmosphere is in the stratosphere (Fig. 4a), where temperatures at the stratopause, 50 to 55 km above Earth's surface, are maintained tens of degrees warmer than temperatures at the tropopause, at 9 to 17 km altitude. This warming is done primarily by solar ultraviolet energy dissociating O_2 and many other chemical species. The stratosphere acts as an "electric" blanket, in the sense that the energy to warm the blanket does not come from the body under the blanket, i.e. from Earth, but from another source, in this case Sun. Temperatures at the stratopause vary greatly with season but commonly range from -13 to $+3\text{ }^{\circ}\text{C}$ in the tropics, -21 to $+7\text{ }^{\circ}\text{C}$ in mid latitudes, and -20 to $+20\text{ }^{\circ}\text{C}$ near the poles (France et al., 2012) and average close to $-15\text{ }^{\circ}\text{C}$ (Wikipedia, 2015b). Thus solar energy causing dissociation of oxygen and other chemical species in the stratosphere appears to play the major role in keeping Earth warmer than it would be in the absence of an atmosphere. The stratopause is the key radiative surface into space of the Earth/atmosphere system and it can continue to radiate only because heat rises continuously through the stratosphere below, replacing the heat radiated.

The observation that EMR travels as frequency, much like the signal from a radio transmitter, rather than as waves, photons, or wave-particle duality, is extremely important for climate change because current computer programs that calculate forcing by greenhouse gases in watts per square meter assume that EMR travels as waves or photons and consequently integrate (sum) across many frequencies (wavelengths) to get total power.

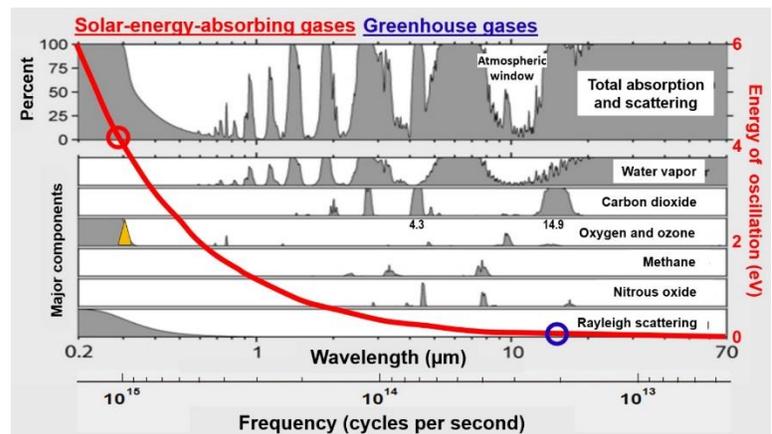


Figure 5. The energy of solar ultraviolet radiation reaching Earth when ozone is depleted (red circle, 4 eV at $0.31\text{ }\mu\text{m}$ wavelength) (Madronich, 1993) is 48 times the energy absorbed most strongly by carbon dioxide (blue circle, 0.083 eV at $14.9\text{ }\mu\text{m}$ wavelength). Shaded grey areas show the bandwidths of absorption by different greenhouse gases. Current computer models calculate radiative forcing by adding up the area under the broadened spectral lines that make up these bandwidths. Net radiative energy, however, is proportional to frequency only (red line), not to amplitude, bandwidth, or amount.

As noted previously, this method leads to erroneous conclusions. The absorption bands for major greenhouse gases are summarized in Fig. 5. Each band consists of numerous individual spectral lines of absorption. Current computer programs essentially sum up the areas under these broadened spectral lines, which total less than the areas of the bands in Fig. 5. For this reason, climatologists concluded long ago that the broad bands of infrared radiation absorbed by CO₂ molecules (grey shaded areas) have much more power (watts = joules of energy per second) than the narrow band of ultraviolet radiation that reaches Earth when ozone is depleted (orange line) (Madronich, 1993). Yet observations in Fig. 2, experience with sunburn, and common sense tell us that ultraviolet-B radiation has much more energy than any infrared radiation. $E=h\nu$ (red line) tells us that ultraviolet radiation reaching Earth when ozone is depleted, centered around wavelengths of 0.31 μm (967 THz) (red circle), has 48 times more energy than the infrared radiation absorbed most strongly by carbon dioxide, centered around wavelengths of 14.9 μm (20.1 THz) (blue circle), no matter how much of either radiation exists. Microscopic thermal energy is a function of frequency, not amount. This is critically important because of the threshold effect inherent in $h\nu$. Below a certain energy level, certain chemical processes cannot occur. Radiation having a lower frequency than radiation being emitted by a receiving body, for example, will be reflected away rather than being absorbed.

10. The global warming “hiatus”

Mean surface temperatures on Earth rose 0.6 °C from 1965 to 1998 but have remained essentially constant since and were essentially constant from 1945 to 1965 (Berkeley Earth, 2015; GISS, 2015; HadCRUT4, 2015; NOAA, 2015b) (Fig. 6) . What caused the two inflection points in temperature around 1965 and during 1998? In the 1960s, chlorofluorocarbons (CFCs) became very popular for use as refrigerants, spray-can propellants, solvents, and fire retardants because they do not interact with most other chemicals. Emissions of these human-manufactured gases began increasing by 1965 (Solomon, 1999). By 1970, total column ozone, measured poleward of the tropics, became depleted by as much as 50% (Staehelin et al., 1998; Hassler et al., 2011), forming the well-known Antarctic Ozone Hole during mid to late local winter, allowing more ultraviolet-B radiation to reach Earth's surface, cooling the lower stratosphere (Randel et al., 2009; Thompson and Solomon, 2009), and warming Earth.

