

ON THE MOLECULAR SPECTROSCOPY OF THE GREENHOUSE EFFECT

Introduction

The greenhouse effect has been in the focus of major political discussions lately. As a physical chemist I have felt the urge to understand the basis of the effect. Even though the effect is well established and extensively discussed scientifically I have tried to approach the problem from the fundamental perspective in order to establish a personal understanding of the phenomenon. There are two obvious objections to this attitude; it can be a waste of time to work out what has already been analyzed and there is always the possibility that one makes a trivial mistake or forgets some important aspect of the problem. The text below should be read with these reservations kept in mind. It is written from a chemistry perspective with the aim of understanding the role of the characteristics of the IR-spectrum of molecules for the greenhouse effect.

The radiation field

The basis of the greenhouse effect is the cooling occurring through emission of radiation. It is thus essential to start with an account of the theory for the description of the radiation field. This is only briefly discussed in chemistry curricula, while it is more extensively described in physics courses. The basic theory was worked out roughly hundred years ago and the derivation of the Planck radiation law 1900 marks the birth of quantum theory. In a confined space of vacuum of macroscopic volume V there are a large number of modes of the radiation field. If the confining walls have a temperature T and there is a mechanism for energy exchange between walls and the field, for example through absorption/emission, there will be an equilibrium between the field and the thermal bath. The different modes are then on average excited to the extent given by the Boltzmann distribution, or more precisely the Bose-Einstein form. This yields the Planck distribution law for the energy dE_{om} in a small frequency interval $d\omega$

$$dE_{om} = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3 d\omega}{\exp\{\hbar\omega/kT\} - 1} \quad (1).$$

Since the function

$$f(x) = x^3 / \{\exp(x) - 1\} \quad (2)$$

has its maximum value for $x_{\max}=2.822$ it follows that the largest contribution to the energy of a thermally equilibrated radiation field comes from frequencies around $\omega_{\max} = 2.822kT/\hbar$. At an ambient temperature of $T=300\text{K}$ the corresponding wavelength is 17 microns or 585 cm^{-1} in wavenumber. Integrating the energy distribution over the whole spectrum gives

$$E = 4\sigma VT^4 / c \quad (3a,b),$$

$$\sigma \equiv \pi^2 k^4 / (60\hbar^3 c^2) = 5.67 \cdot 10^{-2} \text{ kgs}^{-3} \text{ K}^{-4}$$

where σ is called the Stefan-Boltzmann constant. From this the Helmholtz free energy and the entropy can be worked out from standard thermodynamic relations. One can note that the energy of the field increases with the forth power of the temperature. The black body radiation is isotropic and this implies that a volume element dV emits a radiation isotropically in all directions and from the Planck distribution law we have a spectral density

$$e_0(\omega, T) = \frac{1}{4\pi V} \frac{dE_{om}}{d\omega} = \frac{\hbar\omega^3}{4\pi^3 c^3 \{\exp(\hbar\omega/kT) - 1\}} \quad (4)$$

The energy flux leaving a volume element in the solid angle $2\pi d\cos(\theta)$ is then given by $ce_0 2\pi d(\cos(\theta)) d(\omega)$. This will hold also for a volume element in direct vicinity of a surface and we can use the relation to discuss absorption/emission of a body.

Microscopic description of absorption and emission of radiation

Einstein developed the fundamental equations for molecular description of energy exchange between field and molecules. Consider, for simplicity, a system with two energy levels k and l with an energy separation $\Delta E_{kl} = \hbar\omega_{kl}$. Einstein's fundamental contribution was to realize that there are three processes contributing to the energy exchange; absorption, spontaneous emission and stimulated emission. The rate of change of the population in the excited state l can in this picture be written

$$\frac{dP_l}{dt} = I(\omega)B_{lk}P_k - I(\omega)B_{kl}P_l - A_{kl}P_l \quad (5)$$

where $I(\omega)$ denotes the intensity of the radiation field at frequency ω . For a molecule in equilibrium with a radiation field the time derivative should be zero and it follows from this condition that

$$B_{lk} = B_{kl} = \left\{ \pi^2 c^3 / (\hbar \omega_{kl}^3) \right\} A_{kl} \quad (6)$$

where A is called the coefficient of spontaneous emission. When Einstein derived these equalities he used the condition that the expressions had to be consistent with Planck's law. When quantum theory was established the first equality follows from the Hermitian properties of the transition moments, while one arrives at the second equality using quantum electrodynamics.

