

CO₂ infrared absorption

Professor W.J.Witteman [Ref. 1] provides a detailed account of the absorption of thermal emission from the Earth surface by atmospheric CO₂. He found that at atmospheric temperatures only a few low-lying vibrational bands of CO₂ are relevant. Further, it stated that “Especially the absorbed radiation power by the ground state bending mode at about 15 microns is dominant.” The Conclusion states “The absorption of thermal emission from the earth by CO₂ occurs at wavelengths around 15, 5 and 4.3 microns.”

HITRAN CO₂ absorption spectrum

For this study, a spectrum for CO₂ was calculated using the HITRAN web site facility [Ref.2] for the parameters of temperature of 12°C and pressure 0.945 atmospheres being the estimated average conditions at about 500 metres above sea level. The result is shown in Figure 1. The section between wavenumbers 400 to 2600 cm⁻¹ is that referred to in Witteman [Ref.1] as the region of absorption of the thermal emission from the earth.

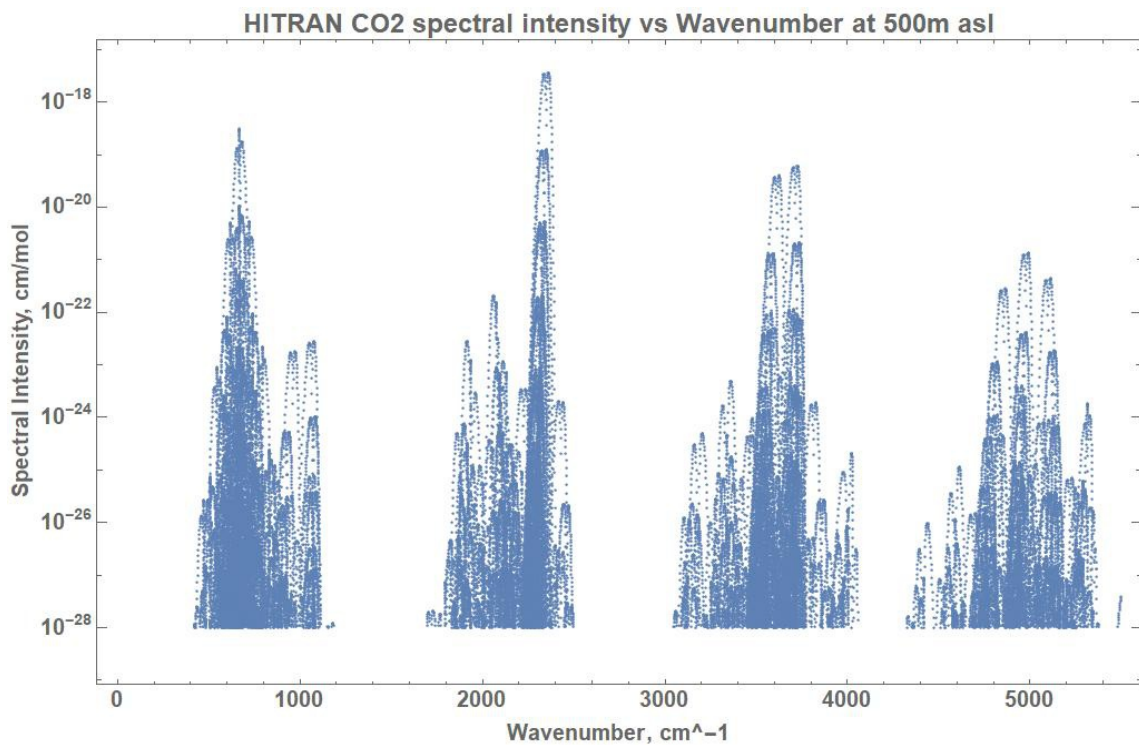


Figure 1.

