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by

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GREENHOUSE MOLECULES, THEIR SPECTRA AND FUNCTION IN THE ATMOSPHERE

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INTRODUCTION

The Earth's atmosphere is largely composed of the diatomic molecules, dinitrogen, N_2, and dioxygen, O_2; 78.08% and 20.93% by volume respectively. They are radiatively inactive as is explained below. The remaining 0.97% is made up from argon (0.93%), carbon dioxide, (CO_2 0.037%), methane, (CH_4 0.00017%), dinitrogen monoxide, (N_2O 0.000032%) and even smaller amounts of carbon monoxide, ozone, (O_3) and the Group 18 inert gases, neon, helium, krypton and xenon. There are also traces of many other volatile compounds. Greenhouse [GH] molecules are those that absorb terrestrial radiation, that which is emitted by the Earth's surface as a result of the warming effect of incoming solar radiation. Their absorption characteristics allow them to act in the retention of heat in the atmosphere and to ensure that the global mean temperature of the atmosphere is tolerable to life – the greenhouse effect. The more important compounds are water, carbon dioxide, methane, dinitrogen monoxide (nitrous oxide), and ozone, in decreasing order of effectiveness, mainly because of their concentrations. This paper outlines the reasons for their effectiveness.

Ozone is a very minor contributor to the greenhouse effect in the troposphere, but has a very important contribution to the properties of the stratosphere. The radiation, known as the electromagnetic spectrum, consists of gamma rays, X-rays, ultra-violet radiation, visible light and infrared radiation, in decreasing order of energy. The vast majority of the highly energetic end of the radiation from the Sun, gamma and X-rays, are absorbed by the upper atmosphere. The ultra-violet region is divided into four parts; UVA (with wavelengths between 320–400 nanometres, 1 nm = 10^{-9} metres), UVB (280–320 nm) and UVC (200–280 nm) and the far-UV (100–200 nm). Far-UV radiation is absorbed in the upper atmosphere (50 km) by dioxygen molecules, as is UVC radiation in the stratosphere (in spite of the claims by the sun protection industry). They cause the oxygen molecules to dissociate to give oxygen atoms, which then combine with the nearest oxygen molecules to produce ozone, O_3 (trioxygen).

$$O_2 \xrightarrow{\text{UV}} 2O$$
$$O + O_2 \longrightarrow O_3$$

Ozone molecules also absorb some of the UVB radiation and protect the Earth's surface, allowing life to persist. The small fraction of UVB radiation that does penetrate to the ground (~1%) should be avoided as it can initiate skin cancers. The less energetic UVA radiation produces temporary sunburn when incident upon skin.

The radiation that does penetrate the stratosphere causes the warming of the lower region, the troposphere in which weather and climate occur. Just why and how the greenhouse molecules act as they do is the main subject of this paper.

INFRARED [IR] SPECTROSCOPY OF GREENHOUSE GASES

This section is limited to the greenhouse gases; water, CO_2, methane and dinitrogen monoxide. First, the reasons why they are greenhouse gases are dealt with and these are followed by their IR spectra with interpretations. Ozone is mentioned briefly.

Why do molecules absorb IR radiation?

In the IR region radiation has sufficient energy to cause molecules to rotate or vibrate or both, dependent upon certain **selection rules**. To acquire rotational energy directly a molecule must have a permanent dipole moment, i.e., there must be a permanent charge separation within the molecule. The rule for acquiring vibrational energy is slightly different; the particular vibration has to be associated with a *change* in dipole moment to be IR active. If a molecule is vibrationally active, it can also acquire and dispense with rotational energy.

The diatomic molecules, N_2 and O_2, have zero dipole moment and do not qualify by either of the rules and cannot interact with IR radiation, hence they are not greenhouse gases, even though they account for 99.93% of the dry atmosphere.

The structures and permanent dipole moments (if any) of the greenhouse gases are shown in Figure 1.

