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The Greenhouse Effect at the Molecular Level

The greenhouse effect is examined at the molecular level for CO_2 and H_2O in terms of the absorption and reemission of radiation. Results show that water vapor and the incoming solar radiation to be the dominant contributors to the greenhouse effect.

Introduction

The greenhouse effect is generally modeled on a macro scale by designating energy balance for the planetary system. This involves the incoming solar radiation, reflected solar energy, absorbed solar energy at the ground, and subsequent re-radiation at longer wavelengths from the ground. The reradiated energy is then either transmitted out of the system or absorbed by the greenhouse gases and thus changing the overall energy balance. This is generally diagrammed as shown below in Figure 1.

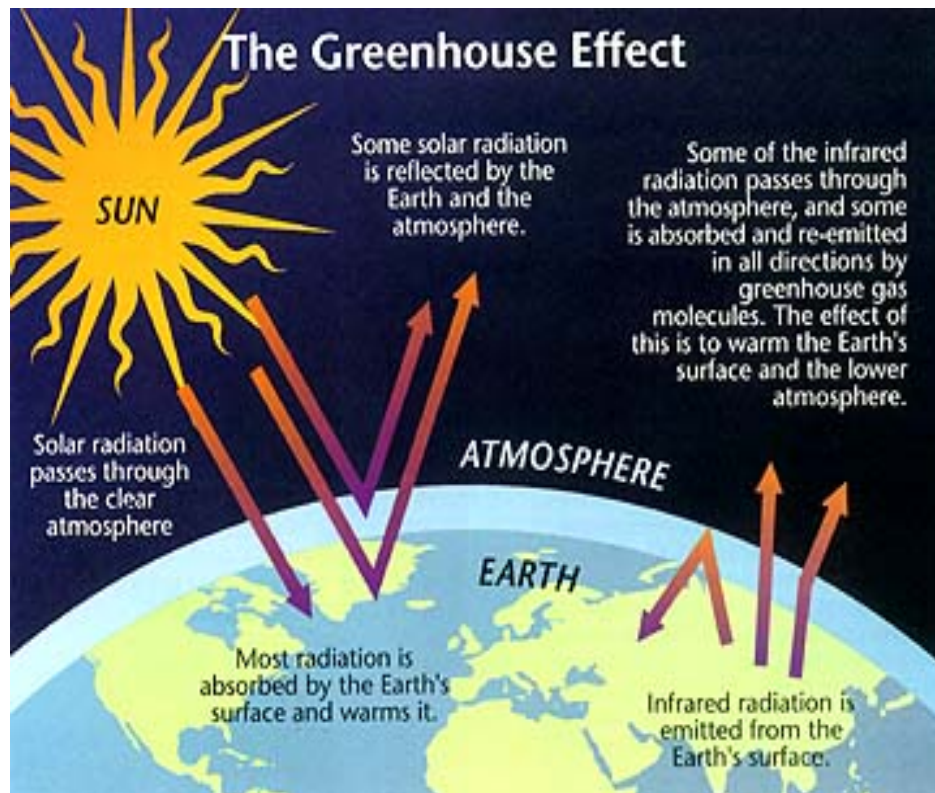


Fig 1. The greenhouse effect as a balance of incoming and outgoing energy flows

However, the entire notion of the effects of so-called greenhouse gases hinges on the absorption and reemission of radiation at the individual molecular level. This paper presents an evaluation of that process by utilizing a different computational technique of Einstein coefficients. This will allow an easier approach to an order of magnitude result as opposed to the more accurate, but tedious and sometime near impossible route of direct integration.

Computation

The quantum mechanically correct, and exact way to approach this problem is to integrate the incoming radiation with respect to the appropriate transitions within each molecule. Then, one must also calculate the resulting emission of radiation from the excited states. It is this approach that Petty [1] outlines with integrals such as:

$$Abs = \int_{\lambda_i}^{\lambda_n} I(\lambda)PS(\lambda)d\lambda \quad (1)$$

where this integral calculates the net absorption of radiation between two wavelength limits. In the equation, I is the incoming radiation intensity, P is the transition probability, and S is the line shape. Once the molecules have been excited by the absorption of the incoming radiation, they will then re-emit the energy through transitions to lower energy states. This process can be calculated via the standard dipole rate equation:

$$R = (constant)|\langle\psi'|er|\psi\rangle|^2 \quad (2)$$

Where the squared matrix element is the dipole transition probability; the same as P in equation (1).