In the macroscopic description of spectroscopy one uses Beer's law

$$I(\omega, z) = I(\omega, 0) \exp\{-\varepsilon(\omega)z\} \quad (7)$$

to describe the absorption. The absorption coefficient $\varepsilon(\omega)$, with the character of an inverse decay length, is in the absence of interactions, proportional to the concentration of the absorbing molecules. It describes the same process as in eq.(5) and to be consistent one has for a transition from state k to state l molecule M

$$\varepsilon_M(\omega - \omega_{kl}) = c_M \alpha_M(\omega - \omega_{kl}) = c_M P_k(T) B'_{kl} L(\omega - \omega_{kl}) \left\{ 1 - \exp[-\hbar \omega_{kl} / (kT)] \right\} \quad (8)$$

Here $L(x)$ represents a normalized line-shape function determined by the relaxation behavior and $P_k(T)$ is the thermally equilibrated population of the initial state k and B'_{kl} is proportional to the Einstein coefficient of eq.(6) and $B'_{kl} = \frac{\hbar \omega_{kl}}{c} B_{kl}$. For transitions where the energy gap is smaller than the thermal energy the absorption can be very low, as is well known in NMR. The absorbtivity α is in chemical literature usually given in terms of the molar absorption coefficient with "units" of area per mol. In the present context it is simpler to describe concentration in terms of area (m^2) per molecule.

The intensity of a spectral transition is always distributed over frequency by some “line-shape” function $L(\omega - \omega_{kl})$. This is affected by intermolecular interactions and change when conditions like pressure changes. However, for a transition of an intramolecular origin the integral over frequency is given by an intramolecular property, like a transition dipole derivative, for vibrations. This quantity is often referred to as the oscillator strength of the transition. Thus as transitions becomes more narrow the absorption coefficient at the maximum increases accordingly. The invariance of the oscillator strength is important for understanding how changes in line-shape affect the net absorption/emission.

Energy exchange between radiation field and a material body

For a radiation field in equilibrium with a piece of matter there is a continuous microscopic exchange of energy but with the net result that there is no energy transfer. Depending on the molecular nature of the matter the absorption is more or less efficient, but the requirement of no energy transfer, in any segment of the spectrum, provides an important consistency relation. Consider a small area dS , of the body. Radiation of orientation $\Omega(\theta, \phi)$ hits the surface and, neglecting scattering, the absorption per unit time and area is

$$dJ_{abs}(\omega, \theta) = 2\pi c e_0(\omega, T) A(\omega, \theta) \cos \theta d \cos \theta d\omega \quad (9)$$

where A is a material specific absorption power. At microscopic equilibrium there is a matching emission J_{em} which amounts to

$$dJ_{em}(\omega, \theta) = 2\pi c e_0(\omega) A(\omega, \theta) \cos \theta d \cos \theta d\omega \quad (10)$$

From eqs.(9,10) we obtain a general relation between emission and absorption which is called Kirchoff's law. It is the macroscopic counterpart of Einstein's relation in eq.(6), which can be used to derive eq.(10) from a microscopic perspective. However, Kirchoff's law predates Einstein's contribution and was (probably) known to Arrhenius in the 1990-ties. A body which completely absorbs all incoming radiation is called a black body. In this case $A=1$ for all frequencies and directions. Such a black body emits radiation as

$$dJ_{em}^{bb}(\omega, \theta) = 2\pi c e_0(\omega, T) \cos \theta d\cos \theta d\omega \quad (11)$$

at given frequency and direction. The total emitted energy per time and area from a flat surface is then obtained by integrating eq.(8) over all frequencies and a hemisphere

$$J_{em}^{bb} = 2\pi c \int_0^{\infty} e_0(\omega, T) d\omega \int_0^1 \cos \theta d\cos \theta = \sigma T^4 \quad (12)$$

One can note that eq.(12) gives an upper bound to emission from a body of temperature T. Since emission and absorption are independent microscopic processes a black body will emit according to eq.(12) even in the case where there is no equilibrium with the radiation field. This is an important conclusion when one wants to understand energy transfer by radiation. A black body at temperature T surrounded by vacuum will emit radiation with an energy per unit area and time according to eq.(12). To maintain its temperature the body has to receive heat from a reservoir or it slowly cools down. For a real body the absorptivity A isn't identically one, but particularly in the infrared region real materials with an inhomogeneous composition and rough surfaces behave similarly to the black body.