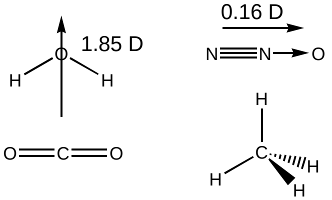

Figure 1: The structures and dipole moments of the greenhouse gas molecules. The non-zero dipole moments are given in units of Debyes [D, 1 D = 3.33564 × 10^{-30} C m (Coulomb metres)] and the arrows point in the direction of the more negative ends of the dipoles. CO_2 and methane do not possess dipole moments

The allowed interactions of the greenhouse gas molecules with IR radiation are as follows.

Water. The molecule has a permanent dipole moment, so rotational changes are allowed and these are spread throughout the IR spectral range. In addition the molecule possesses three fundamental vibration modes, which are shown in Figure 2.

Only the bending vibration at 1595 cm^{-1} is relevant to the absorption of terrestrial radiation.

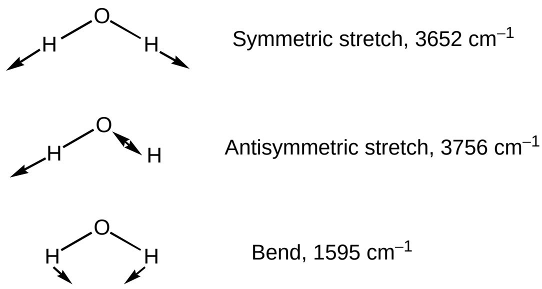

Figure 2: The three fundamental vibrational modes of the water molecule and their wavenumbers

Carbon Dioxide. The molecule is linear and symmetrical about the central carbon atom; its dipole moment is zero because of its symmetry and rotational changes cannot be brought about by the direct absorption of radiation. The three vibrational modes of the molecule are shown in Figure 3, together with their fundamental wavenumbers.

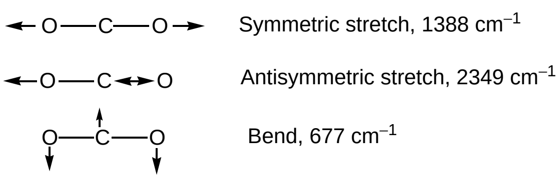

Figure 3: The three fundamental vibrational modes of the CO_2 molecule and their wavenumbers; the bend occurs in two planes at right angles and which contain the molecular axis

The symmetric stretching mode is not associated with a changing dipole moment and is not radiatively active. The other vibrations do cause a change in the dipole moment of the molecule and are active radiatively.

Dinitrogen monoxide. Although the molecule has a permanent dipole moment, this is relatively small and the possible rotational transitions are of no importance in atmospheric spectra because of the very small incidence of the compound. As a linear molecule, N_2O has three fundamental vibrational modes similar to those of CO_2. The symmetric stretch is at 1285 cm^{-1}, the antisymmetric stretch is at 2224 cm^{-1}, and the bend is at 589 cm^{-1}.

Methane. The molecule has a zero dipole moment because of its symmetry and rotational interaction with radiation is not possible. The only fundamental vibration of the methane molecule of interest in the 0–2500 cm^{-1} range is at 1306 cm^{-1} and is a mixture of stretching and bending as depicted in Figure 4.

Ozone. The structure of the molecule is shown in Figure 5; its dipole moment is indicated. The non-linear molecule has a dipole moment of 0.53 D, the terminal oxygen atoms being slightly negatively charged to balance the partial positive charge

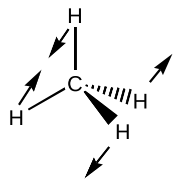

Figure 4: One of the stretching and bending modes of the methane molecule

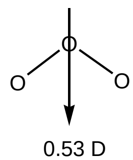

Figure 5: The structure and dipole moment of the ozone molecule

on the central oxygen atom. The absorption spectrum of ozone exhibits a strong absorption at 1043 cm^{-1} that arises mainly from the antisymmetric stretching mode. There are weaker contributions in the same region from the symmetric stretching mode and other weaker bands. Because of its small concentration, ozone contributes to the GH effect in the troposphere to a minor degree. Its role in the stratosphere is much more dominant.