The calculated HITRAN spectrum listing gave the major peaks as:

- wavenumber 667.661 cm⁻¹, that is, wavelength 14.9777 microns, frequency 20.016 Tera Hz, amplitude 3.061×10^{-19} cm/mol, photon energy 1.3263×10^{-20} J
- wavenumber 2361.47 cm⁻¹, that is, wavelength 4.2347 microns, frequency 70.795 Tera Hz, amplitude 3.642×10^{-18} cm/mol, photon energy 4.6909×10^{-20} J
- wavenumber 3727.08 cm⁻¹, that is, wavelength 2.6831 microns, frequency 111.74 Tera Hz, amplitude 6.092×10^{-20} cm/mol, photon energy 7.4035×10^{-20} J
- wavenumber 4989.97 cm⁻¹, that is, wavelength 2.0040 microns, frequency 149.6 Tera Hz, amplitude 1.356×10^{-21} cm/mol, photon energy 9.912×10^{-20} J

From inspection of the HITRAN listing, the absorption bands were chosen by taking one thousandth of the peak line intensity as their outer limits. This gave the absorption band limits to be:

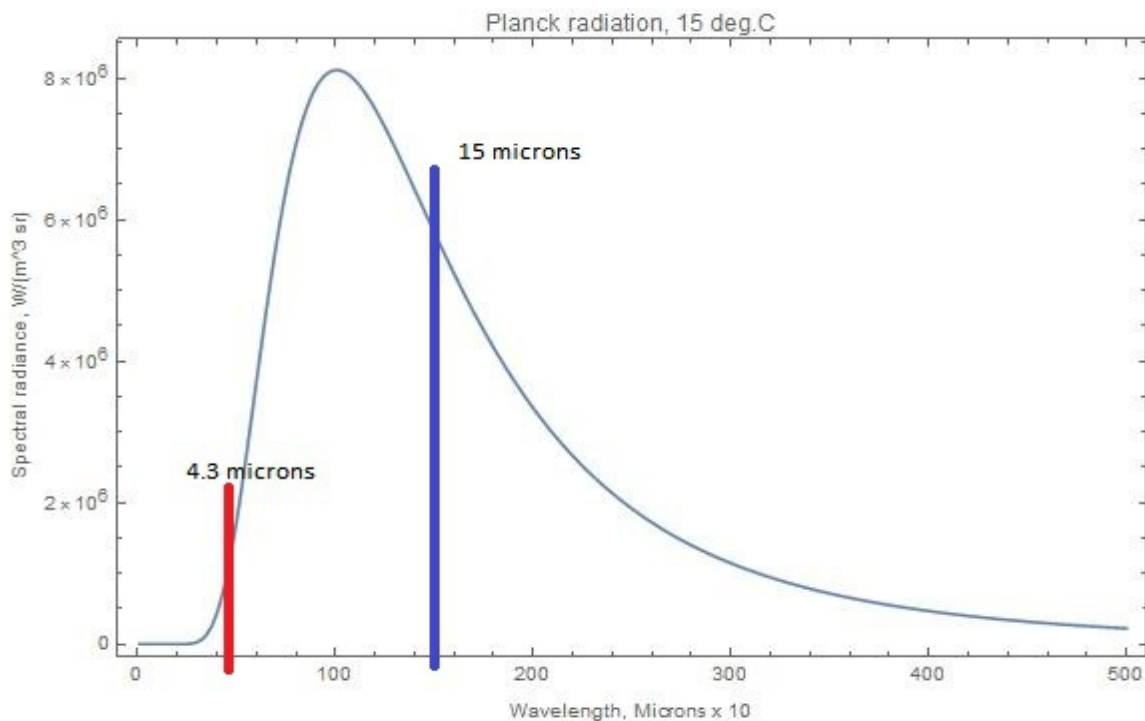
- 13.26 to 17.07 microns,
- 4.189 to 4.377 microns,
- 2.663 to 2.823 microns, and
- 1.995 to 2.036 microns.