It will be noted that in both cases represented by the above equations it is necessary to know the molecular wavefunctions for the states involved, and then to actually evaluate the integrals. While the wavefunctions can be approximated by various techniques, evaluation of the integrals is a long and very tedious process. Just obtaining the approximate wavefunctions for a tri-atomic molecule such as CO₂ and H₂O is very difficult.

I will propose a way around this difficulty by using the technique of Einstein coefficients. This approach, while still an approximation technique, has been successful in the past by being used initially for calculating such quantum probabilities, and was also used in developing the theory behind the laser.

First, let's examine the radiation field we are dealing with and the molecular transitions that are relevant. The radiation field in which a "greenhouse" molecule such as water or carbon dioxide finds itself actually consists of 3 separate fields combined together. They are: the incoming solar radiation, the blackbody radiation emitted from the earth's surface after it absorbs solar radiation, and then the radiation field from the atmospheric molecules radiation after being excited by the solar field and the earth field. All three can be represented by blackbody curves as shown in this diagram from Petty:

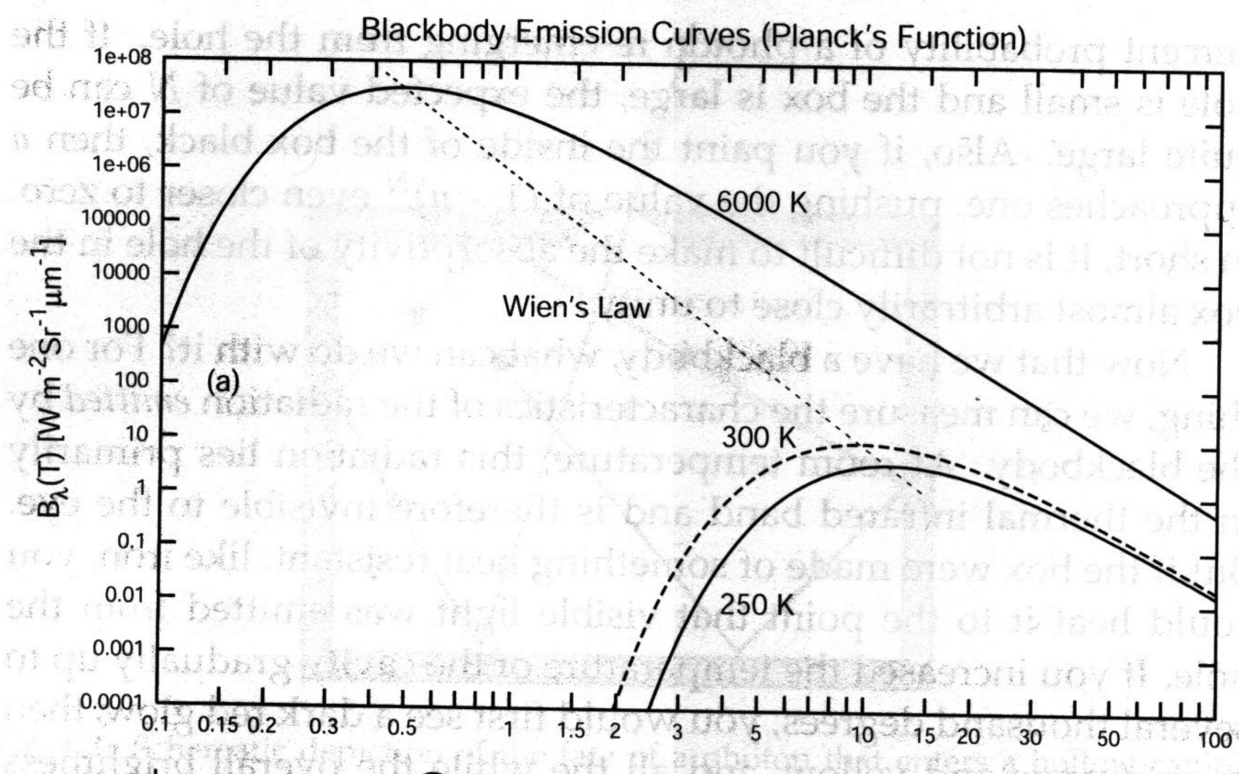


Figure 1. Blackbody radiation curves for the solar radiation field, and the re-emitted earth and atmospheric fields. The solar field at 6000K, and the ground/atmosphere fields at around 300K.

The relevant absorption/emission bands for water and carbon dioxide are shown below, again from Petty:

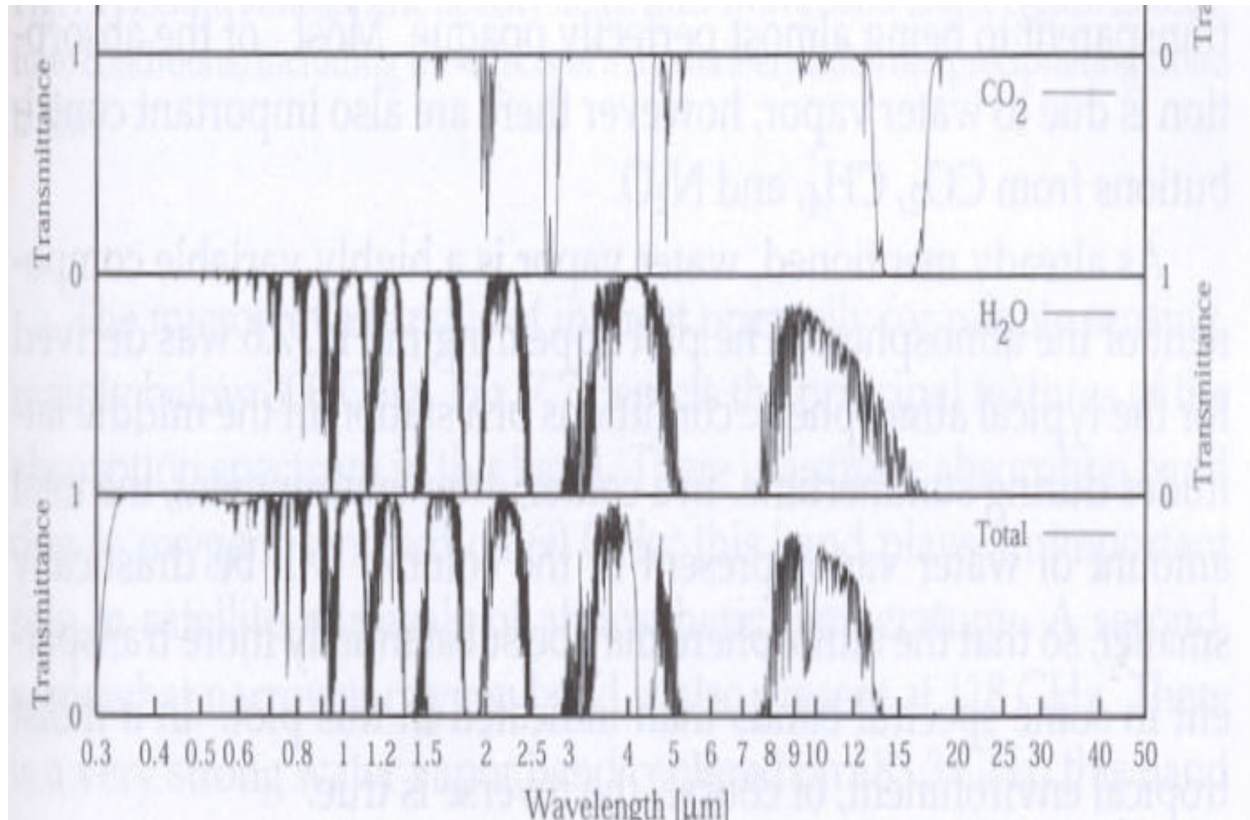


Figure 2. Absorption bands for water and carbon dioxide along with the sum of the two .