The infrared (IR) spectra of the four main GH gases over a 100 metre path length are presented in Figure 6, their concentrations being those that pertain to the atmosphere at sea-level, and in the case of water that which amounts to 45% humidity. One of the conventional methods of representing spectra in the IR is to plot the transmission of the sample against the wavenumber, $1/\lambda = \nu/c$ (λ = wavelength, ν = frequency, c = velocity of light). The transmission (T, sometimes referred to as

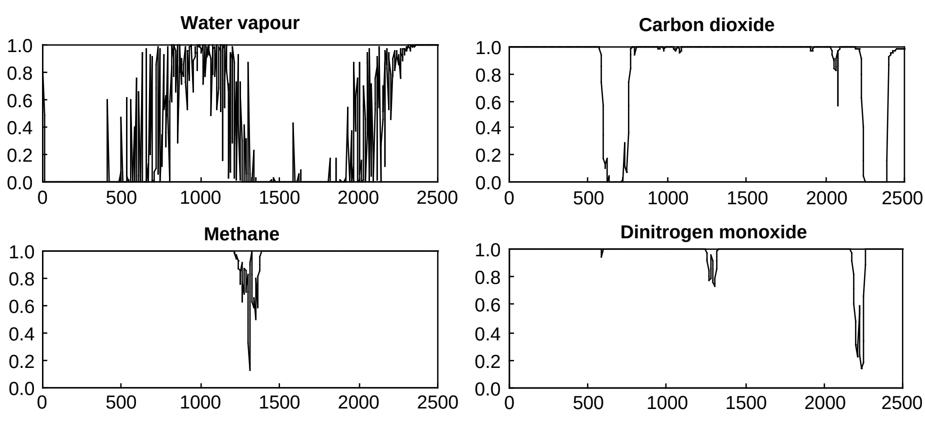

Figure 6: Infrared spectra of the greenhouse gases as calculated using the HITRAN data base[1]; Transmission is plotted against wavenumber (reciprocal cm)

transmittance) is the extent by which the incident radiation at any wavenumber is transmitted by the sample; If all the radiation is absorbed T = 0, if none is absorbed T = 1. The wavenumber is a convenient way of representing the frequency of the radiation. The actual frequencies have units of hertz (Hz) and are too large. To be able to deal with reasonably small numbers, the frequencies are divided by the speed of light (in cm per second) to give the wavenumber. The wavenumber represents the number of waves in a centimetre when expressed as reciprocal centimetres, cm^{-1}. The wavenumber ranges of the spectra are from 0–2500 cm^{-1}. This covers the frequency range of terrestrial radiation that is emitted by the warmed Earth.

The water vapour spectrum indicates almost total absorption from 0–500 cm^{-1}, followed from 500–1300 cm^{-1} by a host of weak rotational bands. From 1300 cm^{-1} the absorption increases to almost total again as the centre of the bending vibrational mode at 1595 cm^{-1} is approached and beyond 1800 cm^{-1} the rotational structure of the bending mode decreases in intensity until 2300 cm^{-1} when the transmission becomes 100%. The CO_2 spectrum is dominated by the bending vibration, centred at 667 cm^{-1} and the antisymmetrical stretching mode at 2349 cm^{-1}. The extra very weak bands arise from further excitations and represent very small absorptions that are, nevertheless significant in calculating the GH effect accurately. The methane spectrum shows the bending/stretching vibration at 1306 cm^{-1} and that of dinitrogen monoxide shows the three bands as described above.

The Earth's surface has a mean global temperature of 288 K and its emission approximates to that of a blackbody at that temperature, consisting of continuous radiation unlike that of the GHGs which is specific to each molecule and made up from discrete rotational or rotation-vibrational bands. The Planck (or blackbody) radiance of the Earth's surface is shown by the heavy smooth curve in Figure 7, together with the combined effects on it of the absorptions of the GHGs.