Molina and Rowland (1974) discovered that CFCs can be broken down by

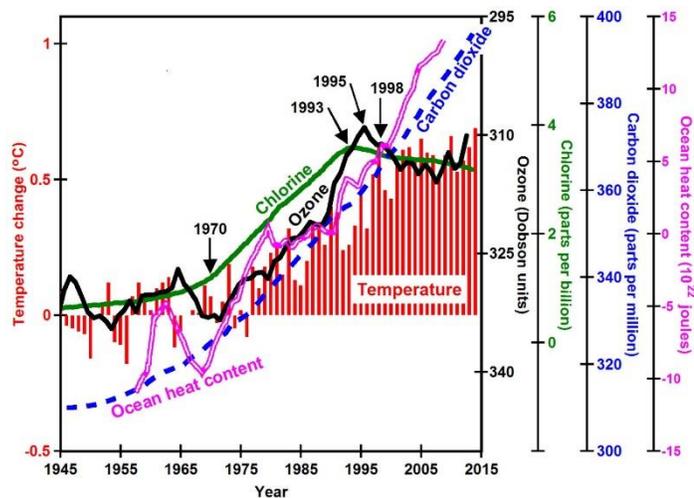


Figure 6. An increase in CFC emissions by 1965 (green line) (Solomon, 1999) led to an increase in ozone depletion by 1968 (black line, y-axis inverted) (Staehelin et al., 1998), which led to an increase in mean global surface temperatures by 1972 (red bars) (NOAA, 2015a). CFC emissions stopped increasing in 1993 as a result of the Montreal Protocol. Ozone depletion stopped increasing in 1995, and temperatures stopped increasing in 1998. Meanwhile, concentrations of CO₂ have continued to rise (dashed blue line) (NOAA, 2015b), perhaps reflecting the continuing increase in ocean heat content (Levitus et al., 2012).

ultraviolet radiation in the very cold lower stratosphere during local late winter and early spring to release chlorine atoms. One atom of chlorine can destroy on the order of 100,000 molecules of ozone through catalytic reactions. After discovery of the Antarctic Ozone Hole (Farman et al., 1985), scientists and politicians worked efficiently together under the Vienna Convention for the Protection of the Ozone Layer to develop the Montreal Protocol on Substances that Deplete the Ozone Layer, which became effective on January 1, 1989. By 1993, subsequent to implementation of this protocol, increases in CFC emissions stopped (Solomon, 1999); increases in ozone depletion stopped by 1995 (Staehelin et al., 1998); and increases in global temperatures stopped by 1998. Increased emissions of CFCs appear to have caused the inflection point around 1965. Decreased emissions of CFCs beginning in 1993 appear to have stopped increases in ozone depletion by 1995 and further increases in temperature by 1998. Because CFC concentrations continue to decrease slowly, increases in temperature due to CFCs are not anticipated.

Annual average ozone concentrations have remained depleted since 1998 by approximately 4% in northern mid-latitudes compared to pre-1970 concentrations (Staehelin et al., 1998; Ward, 2015b). The resulting increased ultraviolet-B radiation continues to increase ocean heat content (Levitus et al., 2012) (Fig. 6) because it penetrates tens of meters into the ocean (Tedetti and Sempéré, 2006), from which depth the energy is not radiated back into the atmosphere at night. The observation that Earth's mean surface temperature increased while ozone depletion was increasing but have remained constant while ozone depletion remains relatively constant suggests that the elevated influx of ultraviolet-B is initially being absorbed in the lower troposphere, possibly by low-level ozone generated by pollution. This could help explain why there was twice as much warming from 1965 to 1998 in the northern hemisphere (0.8 °C) as in the southern hemisphere (0.4 °C), which contains only 32% of the global land area, 12% of the global population, and therefore many times less pollution than the northern hemisphere.

Total column ozone concentrations increase toward the poles in local winter (Fioletov, 2008). Ozone depletion in late winter and early spring occurs within these ozone peaks, explaining why the greatest warming observed has been on the Antarctic Peninsula (Hughes et al., 2007), West Antarctica (Bromwich et al., 2013), and in the Arctic (Trenberth et al., 2007) and why the greatest warming is shown by daily minimum temperatures (Hughes et al., 2007). These annual wintertime increases in total column ozone normally cause warming of the stratosphere and particularly cold temperatures on Earth because more ultraviolet-B radiation is absorbed in the ozone layer and less reaches Earth's surface.