Let us now consider the earth. It is heated on the day side by the sun, but there is continuous emission of a black body character at all times. In the absence of an atmosphere eq.(12) would apply and neglecting other contributions to the energy balance the heating from the sun will balance the cooling from the IR-radiation giving an average steady state temperature (counted on a 24 hour or a yearly basis) Such an energy balance would yield an average temperature clearly lower than actually found. What role can the atmosphere play in this context? There are basically two phenomena to consider for the radiation; absorption/emission and scattering. When considering the emitted IR radiation scattering can be neglected except for the occurrence of clouds or other aerosol particles.

Emission from a black body shielded by an completely absorbing layer.

To illustrate the basic principle behind the "greenhouse effect" consider a large flat surface of a black body of temperature T_B . Above the black body there is a layer of an

absorbing medium of thickness L . This layer is assumed to be thermally insulated from the black body except for the exchange of energy due to emission and absorption of radiation. The medium is also assumed to be in internal thermal equilibrium at temperature T_2 . The medium has an absorption coefficient $\epsilon(\omega)$ and it is assumed that Beer's law can be applied. Now consider the case when $\epsilon(\omega)L \gg 1$ for all frequencies. This implies that all the radiation that comes in from the black body is absorbed in the layer. By Kirchoff's law it also implies that the layer behaves as a black body. It will then emit at both its surfaces. The radiation emitted from the surface facing the black body will be absorbed by the black body, while the radiation emitted from the other surface will leave the system. Since we assumed that the layer was thermally insulated there should be steady state where there is an energy balance for the layer and

$$E(\text{absorbed}) = E(\text{emitted}) \rightarrow \sigma T_B^4 = 2\sigma T_2^4 \rightarrow T_2 = 2^{-1/4} T_B \quad (13)$$

This illustrates how the device with a thermally isolated absorbing layer has two interrelated properties. The radiation provides a cooling of the layer and consequently the radiation energy emitted from the total system decreases by a factor of two, since the temperature of the whole system seen from the outside has decreased with a concomitant decrease in the energy output. Thus the model system provides an illustration of the basis of the "greenhouse effect". Note that it is essential that the layer is thermally isolated from black body. If $T_B = T_2$ there is no change in the emitted energy relative to the case when the layer is absent. If one extends the model to N separate isolated black-body layers the temperature of the outer layer is $N^{-1/4} T_B$ showing that it is potentially possible to reduce the outgoing radiation to very low levels.

Emission from a black body shielded by a partly absorbing layer

In practice one rarely has completely absorbing layers and this is certainly true for the atmosphere. Consider a slightly modification of the model of the completely absorbing layer. Assume that absorption only occurs in a frequency interval, $\omega_1 \leq \omega < \omega_2$, where it is complete, while the layer is fully transparent in the remaining part of the spectrum. It is clear that the emission from the system in the transparent part of the spectrum is from a black body at temperature T_B . For the rest of the spectrum we have in principle

the same description as for the completely absorbing layer. The difference is now that we have to integrate explicitly to calculate the radiation energy of this part of the spectrum.

$$\begin{aligned}
 E(\text{absorbed}) &= \frac{(kT)^4}{4\pi^2 c^3 \hbar^3} \int_{\hbar\omega_1/kT_B}^{\hbar\omega_2/kT_B} \frac{x^3}{\exp(x) - 1} dx \\
 E(\text{emitted}) &= 2 \frac{(kT)^4}{4\pi^2 c^3 \hbar^3} \int_{\hbar\omega_1/kT_2}^{\hbar\omega_2/kT_2} \frac{x^3}{\exp(x) - 1} dx
 \end{aligned} \tag{14}$$

The temperature dependence of these energies is not as simple as in the previous case. We still have a T^4 factor but also the integrals depend on T . According to eq.(13) the temperature of the layer is a factor of $2^{-1/4}$ lower than T_B . In eq.(14) the integrand has a maximum at 2.822 and if the integral covers values lower than that the second integral is the larger, while the opposite is true if the main part of the integration is for high x -values. The ratio of the two temperatures T_2/T_B will accordingly be slightly smaller or larger than $2^{-1/4}$, in the respective cases.