There is considerable absorption of the radiation emitted by the surface and only a significant transmission in the region between 800–1250 cm^{-1} – the so-called *window region* where no molecules absorb significantly. As much as 22.5% of the emitted radiance passes through the window. Unless absorbed by clouds the radiation in the window region escapes to space and does not participate in greenhouse warming.

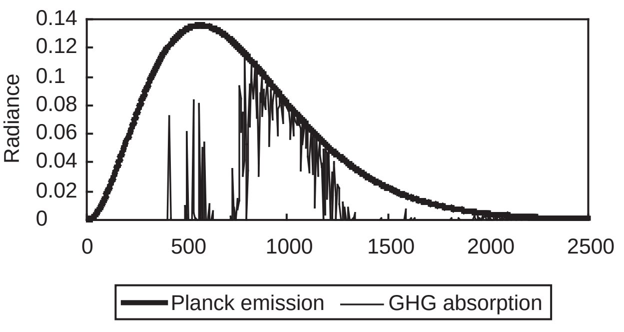

Figure 7: The radiance of the Earth's surface and the absorption of it by the GHGs. The units of radiance are Watts per square metre per cm^{-1} per steradian [solid angle] and the wavenumber axis is as above, reciprocal cm

Table 1: Contributions to the absorption of the Earth's radiance by the first 100 metres of the atmosphere

GHG	% Absorption	Absorption relative To water vapour = 1
Water vapour	68.2	1.000
CO_2 (285 ppmv)	17.0	0.249
CO_2 (570 ppmv)	18.5	0.271
CH_4	1.2	0.018
N_2O	0.5	0.007
Total [water, CO_2 (285 ppmv), CH_4, N_2O]	86.9	
Combination with 285 ppmv CO_2	72.9	1.069
Combination with 570 ppmv CO_2	73.4	1.076

Some idea of the relative contributions to global warming by the GHGs at the Earth's surface may be calculated from the spectral data. Percentage absorption values are useful; they are calculated as %A = 100 – %T (T = transmission). The values for CO_2 in the atmosphere in the pre-industrial era of 285 ppmv and double that value, so crucial to the IPCC arguments, are given in Table 1, together with the contributions from water vapour, N_2O and methane.

The absorption values for the pre-industrial atmosphere add up to 86.9%, significantly lower than the combined value of 72.9%. This occurs because there is considerable overlap between the spectral bands of water vapour and those of the other GHGs. If the concentration of CO_2 were to be doubled in the absence of the other GHGs the increase in absorption would be 1.5%. In the presence of the other GHGs the same doubling of concentration achieves an increase in absorption of only 0.5%, only one third of its effect if it were the only GHG present. Whether this overlap effect is properly built into models of the atmosphere gives rise to some scepticism.

The GHGs absorb 72.9% of the available radiance, leaving 27.1% that is transmitted of which an amount equivalent to 22.5% of the total passes through the window and the other parts of the spectral range transmit only 4.6%. For the doubled CO_2 case this small percentage decreases slightly to 4.1%. These small percentage transmissions are reduced by 72.9% and 73.4% respectively by the second layer of 100 m of the atmosphere so that only ~1% in both cases is transmitted to the region higher than 200 m.

SIZE OF THE GREENHOUSE EFFECT

Incoming solar energy amounts to 342 Watts per square metre (W m^{-2}) of which 107 W m^{-2} are reflected by the atmosphere or the surface. Thus, 235 W m^{-2} contribute to the warming of the Earth. On a long-term basis, the Earth is in radiative equilibrium, i.e., it loses the same amount of radiation to space as it receives. The Stefan-Boltzmann law equates radiation intensity with the temperature of the emitting blackbody:

$$E = \sigma T^4$$

The emitted radiation has an intensity given by the product of the Stefan-Boltzmann constant (5.67×10^{-8} W m^{-2} K^{-4}) and the fourth power of the temperature of the blackbody. Taking the Earth's emission as approximately blackbody radiation, the output of 235 Wm^{-2} is equivalent to a temperature of 253.7 K. The Earth's surface temperature is generally agreed to be 288 K, thus the resultant global warming due to the effects of the GHGs, convection, evaporation of water from the oceans, clouds, aerosols, etc., is 288 – 253.7 = 34.3 K. What that figure will reach if the CO_2 concentration were to become 570 ppmv is the very important question that faces the climatology community.