11. What cools Earth?

Mid- to long-wavelength infrared thermal energy (Table 1) flows upward from Earth's surface through the atmosphere and out to space. Greenhouse gases, such as water vapor, carbon dioxide, methane, and nitrous oxide, absorb many narrow spectral lines of infrared energy because of the large number of degrees of freedom of internal oscillations possible in molecules made up of 3 or more atoms. Greenhouse-gas theory posits that the infrared energy absorbed warms the atmosphere, slowing the rate at which Earth cools, and that this warmer atmosphere also radiates infrared energy back to Earth, warming its surface (Planton, 2013). The Intergovernmental Panel on Climate Change (IPCC, 2014) concludes that “atmospheric

concentrations of carbon dioxide, methane and nitrous oxide ... are extremely likely to have been the dominant cause of the observed warming since the mid-20th century. ... Continued emission of greenhouse gases will cause further warming and long-lasting changes in all components of the climate system, increasing the likelihood of severe, pervasive and irreversible impacts for people and ecosystems. Limiting climate change would require substantial and sustained reductions in greenhouse gas emissions.”

The greenhouse-gas theory of global warming is built on the observation that greenhouse gases absorb narrow bands of infrared energy (Tyndall, 1861). The spectral lines of absorption within these narrow bands have been documented in considerable detail (Rothman et al., 2013).

Greenhouse-gas theory is also based on the assumption that absorption of these narrow bands of infrared radiation raises the temperature of air substantially. Knut Ångström (1900) demonstrated in both field and laboratory experiments that such absorption does not appear to have much effect on air temperature. There are two reasons for this. First, temperature, as we define it (Fig. 2), involves a wide range of frequencies, whereas greenhouse gases absorb only a small subset of these frequencies. Secondly, radiant infrared thermal energy is absorbed in solid matter as internal energy, the oscillatory energy of the bonds holding the absorbing molecules together. Temperature of a gas, however, is proportional to how fast the atoms and molecules are moving through air, i.e., their mean translational kinetic energy. It is customarily assumed that internal energy is redistributed, through intermolecular collisions, among all the degrees of freedom of all atoms and molecules in the gas according to the law of equipartition. But only some degrees of freedom are related to temperature of air and the efficiency of this redistribution and its net effect on temperature are not well measured.

Despite an extensive search, I have been unable to find anyone since Ångström who has reported measuring directly in the laboratory or in the field an increase in air temperature caused by an increase in its greenhouse-gas content. This should not be a difficult experiment. Instead of making direct measurements, climate scientists calculate climate sensitivity simply by assuming that the global warming observed over some period of time was caused primarily by increases in greenhouse gas concentrations observed during the same period of time (PALEOSENS Project Members, 2012). This leads to estimates, in the best controlled situations, of from 2.2 to 4.8 °C temperature increase for a doubling of the atmospheric concentration of carbon dioxide. A simple laboratory experiment should be able to demonstrate whether or not doubling CO₂ concentrations actually leads to some predictable degree of warming. Satellite observations have documented increasing absorption by increasing concentrations of greenhouse gases as predicted by laboratory observations (Harries et al., 2001; Feldman et al., 2015), but the hypothetical conversion of these measurements to radiative forcing or global temperature entails many assumptions based on radiation computer codes that do not treat energy as a function of frequency and are therefore of questionable validity.

There are two basic physical processes by which it is assumed that greenhouse gases cause global warming: (1) infrared radiation absorbed by greenhouse gases is re-radiated in all directions,

slowing the radiative cooling of Earth and (2) infrared radiation absorbed by greenhouse gases is re-radiated back to Earth's surface, where it is re-absorbed, warming Earth (Planton, 2013).

The problem with process 1 is that in the troposphere, the lower 17 km of Earth's atmosphere, which contains 75% of the atmosphere's mass and 99% of its water vapor, heat flows primarily by convection. Convection is driven by the fact that warmer gases are less dense and thus naturally rise because temperature, and hence air density, decrease with altitude. Convection in the troposphere is also inextricably linked to the fact that atmospheric and ocean currents redistribute heat at much greater rates than those at which heat can be radiated. The well-appreciated phenomenon of wind chill confirms that our bodies lose heat most rapidly when the wind is blowing. Earth's weather is the result of the convective redistribution of heat primarily from the warm tropics to the cooler poles. Convection in a storm system can move orders of magnitude more heat per unit time than radiation, and individual storm systems are well below the resolution capabilities of all climate models. Thus, radiation through the troposphere plays only a minor role in cooling Earth's surface.

The problem with process 2 is that it assumes that heat flows from a colder atmosphere to a warmer Earth, and that would violate the second law of thermodynamics. Temperature in the troposphere is well observed to decrease at a lapse rate of 5 to 10 °C per kilometer of increasing altitude depending on water content (red line, Fig. 4a). Thus, all layers of gas in the atmosphere, above any thin, temporary temperature inversion in the boundary layer next to Earth's surface, are observed to be colder than Earth's surface no matter how much infrared thermal energy they absorb. Trenberth et al. (2009) and Trenberth and Fasullo (2012), for example, calculate that within Earth's global annual mean energy budget, 161 W m⁻² of power from Sun is absorbed directly by Earth while assuming that more than twice as much power (333 W m⁻²) is radiated back to Earth from energy absorbed by greenhouse gases and is then re-absorbed by Earth. Wild et al. (2013) argue that even more power (342 W m⁻²) is radiated back to Earth. Heat cannot flow by radiation from cold to hot. You do not get warm by standing next to a cold stove. Even if this back radiation exists, it would be too cold to be absorbed by Earth and would most likely be reflected (Evans and Popp, 1985).