Earth's thermal radiation

Applying these values to the Planck function for an average Earth temperature of 15.5°C (288.5°K) gave the following energy values for the respective absorption bands:

- energy density 9.21554×10^{-7} Joules per cubic metre, being 0.1758 of the total emission and a photon density of $6.948 \times 10^{+13}$ photons per cubic metre,
- energy density 5.723×10^{-9} J/cu.m., being 0.00109 of the total emission and a photon density of $1.220 \times 10^{+11}$ photons per cu. m.,
- energy density 6.666×10^{-11} J/cu.m., being 1.27×10^{-5} of the total emission and a photon density of $9.0038 \times 10^{+8}$ photons per cu. m.,
- energy density 1.11×10^{-13} J/cu.m., being 2.119×10^{-8} of the total emission and a photon density of $1.1199 \times 10^{+6}$ photons per cu. m.,

for a total photon density of $6.9603 \times 10^{+13}$ photons per cu. m. of which the 15 micron band dominates with 99.83% of the total.



Thus the only absorption and re-emission by atmospheric CO₂ of any consequence must be the photons in the 15 micron band.

The source temperatures that radiate at the CO₂ absorption peaks are:

- 193.5°K, ie. -79.5°C,
- 685°K, ie. 412°C,
- 1080°K, ie. 807°C, and

d. 1446°K, ie. 1173°C.

Since 99.83% of the photons that may be absorbed by the atmospheric CO₂ molecules will be from the 15 micron absorption band and these represent radiation from a source at 193.5°K, they will not heat the Earth at its average surface temperature of 288.5°K. Only radiation of a wavelength less than 10.044 microns, the peak of radiation from a source at 288.5°K, will cause heating of the Earth. The absorption of radiation in the three shorter wavelength, 'hot', bands is insignificant.

Temperatures of less than 193.5°K, ie. -79.5°C, occur occasionally in Antarctica and the surface there is too cold to produce any significant radiation in the three shorter wavelength absorption bands.

Absorption and re-emission process

When a CO₂ molecule absorbs a photon it changes to a vibrational mode for the three atoms making up the molecule. This mode depends on the energy of the photon absorbed which must be in one of a limited number of energy levels due to there being a limited number of geometrical vibrational modes available.

On return of an energised molecule to its ground state, it may emit a photon of the original absorbed wavelength (energy) in an arbitrary direction. Otherwise the energised molecule may collide with another atmospheric molecule causing it to emit radiation at a longer wavelength, lesser energy, than that absorbed with the balance of the energy becoming kinetic energy of motion of the pair of colliding molecules or no radiation, merely a transfer of state to kinetic energy.

In every case the total energy involved does not change. There is no additional energy created by the action so there is no heating generated by the CO₂ molecule. Any change of kinetic energy becomes part of the normal convective process of cooling the Earth's surface.

The laws of thermodynamics mandate that heat cannot flow from cold to hot so the return of some radiation back towards the Earth cannot cause surface heating as it is only a fraction of the energy being emitted from the surface. It is not heat from a hotter source so there is no surface heating as proposed by the Greenhouse Effect.

Sun's radiation

Applying the same absorption bands to the Planck function for the Sun's radiation at 5772°K adjusted by a divisor of 46,238.8 to provide for the decrease in intensity by the square of the distance apart, gave the following energy values for the respective absorption bands at the Earth's average distance from the Sun:

- a. energy density 3.0256×10^{-9} Joules per cubic metre, being 1.661×10^{-4} of the total emission and a photon density of $2.2812 \times 10^{+11}$ photons per cubic metre,
- b. energy density 1.789×10^{-8} J/cu.m., being 9.8506×10^{-4} of the total emission and a photon density of $3.8137 \times 10^{+11}$ photons per cu. m.,
- c. energy density 7.5175×10^{-8} J/cu.m., being 4.139×10^{-3} of the total emission and a photon density of $1.0154 \times 10^{+12}$ photons per cu. m.,
- d. energy density 5.53×10^{-8} J/cu.m., being 3.046×10^{-3} of the total emission and a photon density of $5.5789 \times 10^{+11}$ photons per cu. m.

All three of the shorter wavelength, 'hot', absorption bands have greater energy density emanating from the Sun than that from the Earth. The greenhouse effect would apply equally well to this incoming

radiation and should have caused the Earth to cool as the concentration of atmospheric CO₂ increased due to an increase in the amount of radiation back into space before it could warm the Earth.