For this discussion it is important to note the differences between the absorption bands of water and CO₂. Carbon dioxide's absorption is in large part due to the well-known band at 15μ, with several much smaller bands in the near IR. Water, in contrast, has numerous bands in the near IR, and very strong bands at 1.3, 1.7, 2.5 microns. A very large absorption band exists at 6.5 microns and then from 15 microns and to higher wavelengths, water is completely opaque.

We begin the calculation by first noting the radiations fields present: consider a gas in a total radiation field consisting of 3 sources:

$$\rho(\nu)_{\text{sun}} , \quad \rho(\nu)_{\text{ground}} , \quad \rho(\nu)_{\text{gas}}$$

which are expressly given by the blackbody curves shown in Figure 1. The rate of absorption per molecule between the lower state 1 and the higher state 2 is

$$R_{12} = B_{12} [\rho(\nu)_{\text{sun}} + \rho(\nu)_{\text{grd}} + \rho(\nu)_{\text{gas}}] \quad (3)$$

where B_{12} is the Einstein coefficient for absorption (can be calculated from the wavefunctions of the molecule).

The rate of emission is then,

$$R_{21} = A_{21} + B_{21} [\rho(\nu)_{\text{sun}} + \rho(\nu)_{\text{grd}} + \rho(\nu)_{\text{gas}}] \quad (4)$$

where A_{21} is the coefficient for spontaneous emission, and B_{21} is the coefficient for stimulated emission. The total absorption and emission is then given by multiplying by the total number of molecules in each state:

$$N_1 R_{12} = \text{absorption} \quad \text{and} \quad N_2 R_{21} = \text{emission} \quad (5)$$

At this point, when one has a case of constant temperature, the total absorption and emission are equated to each other as we would be dealing with an equilibrium situation. However, here we are interested in cases where the relative processes could cause a temperature change, so instead we will look at the ratio of absorption to emission:

$$Abs / Emis = \frac{N_1 B_{12} (\rho(\nu)_{\text{sun}} + \rho(\nu)_{\text{grd}} + \rho(\nu)_{\text{gas}})}{N_2 A_{21} + N_2 B_{21} (\rho(\nu)_{\text{sun}} + \rho(\nu)_{\text{grd}} + \rho(\nu)_{\text{gas}})} \quad (6)$$

To make the numerical calculation more tractable, we will calculate this ratio for each respective radiation field, then combine the results. We can then express eqn. 6, for a single radiation field as

$$\frac{Abs}{Emis} = \frac{N_1 B_{12} \rho}{N_2 A_{21} + N_2 B_{21} \rho} \quad (7)$$

where ρ is the radiation field under investigation. From more complete quantum mechanical description of atomic and molecular transitions we know that the coefficients for stimulated absorption and emission are equal; i.e. $B_{12} = B_{21}$ [2]. So,

$$\frac{Abs}{Emis} = \frac{(N_1 / N_2) B \rho}{A_{21} + B \rho} \quad (8)$$

And the ratio of the spontaneous coefficient to the stimulated coefficient is given by:

$$\frac{A}{B} = \frac{8\pi h \nu^3}{c^3} \quad (9)$$

And inserting eqn. 9 into eqn. 8 yields:

$$\frac{Abs}{Emis} = \frac{N_1}{N_2} \left[\frac{\rho}{\rho + \frac{8\pi h \nu^3}{c^3}} \right] = \frac{N_1}{N_2} \left[\frac{1}{1 + \frac{8\pi h \nu^3}{c^3 \rho}} \right] \quad (10)$$

And, for the radiation field we will use the usual blackbody expression:

$$\rho(\nu) = \frac{8\pi h \nu^3}{c^3} \left(\frac{1}{e^{\frac{h\nu}{kT}} - 1} \right) \quad (11)$$

Inserting eqn.11 into eqn. 10 will yield the ratio of Absorption to Emission for the particular radiation field.