The primary problem with greenhouse-gas theory is, if energy is equal to frequency times the Planck constant ($E=h\nu$), then there simply is not enough energy in infrared radiation absorbed by greenhouse gases compared to the energy available in ultraviolet-B radiation when ozone is depleted to play a major role in global warming.

A second major problem with greenhouse-gas theory is that a thermal mass cannot warm itself. Note in Fig. 2, that in order to warm a body, you must increase the amplitudes of oscillation at all frequencies and increase the frequency that has the greatest amplitude. This means that radiation from Earth, no matter how efficiently it is re-radiated back to Earth, cannot warm Earth's surface – it does not have large enough amplitudes at all frequencies to drive resonance. Heat can only flow from a warmer body to a colder body. The color temperature axis at the top of Fig. 2 shows the temperature of any given body of matter whose maximum amplitude is at the

frequency shown. This is the maximum temperature to which sufficient radiation from this body can raise another body and is referred to as the color temperature (Table 1).

A third problem with greenhouse-gas theory is that it is unable to explain the inflection points in the temperature trend around 1965 and at 1998 shown in Fig. 6. More than 50 papers have been published by the end of 2014 trying to explain the so-called “global warming hiatus” (as if warming is expected to resume) since 1998 in terms of natural variations within the climate system, including a prolonged minimum in the solar cycle, increased aerosols, decreased stratospheric water vapor, and changes in ocean currents, ocean heat uptake, ocean stratification, trade winds, and Ekman downwelling. Differentiating between cause and effect for many of these observed variations can be difficult. Furthermore, the probability that multiple independent factors would spontaneously coordinate to suppress global warming all at the same time is vanishingly small. Alternatively, and far more reasonably, these observations could simply reflect changes caused by the single factor of ozone depletion. The most straightforward explanation for the distinct divergence of increasing CO₂ concentrations with constant temperatures since 1998 is that something other than increasing greenhouse gas concentration is the primary cause of global warming. Ozone depletion seems to be the most likely candidate.

Note in Fig. 6 that CO₂ concentration has continued to increase with increasing ocean heat content. Could atmospheric CO₂ concentration be primarily a reflection of the decreasing solubility of CO₂ in a warming ocean and thus be a proxy for ocean temperature? The eruption of Pinatubo in 1991 ejected 42 to 234 megatons of CO₂ into the atmosphere (Self et al., 1996), yet atmospheric concentration of CO₂ increased at slower rates than usual for several years following the eruption (NOAA, 2015a), over the same time interval in which global temperatures decreased 0.5 °C because of the effects of aerosols formed by eruption of sulfur dioxide and water vapor into the lower stratosphere. This appears to suggest that it was actually the decreasing temperature of the ocean surface that reduced the atmospheric concentration of CO₂.

Arctic amplification of global warming (Serreze and Barry, 2011) is also difficult to explain by greenhouse-gas theory, but it is explained quite clearly by ozone depletion theory, as depletion has been most intense in the circumpolar regions.

12. Ozone depletion theory

Ward (2015a) provides a clear, straightforward, and intuitive explanation for most observations of changes in ozone and related changes in climate (WMO, 2014). Ozone depletion and warming began after 1965 with increased use of chlorofluorocarbons (CFCs) that release chlorine in the cold, circumpolar stratosphere, leading to ozone depletion at northern mid-latitudes of approximately 4%. Ozone depletion and associated warming stopped increasing when the Montreal Protocol on Substances that Deplete the Ozone Layer limited further emissions of CFCs. Volcanic eruptions, even small ones, also deplete ozone by up to 6% per eruption, causing warming for the better part of a decade. Major explosive eruptions, however, also eject megatons of sulfur dioxide and water vapor into the lower stratosphere, where they form aerosols whose particle sizes grow large enough to reflect and scatter sunlight, causing net global cooling for typically three years, as summarized in Fig. 7. Note that as the particle sizes of the