Seen from outside this system will emit as one black body in certain frequency ranges and as another at other frequencies. The totally emitted radiation will lie in between that of the two previous cases, as is intuitively obvious.

Emission from a black body shielded by an absorbing layer. General case.

In the general case the extinction coefficient $\varepsilon(\omega)$ is smoothly varying with frequency. Then the layer is neither completely absorbing nor completely transparent. Since the path-length through the layer depends on the angle of the radiation it is necessary to explicitly consider the angular dependence. Per unit area the black body emits radiation at an angle θ according to eq.(11). This radiation energy will be partly absorbed by the layer and the outgoing unaffected part is

$$J_{out}^B(\omega, \theta) = J_{em}^B(\omega, \theta) \exp[-\varepsilon(\omega)L/\cos\theta] \tag{15}.$$

The layer also emits and for given frequency and direction one has

$$J_2^{out}(\omega, \theta) = 2\pi c e_0(\omega, T_2) \{1 - \exp[-\varepsilon(\omega)L/\cos\theta]\} \tag{16}$$

The same relation holds for the radiation going in the opposite direction towards the black body. The total radiation energy emitted by the system is then

$$J_{out} = \int_0^{\infty} \int_0^1 2\pi c \left\{ e_0(\omega, T_B) \exp[-\varepsilon(\omega)L/\cos\theta] + e_0(\omega, T_2) [1 - \exp\{-\varepsilon(\omega)L/\cos\theta\}] \right\} \cos\theta d\cos\theta d\omega \quad (17)$$

For the case when the two temperatures T_B and T_2 are equal we regain the normal black body result. However, eq.(17) shows that in general the layer has an insulating effect in a way that depends on the absorption coefficient. This in turn depends on the chemical composition of the layer. If we consider the layer to consist of a gas enclosed between transparent walls it is clear that the insulating effect depends on the spectrum of the components and their amounts. For a black body around 300K the dominant contribution to the energy of the radiation field comes from IR-region and it is consequently the spectrum in the IR range that is most relevant. In this part of the spectrum it is the vibration that is the relevant molecular degree of freedom.

Emission from a black body shielded by an absorbing gas atmosphere.

The model calculations above have demonstrated most of the essential qualitative features of the "greenhouse effect". Consider now a slightly more realistic model with a gas-phase atmosphere above the black body radiator. We allow the temperature and composition vary with the height z above the solid body. For the case where the gas layer is finite (counted in molecules per area) a fraction of the original black body radiation will pass through unaffected. In analogy with eq.(15) we have

$$J_{out}^B(\omega, \theta) = J_{em}^B(\omega, \theta) \exp\left\{ -\int_0^{\infty} \varepsilon(\omega, z) dz / \cos\theta \right\} \quad (18)$$

In addition there will be emission/absorption in each layer of thickness dz . For a layer at z there is an emission using Kirchoff's law ($A(\omega, z, \theta) = \varepsilon(\omega, z) / \cos\theta dz$) of

$$dJ_{em}(\omega, \theta, z) = 2\pi c e_0(\omega, T) \varepsilon(\omega, z) d\cos\theta dz \quad (19).$$

Only a fraction of this radiation reaches outside the gas atmosphere

$$dJ_{out}(\omega, \theta, z) = 2\pi c e_0(\omega, T) \varepsilon(\omega, z) \exp\left[-\int_z^\infty \varepsilon(\omega, z') dz' / \cos\theta\right] d\cos\theta dz d\omega \quad (20).$$