Taking the fractions of terrestrial radiation absorbed by the GHGs as representative, their contributions to the GH effect are given in Table 2.

Table 2: Contributions of GHGs to the GH effect

GHG	% Contribution to GH effect	
	285 ppmv CO_2	570 ppmv CO_2
Water vapour	78.5	77.1
CO_2	19.6	20.9
CH_4	1.4	1.4
N_2O	0.6	0.6

The contribution of carbon dioxide to the total global warming of 34.2 K may be calculated to be 6.7 K from the results of Table 2. That assumes that radiative transfer is the only mechanism whereby heat is transferred from the surface to the atmosphere. The global energy budget[2] indicates that the warming of the atmosphere has a major contribution from the latent heat of evaporated water of 78 W m^{-2}. If this is converted into a radiative flux, the total radiative flux would be 390 + 78 = 468 W m^{-2} which would be emitted by a surface with a Stefan-Boltzmann temperature of 301.4 K, a global warming effect of 301.4 – 253.7 = 47.7 K. Thus, the effect of water evaporation is to cool the surface by 47.7 – 34.3 = 13.4 K. These results are shown in Figure 8.

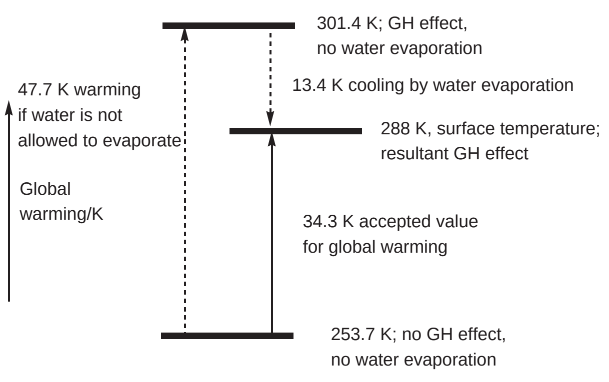

Figure 8: A calculation of the cooling effect of water evaporation on the Earth's surface temperature

On a radiative-alone basis, the 47.7 K of warming may be divided up into contributions from water and carbon dioxide from the figures given in Table 2 and amount to 37.4 K from water and 9.3 K from carbon dioxide. The water contribution should then be reduced by the cooling effect from evaporation to 24.0 K. The above calculations apply only to the first 100 m of the atmosphere and water is less and less effective in comparison to carbon dioxide as altitude increases. This is because the contribution to the atmospheric content of water reduces very rapidly with altitude, the ever-lower temperatures determining that the water vapour content decreases, that of carbon dioxide only decreasing with the decreasing pressure. At sea level the mean molecular ratio of water vapour to CO_2 is around 23, but at an altitude of 10 km the value is as low as 0.2. It would be expected that more CO_2 would have a greater effect on atmospheric warming at higher altitudes, but this seems not to be occurring in spite of the predictions of most GCMs.