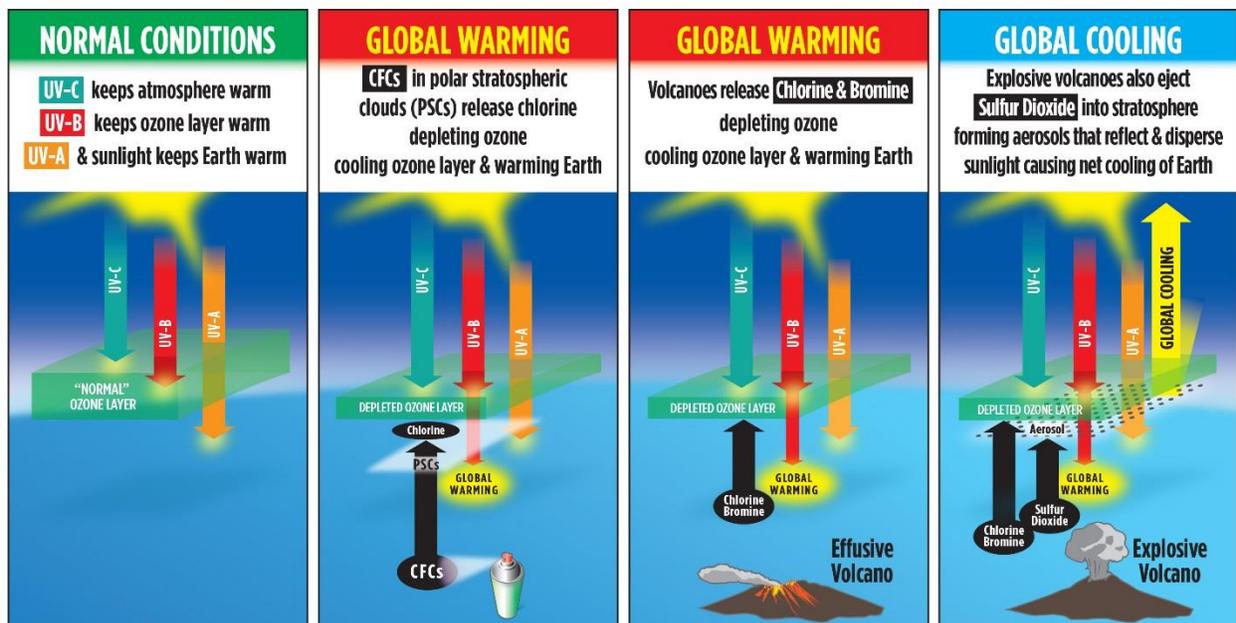


Figure 7. Under conditions normal before 1965, ultraviolet-C (UV-C) warmed the upper atmosphere, UV-B primarily warmed the ozone layer, and UV-A and visible light warmed Earth. CFCs, when they rise to the level of very cold polar stratospheric clouds (PSCs), release chlorine that depletes ozone, causing more UV-B than usual to reach Earth's surface, thus cooling the ozone layer and warming Earth. Effusive volcanoes emit chlorine and bromine that deplete ozone, leading to global warming. Explosive volcanoes similarly deplete ozone, but also eject megatons of water and sulfur dioxide into the lower stratosphere, forming globe-encircling aerosols that become extensive enough to reflect and scatter sunlight, causing net global cooling.

aerosol grow, it is the highest frequency ultraviolet-B radiation that is reflected and scattered first.

Climate change throughout geologic time appears to have resulted from changes in ozone concentration caused by changes in the rates and volumes of volcanic eruptions, and by the ratio of effusive, basaltic eruptions causing warming to explosive eruptions causing cooling. These rates are determined by plate tectonics. If there is a major increase in basaltic, effusive volcanic eruptions such as from central Iceland's Bárðarbunga, which began erupting in August, 2014, with lava flows covering more than 85 km² within 5 months (Wikipedia, 2015a), then future warming is likely. But Bárðarbunga appears to have stopped erupting on February 27, 2015. For more detail, see ozonedepletiontheory.info and a YouTube talk at tinyurl.com/ozonedepletiontheory.

13. Implications

Manufacturing of CFCs began increasing substantially by 1965 (Solomon, 1999), causing major increases in ozone depletion (Staelin et al., 1998), especially within the Antarctic ozone hole (Farman et al., 1985). For every 1% decrease in ozone in the stratosphere, an additional 1 to 2% of ultraviolet-B radiation reaches Earth (Moore et al., 2007; Herman, 2010; McKenzie et al., 2011; Bais et al., 2015), warming global mean surface temperature 0.6 °C from 1965 to 1998 (NOAA, 2015b) and regional minimum temperatures as much as 6.7 °C, as on the Antarctic Peninsula (Hughes et al., 2007). This warming, therefore, appears to have been caused by humans

manufacturing and using CFCs. Humans also began correcting the problem by 1989 via the Montreal Protocol. This warming has not yet reached thermal equilibrium, so its effects on such things as glaciers, sea level, biota, and weather may continue for some time. More disturbing is the fact that humans have moved Earth's thermostat upward about 0.6 °C by increasing the heat content of the oceans. There is no natural way to move the thermostat back down to temperature levels typical before 1965 without a rapid sequence of major explosive volcanic eruptions.

14. Conclusions

Thermal energy in matter is a broad distribution of amplitudes of oscillation of all the bonds holding matter together as a function of the various frequencies of these oscillations. This spectral distribution, at thermal equilibrium, is described by Planck's empirical law as a function of temperature. These oscillations on the surface of matter transmit, through the motion of charge, electromagnetic radiation that travels through air and space simply as frequencies and amplitudes, not as waves or photons. The thermal energy of any frequency component of this radiation is equal to the frequency times the Planck constant and is not a function of amount, amplitude, or bandwidth, as is currently assumed in climate models. A molecule of any greenhouse gas can extract from radiation only those frequencies that are characteristic of the normal modes of oscillation of the molecule. When radiation is absorbed by matter that is colder than the radiation, it increases the amplitudes and frequencies of oscillation in the absorbing matter, thereby raising its temperature.

Global climate change is caused primarily by changes in the highest-frequency, highest-energy, hottest, most chemically active solar radiation that is able to penetrate through Earth's atmosphere to the surface. Warming since 1965 was caused by emissions of CFCs that depleted ozone, allowing more than the usual dose of high-energy, high-temperature, ultraviolet-B radiation to reach Earth's surface. Global warming over geologic time appears to have been caused by long periods of major effusive, basaltic volcanism depleting ozone and thereby causing warming. Global cooling occurs when major explosive volcanic eruptions occur every decade or so, rather than at current rates of one or two per century. This kind of eruption depletes ozone, causing warming, but it also forms aerosols in the lower stratosphere that reflect and scatter solar radiation, causing net cooling for about three years.