Molecular density:

In the abstract, Witteman [Ref.1], it states:

“Roughly, only 10% of its spectrum is active and the thermal radiation that falls within these regions is fully absorbed. This is not only the case for 400 ppm of CO₂ in the atmosphere but also for much smaller concentration values.”

Further on in the text, it states:

“The air density is about 2.78×10^{19} molecules per cm³. The present content of CO₂ is 400 ppm or 0.04% so that $N_{\text{CO}_2} = 1.1 \times 10^{16}$ cm³. At atmospheric temperatures practically all molecules are in the vibrational ground state.”

The total photon density from the four emission bands is shown above to be of $6.929 \times 10^{+7}$ photons per cm³, that is, at 400 ppm CO₂ concentration there is only one photon for every 158,750,000 CO₂ molecules. The effect of the absorption and re-emission of the Earth's radiation at this rate of photons must be completely insignificant as is the current rate of increase in CO₂ of 3.4 ppm per annum. Furthermore all of the radiation emitted by the surface must be absorbed within a few hundred metres of the surface so increasing the CO₂ concentration will not cause any change as all of the emitted radiation that can be absorbed, is already completely absorbed at the lower concentration.

Conclusion:

The Executive Summary, page xi, of the UN IPCC report “Climate Change - The IPCC Scientific Assessment” 1990, stated:

“We calculate with confidence that:

- some gases are potentially more effective than others at changing climate, and their relative effectiveness can be estimated Carbon dioxide has been responsible for over half the enhanced greenhouse effect in the past, and is likely to remain so in the future.”

Then in the Policymaker's Summary, page xiii, it stated:

“What natural factors are important?

One of the most important factors is the **greenhouse effect**, a simplified explanation of which is as follows Short-wave solar radiation can pass through the clear atmosphere relatively unimpeded But long-wave terrestrial radiation emitted by the warm surface of the Earth is partially absorbed and then re-emitted by a number of trace gases in the cooler atmosphere above. Since, on average, the outgoing long wave radiation balances the incoming solar radiation both the atmosphere and the surface will be warmer than they would be without the greenhouse gases”

Later reports have continued on this theme with an emphasis on the dire consequences that will arise from global warming and the associated climate change. They fail to reveal to the reader that infrared radiation forms 52% of the Sun's emitted radiation.

This analysis has shown that the greenhouse effect arising from the dominant long wavelength CO₂ absorption band emanating from the Earth's surface at 288°K cannot cause warming of the surface.

However, radiation back into space from the shorter wavelength CO₂ absorption bands, emitted from the Sun, should have caused the Earth's temperature to decrease as the CO₂ concentration increased.

Within the limits of measurement, neither of these events have taken place thereby negating the UN IPCC proposition that CO₂ has caused global warming or climate change. The factor of the order

of 10^8 between the CO_2 molecular density in the atmosphere relative to the photon emission from the Earth's surface shows why there is no measurable effect. This supports the findings from the analysis of climate data from stations across the globe that have shown that the atmospheric temperature is independent of the CO_2 concentration but correlates with the annual rate of change of CO_2 concentration due to climate change driving the change in CO_2 .

It is important to be aware that the above discussion only deals with the radiative effect of CO_2 whereby it absorbs and releases heat energy from the Sun and the Earth's surface. It is a simple, stable molecule that does not, of itself generate any heat so it cannot increase the temperature of anything, it passes on part of the heat energy already present in the environment.

References:

1. W.J.Witteman, The absorption of thermal emitted infrared radiation by CO_2 .
<https://principia-scientific.org/the-absorption-of-thermal-emitted-infrared-radiation-by-co2/>
2. HITRAN website, <http://www.hitran.ioa.ru> , a collaboration between Harvard-Smithsonian Center for Astrophysics (CFA), Cambridge, MA, USA, V.E. Zuev Institute of Atmospheric Optics (IAO), Tomsk, Russia National Research Tomsk State University (TSU), Tomsk, Russia