By integrating over all layers and adding the radiation emanating from the black body we obtain the total radiation energy reaching through the gas per unit time as

$$J_{out}[T_B, T(z), \varepsilon(\omega, z)] = 2\pi c \int_0^1 \int_0^\infty e_0(\omega, T_B) \exp\left[-\int_0^\infty \varepsilon(\omega, z) dz / \cos\theta\right] \cos\theta d\cos\theta d\omega \\ + 2\pi c \int_0^\infty \int_0^1 \int_0^\infty e_0[\omega, T(z)] \varepsilon(\omega, z) \exp\left[-\int_z^\infty \varepsilon(\omega, z') dz' / \cos\theta\right] dz d\cos\theta d\omega \quad (21).$$

For the case when the temperature is homogeneous and independent of z the eq.(21) reduces to the ordinary expression for the radiation from a black body of $T=T_B$. (The integral over z can be performed analytically in this case) If one assumes no other energy transfer than the radiation one can write down an expression for the energy balance of each layer dz and obtain an equation determining also the temperature profile. The principles are the same as for the more simple models discussed above. (An explicit calculation leading to an integral equation for the temperature profile is found in additional material at the end.)

The role of the absorption spectrum

When applying the expressions derived above to actual calculations on how the energy balance is affected by different molecules the absorption spectrum is the most crucial input parameter. Experimental recordings from outside the earth show that there is a characteristic spectral variation of the emitted IR radiation. (See figure 1) One approach to understanding the role of different molecules in the energy balance is to experimentally record the spectrum for a range of temperatures and pressures. This data can then be used as input to numerical calculations. However, in order to establish an understanding of the mechanisms it is often more helpful to develop approximate analytical results. A measure of how transparent the atmosphere is at different wavelengths and heights is obtained from

$$\Sigma(\omega, z) \equiv \int_z^\infty \varepsilon(\omega, z') dz' \quad (22).$$

If $\Sigma(\omega, 0) \gg 1$ it is the molecules in the atmosphere that emits the outgoing radiation, while in the opposite limit $\Sigma(\omega, 0) \ll 1$ the atmosphere is transparent and the radiation

emanates from the ground. It is important to make the distinction between the integral contribution of a certain compound to the cooling effect and the consequence of adding more of such a compound. Intuitively it is obvious that adding a compound with an absorption in a range where $\Sigma(\omega,0)$ is small provides a large effect, while for a compound with an absorption where $\Sigma(\omega,0)$ is already large should have a smaller effect. One important part of this work is how to quantify this argument. In the atmosphere the pressure at ground level is around 10^5Pa and decreases by an order of magnitude for approximately every 10^4m in height. Thus we have

$$\begin{aligned} p(z) &\approx p(0)\exp(-\lambda z) \\ 1/\lambda &\approx 6000\text{m} \end{aligned} \quad (23)$$

For the typically small molecules of the atmosphere like carbon dioxide, water or methane the intermolecular interactions are weak enough that the rotational pattern is resolved at the relevant pressures. Furthermore the lower the pressure the more narrow are the spectral lines. This results in a non-trivial z-dependence of the absorption coefficient $\varepsilon(\omega)$.

Figure 2 shows schematically how the temperature varies with height. There is a nearly linear decrease in T from around 300K on the surface to 210K at 12km, where there is a change to a slow increase with a maximum around 270K at 50km where the temperature decreases again. In a linear approximation one can write for $z < 12000\text{m}$

$$T(z) \approx T(0) + \left\langle \frac{dT}{dz} \right\rangle_{av} z \approx T(0) - 7.5 \times 10^{-3} z \quad (24)$$

The most obvious explanation of the initial drop in temperature is that it is caused by the greenhouse effect. The interpretation of the turnaround in temperature above 12km is that heating mechanisms, emanating for example from absorption of UV-light by ozone and from cosmic radiation dominates over the cooling from IR emission. The lower the pressure the fewer molecules and the less energy is emitted.