To begin, we will start with the solar field. However, the blackbody expression given by eqn. 11, is for the radiation field at the surface of the blackbody. This is not correct when we are dealing with the incoming solar radiation at the earth. In that case the radiation field must be decreased by the simple geometric factor of the ratio of the area of the earth compared to the surface area of a sphere of radius of the earth's orbit. This gives a factor of about 10^{-5} . In fact the expression for the solar field's contribution to the ratio then becomes:

$$\frac{Abs}{Emis} = (1.87 \times 10^{-5}) \frac{N_1}{N_2} e^{\frac{-hv}{kT_{sun}}} \quad (12)$$

Now we will do the same for the ground/gas fields. We combine them into one relation as the temperatures of the two fields are almost identical:

$$\frac{Abs}{Emis} = \frac{N_1 B_{12} [\rho_g + \rho_{gas}]}{N_2 A_{21} + N_2 B_{21} [\rho_g + \rho_{gas}]} \quad (13)$$

Again subbing for the A's and B's, and doing some algebra,

$$\frac{Abs}{Emis} = \frac{N_1}{N_2} \left[\frac{[\rho'_g + \rho'_{gas}]}{1 + [\rho'_g + \rho'_{gas}]} \right] \quad (14)$$

where $\rho' = \left(e^{\frac{hv}{kT}} - 1 \right)^{-1}$, and T is the temperature of either the ground or the gas.

The numerical part of the calculation begins with the radiation field intensities for each of the major bands of water and CO₂. The following tables are the results for these fields from eqn. 11:

| CO ₂ bands μm | ρ _{sun} eVsec/m ³ -μm | ρ _{grnd,gas} eVsec/m ³ -μm |
|-----------------------------|---|--|
| 14.9 | 0.003353255 | 1.11136132 |
| 7.8 | 0.011336263 | 0.34646715 |
| 7.2 | 0.013125366 | 0.25714787 |
| 5.17 | 0.023735425 | 0.04462181 |
| 4.82 | 0.026813591 | 0.02715957 |
| 4.25 | 0.033253879 | 0.00976793 |
| 2.7 | 0.068674315 | 4.2555E-05 |
| 1.95 | 0.107660538 | 8.7071E-08 |

Table 1: radiation fields for carbon dioxide bands.

| H ₂ O bands μm | ρ_{sun} eVsec/m ³ -μm | $\rho_{\text{grnd,gas}}$ eVsec/m ³ -μm |
|------------------------------|--|---|
| 25 | 0.001231502 | 1.026453257 |
| 20 | 0.00190079 | 1.142417667 |
| 17 | 0.002602459 | 1.156826791 |
| 6.26 | 0.016907356 | 0.136907152 |
| 3.17 | 0.053704229 | 0.000416794 |
| 2.74 | 0.067182818 | 5.34509E-05 |
| 2.66 | 0.070213009 | 3.36269E-05 |
| 1.88 | 0.112665723 | 3.71725E-08 |
| 1.34 | 0.160781953 | 2.12301E-12 |
| 1.13 | 0.18175628 | 3.29762E-15 |
| 0.94 | 0.196036562 | 7.06298E-19 |
| 0.906 | 0.197371443 | 1.05809E-19 |
| 0.82 | 0.197843096 | 4.21395E-22 |

Table 2: radiation fields for water bands.

Now let's calculate these ratios explicitly leaving out the factor of N_1/N_2 for the moment; it will be reinserted into the equation later. First for the solar radiation field:

| Abs/Emis H ₂ O sun | Abs/Emis CO ₂ sun |
|---------------------------------|--------------------------------|
| 1.69835E-05 | 1.59105E-05 |
| 1.65796E-05 | 1.37349E-05 |
| 1.62312E-05 | 1.33862E-05 |
| 1.27308E-05 | 1.17395E-05 |
| 8.7515E-06 | 1.13492E-05 |
| 7.7684E-06 | 1.0614E-05 |
| 7.56585E-06 | 7.66796E-06 |
| 5.1977E-06 | 5.44216E-06 |
| 3.1027E-06 | |
| 2.22211E-06 | |
| 1.44471E-06 | |
| 1.31235E-06 | |
| 9.93209E-07 | |
| | |

Table 3: Absorption/Emission ratios for each molecular band due to the incoming solar radiation.