Greenhouse-gas theory is physically impossible. The assumption of back-radiation warming Earth violates the second law of thermodynamics. Greenhouse-gas theory relies on assumptions described in this paper that are not supported by observation. The only direct measurement of how much an increase in carbon dioxide concentration actually causes an increase in air temperature was in 1900 by a well-known physicist, and it showed little effect. Those who support greenhouse-gas theory should undertake similar experimental measurements; they should not be overly difficult.

Major warming predicted by models based on greenhouse-gas theory has not occurred since 1998 and is unlikely to occur in the future. Reducing carbon dioxide emissions is not likely to reduce global warming, although it might reduce ocean acidity. Maintaining global vigilance

against the future production and release of ozone depleting substances, however, remains a critical concern.

References

- Ångström, K., 1900, Ueber die Bedeutung des Wasserdampfes und der Kohlensäure bei der Absorption der Erdatmosphäre: *Annalen der Physik*, v. 308, no. 12, p. 720-732. In English at ozonedepletiontheory.info/Papers/Angstrom1900-English.pdf, doi:10.1002/andp.19003081208.
- Bais, A., McKenzie, R., Bernhard, G., Aucamp, P., Ilyas, M., Madronich, S., and Tourpali, K., 2015, Ozone depletion and climate change: Impacts on UV radiation: *Photochemical & Photobiological Sciences*, v. 14, no. 1, p. 19-52, doi:10.1039/c4pp90032d.
- Berkeley Earth, 2015, berkeleyearth.lbl.gov/auto/Global/Land_and_Ocean_complete.txt.
- Bromwich, D. H., Nicolas, J. P., Monaghan, A. J., Lazzara, M. A., Keller, L. M., Weidner, G. A., and Wilson, A. B., 2013, Central West Antarctica among the most rapidly warming regions on Earth: *Nature Geoscience*, v. 6, p. 139-145, doi:10.1038/ngeo1671.
- Coopersmith, J., 2010, *Energy, the Subtle Concept: The discovery of Feynman's blocks from Leibniz to Einstein*, Oxford University Press 400 p.
- Einstein, A., 1905a, Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt: *Annalen der Physik*, v. 322, no. 6, p. 132-148. In English at en.wikisource.org/wiki/A_Heuristic_Model_of_the_Creation_and_Transformation_of_Light, doi:10.1002/andp.19053220607, in English at en.wikisource.org/wiki/A_Heuristic_Model_of_the_Creation_and_Transformation_of_Light.
- Einstein, A., 1905b, Zur elektrodynamik bewegter körper: *Annalen der Physik*, v. 322, no. 10, p. 891-921, doi:10.1002/andp.19053221004, in English at www.fourmilab.ch/etexts/einstein/specrel/www/.
- Evans, J., and Popp, B., 1985, Pictet's experiment: the apparent radiation and reflection of cold: *American Journal of Physics*, v. 53, p. 737, doi:10.1119/1.14305.
- Faraday, M., 1849, The bakerian lecture: Experimental researches in electricity. twenty-second series: *Philosophical Transactions of the Royal Society of London*, v. 139, p. 1-18, doi:10.1098/rstl.1849.0001.
- Farman, J. C., Gardiner, B. G., and Shanklin, J. D., 1985, Large losses of total O₃ in atmosphere reveal seasonal ClO_x/NO_x interaction: *Nature*, v. 315, p. 207-210, doi:10.1038/315207a0.
- Feldman, D. R., Collins, W. D., Gero, P. J., Torn, M. S., Mlawer, E. J., and Shippert, T. R., 2015, Observational determination of surface radiative forcing by CO₂ from 2000 to 2010: *Nature*, doi:10.1038/nature14240.
- Feynman, R. P., Leighton, R. B., and Sands, M., 1963, *Feynman lectures on physics. vol. 1: Mainly mechanics, radiation and heat*, Addison-Wesley, 4-1 p.
- Fioletov, V., 2008, Ozone climatology, trends, and substances that control ozone: *Atmosphere-Ocean*, v. 46, no. 1, p. 39-67, doi:10.3137/ao.460103.