The vibration rotation of carbon dioxide

Carbon dioxide is a linear molecule and with three atoms there are $9-5=4$ vibrational degrees of freedom. There is a symmetric stretch, which is not infrared active. There is an asymmetric stretch with its basic frequency at 2349cm^{-1} and a degenerate bending mode at frequency 667cm^{-1} . (See Figure 4) The latter is particularly important since the absorption corresponds to the frequency range close to the maximum output energy for a black body radiator at 300K. Figure 5 shows a quantitative estimate of the absorption characteristics of carbon dioxide at a pressure of $1 \times 10^5 \text{Pa}$. The measured absorption coefficient provides a basis for estimating at which frequencies carbon dioxide can absorb and reemit. At the surface of the earth the CO_2 content is around 350 ppm (volume/volume). To a good approximation CO_2 is distributed in the gravitational field with a Boltzmann weight

$$c_{\text{CO}_2}(z) = c_{\text{CO}_2}(0) \exp(-m_{\text{CO}_2}gz/kT) \approx c_{\text{CO}_2}(0) \exp(-z/5000); T \approx 270\text{K} \quad (25)$$

Integrating the absorption through the atmosphere with its decaying content of CO_2 yields

$$\Sigma(\omega, \theta) = \int_0^{\infty} \varepsilon(\omega, z) / \cos(\theta) dz = \alpha(\omega) / \cos(\theta) \int_0^{\infty} c_{\text{CO}_2}(z) dz \approx \frac{\alpha(\omega) c_{\text{CO}_2}(0)}{\lambda \cos \theta} \approx 2.25 \alpha(\omega) / \cos(\theta) \quad (26)$$

Thus when the absorption coefficient $\alpha < 0.4(\text{m}^2/\text{kg})$ absorption/reemission is small. For $\alpha > 0.4$ such processes are important. With this measure the ranges 500 to 800cm^{-1} and 2250 to 2450cm^{-1} are the important frequency ranges. Even though there are peaks and valleys in these ranges these do not reach as low level as 0.4. However, the data of Figure 5 is relevant for atmospheric pressure and for lower pressures peaks and valleys are more pronounced so one has to treat the conclusion with some care. Around 1100cm^{-1} there is a weak absorption band due to overtones. It appears to be below the limit $\alpha < 0.4(\text{m}^2/\text{kg})$ and thus giving only small contributions to the overall effect.

In a gas where the rotational relaxation isn't too fast the spectrum can be analyzed as exchange of combined vibrational and rotational energy. There is a technical difference between the two IR-active modes in that the stretch conserves the linear symmetry, but not the bend. Accordingly the selection rule is $\Delta J = \pm 1$ (P and R-branches) for the stretch,

while for the bend a change in vibrational energy can occur without a change in the rotation so that $\Delta J=0$ is also allowed (Q-branch). Furthermore there is an occurrence of 1.1% of ^{13}C . The effect on the reduced mass of the bending motion results in a shift of 19cm^{-1} of the vibrational frequency. This also gives rise to satellites in the spectrum. The IR spectrum of carbon dioxide around 667cm^{-1} is composed of a strong central peak, labeled Q, due to the $\Delta J=0$ transition. Since rotational constants are slightly different in the ground and excited vibrational states this peak has satellites due to the populations of the thermally excited vibrational states. At 300K the calculated populations of the degenerate energy level is around 8%, while for 210K it is only 2%. In addition to the central Q peak there are the P, $\Delta J=1$, and R, $\Delta J=-1$, branches that cover a broader frequency range covering around 100cm^{-1} of resolved rotational lines on each side of the Q-peak. These peaks also have satellites due to the vibrationally excited level. The IR spectrum of carbon dioxide around 667cm^{-1} thus consists of a number of strong absorption peaks separated by 1.6cm^{-1} , which overlap slightly at atmospheric pressure where the width at half height is around 0.1 to 0.2cm^{-1} . In addition there are a large number of weaker satellite peaks, due to isotope substitutions and hot bands, shifted from the main ones. These contribute to cover the spectrum to give an absorption that ensures that the condition $\Sigma(\omega,0) > 1$ over a broad range $500\text{-}800\text{cm}^{-1}$. Thus the presence of carbon dioxide has the consequence that the IR radiation, in this frequency range, sent from the surface of the earth is absorbed in the atmosphere and then reemitted from a body that has a lower temperature. In this way carbon dioxide contributes to the greenhouse effect in the radiation energy balance of the earth.