Now we need to account for the relative populations of molecules, N_1/N_2 . For there to be a net absorption of radiation, the ratio N_1/N_2 must be greater than, or equal to, the inverse of the above numbers. This implies that there are more molecules in the lower state than the upper state. We then must have the temperature of the atmosphere such that this requirement is satisfied.

The ratio is given by the Boltzmann factor $N_1/N_2 = e^{h\nu/kT_{\text{atm}}}$, then the temperature of the atmosphere must satisfy:

$$T_{\text{atm}} \leq \frac{h\nu}{k \ln(\text{Emis} / \text{Abs})} \quad (15)$$

which yields for the above Emis/Abs ratios a temperature near 6000 K, so the atmosphere is certainly absorbent as its temperature is close to 300 K. In fact for $T = 300$ K, we get for N_1/N_2 of around 7 at 25 microns, to over 1025 in the visible region. Thus, we can finally get the total Abs/Emis by multiplying with the N ratio:

| Band H ₂ O μm | Abs/Emis H ₂ O total sun | Band CO ₂ μm | Abs/Emis CO ₂ total sun |
|-------------------------------------|-------------------------------------|------------------------------------|------------------------------------|
| 25 | 0.000127109 | 14.9 | 0.000465992 |
| 20 | 0.00020524 | 7.8 | 0.008701302 |
| 17 | 0.000313231 | 7.2 | 0.014517644 |
| 6.26 | 0.039433559 | 5.17 | 0.198004819 |
| 3.17 | 68.54934408 | 4.82 | 0.388092726 |
| 2.74 | 734.7599361 | 4.25 | 1.472088697 |
| 2.66 | 1243.213117 | 2.7 | 952.0366622 |
| 1.88 | 2188444.473 | 1.95 | 876621.5852 |
| 1.34 | 63167368555 | | |
| 1.13 | 4.85678E+13 | | |
| 0.94 | 2.56112E+17 | | |
| 0.906 | 1.73445E+18 | | |
| 0.82 | 4.4456E+20 | | |

Table 4: Total ratio of Abs/Emis of both molecules in the presence of the solar radiation field.

To put the numbers presented in Table 4 in context, if the ratio is less than 1, then the molecule is emitting more radiation than it is absorbing for that band. Both molecules become net absorbers at around the 3-4 micron region and lower.

This is not surprising when considering the net incoming radiation from the sun as given by its blackbody curve where the solar radiation increases rapidly from the IR into the visible and UV regions.

Now we need to do the same for the ground/gas field using eqn. 6. Here we will explicitly put in the fact that the ground and the air are at slightly different temperatures. From Petty, and also ucar.edu, we have the following for the surface temperature and the air temperature on average:

Surface temp = 289 K, air temp = 287 K,

from which we can then get the respective ρ 's. And then using the Boltzmann factor again for the N_1/N_2 ratio we get the Abs/Emis ratios:

| Band H ₂ O μm | Abs/Emis ground gas H ₂ O | Band CO ₂ μm | Abs/Emis ground gas CO ₂ |
|-------------------------------------|--------------------------------------|------------------------------------|-------------------------------------|
| 25 | 1.764269511 | 14.9 | 1.933967766 |
| 20 | 1.850512284 | 7.8 | 1.99684801 |
| 17 | 1.901468381 | 7.2 | 1.998157576 |
| 6.26 | 1.999354526 | 5.17 | 1.999881429 |
| 3.17 | 1.999999745 | 4.82 | 1.999941514 |
| 2.74 | 1.999999979 | 4.25 | 1.99998558 |
| 2.66 | 1.999999988 | 2.7 | 1.999999984 |
| 1.88 | 2 | 1.95 | 2 |
| 1.34 | 2 | | |
| 1.13 | 2 | | |
| 0.94 | 2 | | |
| 0.906 | 2 | | |
| 0.82 | 2 | | |

Table 5: Absorption/Emission ratio for the two molecules in the presence of radiation fields due to the earth's surface, and the surrounding atmosphere.