- France, J., Harvey, V., Randall, C., Hitchman, M., and Schwartz, M., 2012, A climatology of stratopause temperature and height in the polar vortex and anticyclones: *Journal of Geophysical Research: Atmospheres*, v. 117, no. D6, doi:10.1029/2011JD016893.
- Fresnel, A., Lettre d'Augustin Fresnel à François Arago sur l'influence du mouvement terrestre dans quelques phénomènes d'optique, *in Proceedings Annales de chimie et de physique* 1818, Volume 9, p. 57-66.
- Gearhart, C. A., 2008, Max Planck and black-body radiation, *in Hoffmann, D., ed., Max Planck: Annalen Papers*, Wiley-VCH, p. 395-418.
- GISS, 2015, data.giss.nasa.gov/gistemp/abs_temp.html.
- Grossman, J. C., 2014, Thermodynamics: Four laws that move the Universe, *The Great Courses*, Course 1291.
- HadCRUT4, 2015, www.cru.uea.ac.uk/cru/data/temperature/.
- Halliday, D., Resnick, R., and Walker, J., 2013, *Fundamentals of Physics*, 10th edition, Wiley, 1232 p.
- Harries, J. E., Brindley, H. E., Sahoo, P. J., and Bantges, R. J., 2001, Increases in greenhouse forcing inferred from the outgoing longwave radiation spectra of the Earth in 1970 and 1997: *Nature*, v. 410, no. 6826, p. 355-357, doi:10.1038/35066553.
- Hassler, B., Bodeker, G., Solomon, S., and Young, P., 2011, Changes in the polar vortex: Effects on Antarctic total ozone observations at various stations: *Geophysical Research Letters*, v. 38, no. 1, p. L01805, doi:10.1029/2010GL045542.
- Herman, J. R., 2010, Global increase in UV irradiance during the past 30 years (1979–2008) estimated from satellite data: *J. Geophys. Res.*, v. 115, p. D04203, doi:10.1029/2009JD012219.
- Hughes, G. L., Rao, S. S., and Rao, T. S., 2007, Statistical analysis and time-series models for minimum/maximum temperatures in the Antarctic Peninsula: *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Science*, v. 463, no. 2077, p. 241-259, doi:10.1098/rspa.2006.1766.
- IPCC, 2014, *Climate Change 2014: Synthesis Report*, www.ipcc.ch/report/ar5/syr/.
- Knight, R. D., 2012, *Physics for Scientists and Engineers: A Strategic Approach with Modern Physics* (3rd Edition), Addison-Wesley, 1376 p.
- Kuhn, T. S., 1987, Black-Body Theory and the Quantum Discontinuity, 1894-1912, 398 p.
- Lenard, P., 1902, Ueber die lichtelektrische Wirkung: *Annalen der Physik*, v. 313, no. 5, p. 149-198, doi:10.1002/andp.19023130510.
- Levitus, S., Antonov, J., Boyer, T., Baranova, O., Garcia, H., Locarnini, R., Mishonov, A., Reagan, J., Seidov, D., and Yarosh, E., 2012, World ocean heat content and thermocline sea level change (0-2000 m), 1955-2010: *Geophysical Research Letters*, v. 39, no. 10, p. L10603, doi:10.1029/2012GL051106.
- Lewis, G. N., 1926, The conservation of photons: *Nature*, v. 118, p. 874-875, doi:10.1038/118874a0.
- Lummer, O., and Pringsheim, E., 1899, Die Vertheilung der Energie im Spectrum des schwarzen Körpers und des blanken Platins; Temperaturbestimmung fester glühender Körper: *Verhandlungen der Deutschen Physikalischen Gesellschaft*, v. 1, p. 215-235.

- Madronich, S., 1993, Trends and predictions in global UV, *in* Chanin, M. L., ed., *The Role of the Stratosphere in Global Change*, Volume 8, NATO ASI Series I: Global Environmental Change: Berlin, Springer-Verlag, p. 463-471.
- Maxwell, J. C., 1865, A dynamical theory of the electromagnetic field: *Philosophical Transactions of the Royal Society of London*, v. 155, p. 459-512, doi:10.1098/rstl.1865.0008.
- Maxwell, J. C., 1873, *A treatise on electricity and magnetism*, Oxford, Clarendon Press, 560 p.
- McKenzie, R. L., Aucamp, P. J., Bais, A. F., Björn, L. O., Ilyas, M., and Madronich, S., 2011, Ozone depletion and climate change: impacts on UV radiation: *Photochemical & Photobiological Sciences*, v. 10, no. 2, p. 182-198, doi:10.1039/c0pp90034f.
- Michelson, A. A., and Morley, E. W., 1887, On the relative motion of the earth and the luminiferous ether: *American journal of science*, v. 34, no. 203, p. 333-345, doi:10.2475/ajs.s3-34.203.333
- Molina, M. J., and Rowland, F. S., 1974, Stratospheric sink for chlorofluoromethanes: Chlorine catalysed destruction of ozone: *Nature*, v. 249, p. 810-814, doi:10.1038/249810a0.
- Moore, J. W., Stanitski, C. L., and Jurs, P. C., 2007, *Chemistry: The Molecular Science*, Volume I, Chapters 1-12, Brooks Cole, 912 p.
- NOAA, 2015a, Annual mean CO₂ at Mauna Loa.
- NOAA, 2015b, www.ncdc.noaa.gov/cag/time-series/global.
- PALEOSENS Project Members, 2012, Making sense of palaeoclimate sensitivity: *Nature*, v. 491, no. 7426, p. 683-691, doi:10.1038/nature11574.
- Planck, M., 1900, Entropie und temperatur strahlender wärme: *Annalen der Physik*, v. 306, no. 4, p. 719-737, doi:10.1002/andp.19003060410.
- Planton, S., 2013, Annex III: Glossary, *in* Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and P.M. Midgley (eds.), eds., *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*: Cambridge, United Kingdom and New York, NY, USA, Cambridge University Press.
- Randel, W. J., Shine, K. P., Austin, J., Barnett, J., Claud, C., Gillett, N. P., Keckhut, P., Langematz, U., Lin, R., Long, C., Mears, C., Miller, A., Nash, J., Seidel, D. J., Thompson, D. W. J., Wu, F., and Yoden, S., 2009, An update of observed stratospheric temperature trends: *Journal of Geophysical Research*, v. 114, no. D2, doi:10.1029/2008jd010421.
- Rothman, L., Rothman, L. S., Gordon, I. E., Babikov, Y., Barbe, A., Benner, D. C., Bernath, P. F., Birk, M., Bizzocchi, L., Boudon, V., Brown, L. R., Campargue, A., Chance, K., Cohen, E. A., Coudert, L. H., Devi, V. M., Drouin, B. J., Fayt, A., Flaud, J.-M., Gamache, R. R., Harrison, J. J., Hartmann, J.-M., Hill, C., Hodges, J. T., Jacquemart, D., Jolly, A., Lamouroux, J., Roy, R. J. L., Li, G., Long, D. A., Lyulin, O. M., Mackie, C. J., Massie, S. T., Mikhailenko, S., Müller, H. S. P., Naumenko, O. V., Nikitin, A. V., Orphal, J., Perevalov, V., Perrin, A., Polovtseva, E. R., Richard, C., Smith, M. A. H., Starikova, E., Sung, K., Tashkun, S., Tennyson, J., Toon, G. C., Tyuterev, V. G., and Wagner, G., 2013, The HITRAN2012 molecular spectroscopic database: *Journal of Quantitative Spectroscopy and Radiative Transfer*, v. 130, p. 4-50, doi:10.1016/j.jqsrt.2013.07.002.
- Self, S., Zhao, J.-X., Holasek, R. E., Torres, R. C., and King, A. J., 1996, The atmospheric impact of the 1991 Mount Pinatubo eruption, *in* Newhall, C. G., and Punongbayan, R. S., eds., *Fire*