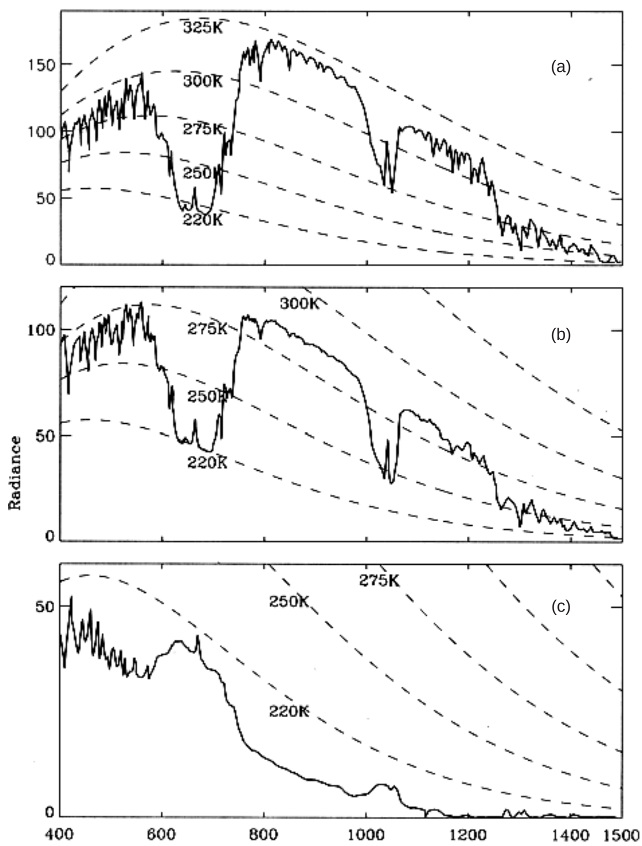

Figure 9: Emission spectra of the Earth taken by the Nimbus 4 satellite. The radiance units are milliWatts per square metre per cm^{-1} per steradian. Spectrum (a) is measured over the Sahara Desert, spectrum (b) over the Mediterranean, and spectrum (c) over the Antarctic

A fairly accurate estimate of the importance of the various greenhouse gases may be made by an analysis of emission spectra of the Earth as recorded by satellites. Three examples are given in Figure 9.

From 400 cm^{-1} to 600 cm^{-1} the spectra consist of rotational transitions of water molecules, and the regions from 600 cm^{-1} to 800 cm^{-1} are dominated by the main bending mode of carbon dioxide and some combination bands (i.e., mixtures of bends and stretches) that are of smaller intensity, together with some of the water rotation bands which overlap with the carbon dioxide bands. From 800 to 1300 cm^{-1} are the IR window regions with some ozone absorption and emission spectra at around 1043 cm^{-1} and essentially demonstrate the temperature of the surface when compared to the Planck emission spectra that are incorporated into each spectrum. The Saharan surface temperature is around 320 K, that of the Mediterranean is around 285 K and that of the Antarctic is around 210 K. From 1300 cm^{-1} the spectra consist of vibration-rotation bands of water molecules, and the bending vibrations of methane and dinitrogen monoxide molecules.

The influence of carbon dioxide can be seen from the Saharan and Mediterranean spectra as absorbing all of the radiation in the 600–800 cm^{-1} regions and emitting about 25% of it. The large absorption areas in the two spectra show how carbon dioxide is an important GHG. Spectrum (c) shows that emission by carbon dioxide in the Polar Regions is relatively more important and arises because of the low water vapour pressure. A detailed estimate of the effects of the GHGs from the analysis of spectra such as those shown in Figure 9 indicates that carbon dioxide provides about 7–8ºC of global warming, much the same conclusion that comes from a study of its absorption characteristics.

CONCLUDING REMARKS

The main GHG's spectra have been described and explained. The absorption characteristics of the GHGs indicate their relative importance in GH warming. The discussion is restricted to only a 100 m path length, the whole atmosphere being equivalent to one of 8 km at a pressure of 1000 mb and a temperature of 288 K. The basic spectroscopic data are presented and from these the absorption properties of the atmosphere are derived in the general circulation models. In addition to the properties of the GHGs, those of clouds, other aerosols and particulate matter are built into model programmes with a considerable degree of parametric uncertainty. The GCMs take feedbacks into account, such as the supposed positive feedback from extra warming caused by the absorption of radiation by extra water vapour. Such feedbacks have to be parameterised and although they may contribute a greater reality to the models, they also introduce extra uncertainties.

REFERENCES

1. The HITRAN database is used universally as the basis for simulations of spectra; it is constructed from experimental data and supplied by the University of South Florida.
2. See Kiehl, J. T., and K. E. Trenberth, *Bull. Am. Met. Soc.*, **78**, 197 (1997).