In Table 5, it is seen that the ratio quickly approaches an asymptotic value of 2. This is due to the fact that the atmospheric temperature and the earth surface temperature differ only by a small amount. As such, the expression becomes:

$$\frac{Abs}{Emis} = \frac{N_1}{N_2} \left[\frac{2}{e^{\frac{h\nu}{kT}} + 1} \right] \quad (16)$$

and with $N_1/N_2 = e^{h\nu/kT}$ we quickly get,

$$\frac{Abs}{Emis} = \left[\frac{2}{e^{\frac{-h\nu}{kT}} + 1} \right] \quad (17)$$

where the exponential term quickly approaches zero as the frequency increases.

What we have now is the total ratio of absorption to emission due to the presence of the sun, gas, and ground radiation fields for both water and CO₂. However, as we are interested in the effect these molecules have on the net temperature of the atmosphere, we need to convert this to energy. To find what this represents in terms of energy we must multiply by the energy of the photons in each band. Further, we must take into account whether there is absorption or emission. As stated before, this depends on whether the ratio is greater than or less than 1. If $A/E > 1$ for a band, take that ratio, multiply by $h\nu$ and add. If $A/E < 1$, invert the ratio, multiply by $h\nu$ again and then SUBTRACT from the previous sum. That would yield an indication of net energy loss/gain over the entire spectral region. The following is the result:

| Total H₂O sun(eV) | Total CO₂sun(eV) | Total H₂Og(eV) | Total CO₂g(eV) |
|-------------------------------------|------------------------------------|----------------------------------|----------------------------------|
| 6.76E+20 | 558567 | 17.148 | 4.597 |

Table 6: net total energy integrated over all the bands.

Table 6 gives a relative indication of the net contribution to atmospheric energy absorption due to the two molecules as well as the relative effect of the radiation fields. First of all, the net energy for both molecules is positive, which means both molecules are net absorbers of energy while in the atmosphere, and thus will contribute to a temperature increase via re-radiation and collisions. It should be noted immediately that the solar radiation field is dominant by a large factor for both molecules. In fact, the net contribution of the earth surface and the surrounding gas primarily in the infrared region is essentially non-existent when compared to the solar field. This result gives doubt to the whole model of the so-called “greenhouse effect” where it is usually stated that the outgoing IR from the surface contributes significantly to the net temperature. The last two columns of the table show that this is indeed occurring, but is very insignificant compared the overall effect of the solar radiation.

In the above calculation it is assumed that both gases occur in equal amounts. However the CO₂ energy numbers must be decreased by the average relative proportion of the gases; vis. .038%/3% = .013. Using this result we can then calculate the total energy Abs/Emis for the two gases:

$$\text{Total H}_2\text{O} = 6.76 \times 10^{20} \text{ eV}$$

$$\text{Total CO}_2 = 5.5 \times 10^5 * .013 = 7200 \text{ eV}$$

These numbers point out quite clearly that water is the very dominant (by a factor of 10¹⁷!!) “greenhouse gas”.

The above numbers represent an order of magnitude calculation. However, it also is a calculation that delves directly into the molecular absorption and emission processes which are claimed to be at the center of the planetary “greenhouse” effect. They quite clearly show that the earth’s temperature is primarily a result of the presence of water vapor and its interaction with the incoming solar radiation.

Collaborators and References

- Jim Barrante, Phys. Chem. Southern CT St. Univ.
- Larry Gould, Physics, U. Hartford
- Steve Zell, Env. Engineer, TRC Environmental, Windsor, CT

[1] Petty, Atm. Radiation, 2nd Ed, Sundog Pub. 2006, Madison, WI

[2] Howell & Siegel, Thermal Rad. Transfer, NASA, 1969, Wash. DC