- and Mud: Eruptions and lahars of Mount Pinatubo, Philippines, Philippine Institute of Volcanology and Seismology and University of Washington Press, pubs.usgs.gov/pinatubo/self/, p. 1089-1115.
- Serreze, M. C., and Barry, R. G., 2011, Processes and impacts of Arctic amplification: A research synthesis: *Global and Planetary Change*, v. 77, no. 1, p. 85-96, doi:10.1016/j.gloplacha.2011.03.004.
- Solomon, S., 1999, Stratospheric ozone depletion: A review of concepts and history: *Reviews of Geophysics*, v. 37, no. 3, p. 275-316, doi:10.1029/1999RG900008.
- Staehelin, J., Renaud, A., Bader, J., McPeters, R., Viatte, P., Hoegger, B., Bugnion, V., Giroud, M., and Schill, H., 1998, Total ozone series at Arosa (Switzerland): Homogenization and data comparison: *Journal of Geophysical Research*, v. 103, no. D5, p. 5827-5841, doi:10.1029/97JD02402.
- Tedetti, M., and Sempéré, R., 2006, Penetration of ultraviolet radiation in the marine environment. A review: *Photochemistry and Photobiology*, v. 82, no. 2, p. 389-397, doi:10.1562/2005-11-09-IR-733.
- Thompson, D. W. J., and Solomon, S., 2009, Understanding recent stratospheric climate change: *Journal of Climate*, v. 22, no. 8, p. 1934-1943, doi:10.1175/2008JCLI2482.1.
- Trenberth, K. E., and Fasullo, J. T., 2012, Tracking Earth's energy: From El Niño to global warming: *Surveys in Geophysics*, v. 33, no. 3-4, p. 413-426, doi:10.1007/s10712-011-9150-2.
- Trenberth, K. E., Fasullo, J. T., and Kiehl, J., 2009, Earth's global energy budget: *Bulletin of the American Meteorological Society*, v. 90, no. 3, p. 311-323, doi:10.1175/2008bams2634.1.
- Trenberth, K. E., Jones, P. D., Ambenje, P., Bojariu, R., Easterling, D., Tank, A. K., Parker, D., Rahimzadeh, F., Renwick, J. A., Rusticucci, M., Soden, B., and Zhai, P., 2007, Observations: Surface and Atmospheric Climate Change, *in* Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., eds., *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, p. 235-336.
- Tyndall, J., 1861, The Bakerian Lecture: on the absorption and radiation of heat by gases and vapours, and on the physical connexion of radiation, absorption, and conduction: *Philosophical Transactions of the Royal Society of London*, v. 151, p. 1-36, doi:10.1098/rstl.1861.0001.
- Ward, P. L., 2015a, ozonedepletiontheory.info.
- Ward, P. L., 2015b, ozonedepletiontheory.info/ozone-depletion.html.
- Wikipedia, 2015a, en.wikipedia.org/wiki/Holuhraun.
- Wikipedia, 2015b, en.wikipedia.org/wiki/Stratopause.
- Wild, M., Folini, D., Schär, C., Loeb, N., Dutton, E. G., and König-Langlo, G., 2013, The global energy balance from a surface perspective: *Climate dynamics*, v. 40, no. 11-12, p. 3107-3134, doi:10.1007/s00382-012-1569-8.
- WMO, 2014, Scientific Assessment of Ozone Depletion: 2014, World Meteorological Organization, Global Ozone Research and Monitoring Project—Report No. 55, www.esrl.noaa.gov/csd/assessments/ozone/2014/report.html, 416 p.