The stretching vibration at 2349cm^{-1} has only a P- and a R-branch. They have the same characteristics as for the bending vibration, since the rotational motion is (essentially) the same. Consequently one has absorption in a range $\pm 100\text{cm}^{-1}$ around 2350cm^{-1} . The potential effect on the energy balance is different though since the contribution to the black body radiation is smaller in this region. We have the ratio

$$\tilde{\nu} = 667\text{cm}^{-1} \leftrightarrow 3.2kT; \tilde{\nu} = 2349\text{cm}^{-1} \leftrightarrow 11.3kT \rightarrow$$

$$\frac{e_0(2349)}{e_0(667)} = \frac{11.3^3[\exp(3.2) - 1]}{3.2^3[\exp(11.3) - 1]} = 0.013 \quad (27)$$

indicating that the absorbance in this region has a much lesser effect on the energy balance.

Contributions from water molecules

Water is a bent molecule with only three vibrational modes. There are two stretch modes; one at basic frequency of 3757cm^{-1} (asymmetric stretch, IR active) and one at 3652cm^{-1} (symmetric stretch). There is also a bending mode around 1540cm^{-1} . All these frequencies refer to isolated molecules in the gas phase. A spectrum is shown in Figure 6a. The water molecule is an asymmetric top (the three moments of inertia all different) and the rotational spectrum contains a large number of transitions. However, the width of the spectrum is largely determined by kT but the strong intensity makes the absorption significant up to $\pm 200\text{cm}^{-1}$ from the center of the transition. The rotational constants are substantially larger for water than for carbon dioxide making the intrinsic splittings between lines larger, but this effect is compensated by the fact that there are many more transitions while the Q-branch is absent. For water there is also the odd molecule that has a deuterium rather than a proton. This strongly affects the spectrum through both the exclusion principle and through the change in moment of inertia. The bending mode of water is at the high end of the energy distribution at 300K. Compared to carbon dioxide and a calculation as in eq.(25) yields $e_0(1540)/e_0(667)=0.18$ ($T=300\text{K}$). Both water and carbon dioxide is present in substantial amounts in the atmosphere and they both contribute to the “greenhouse effect”. For the case when the spectral region around the respective bending modes dominate one would conclude that carbon dioxide contributes more due to the higher energy density in the relevant frequency range. However, for water intermolecular interactions provides important complications to this simplistic picture. The concentration profile of water in the atmosphere is very different from the other components. At ground level the relative humidity is typically in the range 40-90%, which at $T=300\text{K}$ corresponds to a partial pressure of 1.5-3. kPa, which is much higher than for carbon dioxide. On the other hand at $T=210\text{K}$, corresponding to a height of 12km, the saturation pressure is 0.8Pa, which is of the same order as the carbon dioxide pressure at this height. At all heights of 12km and below the water can be near saturation. Close to phase separation there appears clusters, dimers, trimers etc in the gas phase. These generate IR absorption/emission from intermolecular motions, librations, in the frequency range $400\text{-}700\text{cm}^{-1}$. The

appearance of such species depends strongly on temperature and partial pressure of the water making it difficult to make general statements on how important they are for the greenhouse effect. However, if they occur in substantial amounts there is a major overlap with the spectrum of the bending vibrations of carbon dioxide. This could to some extent mask the effect of CO₂.

When water condenses to a liquid (or solid) phase the stretching vibrations cover a large frequency range around 2600cm⁻¹ and up. (See Figure 6b) This absorption is wide enough to give a noticeable contribution to the energy balance, in spite of the high frequency. For the bending mode on the other hand condensation gives a narrowing. An additional most significant effect is that on condensing to a liquid there appear low frequency librational modes due to intermolecular motions. They give a strong absorption from around 700cm⁻¹ and below and when liquid water is present these modes are important for the energy balance. Thus if clouds are present they strongly influence the IR radiation. In addition to the absorption/emission clouds also generate scattering in the IR regime.

Other gases contributing to the greenhouse effect

Nitrogen and oxygen are infrared inactive, but there are several other components of the atmosphere that potentially could contribute to the greenhouse effect in addition to carbon dioxide and water. Ozone is present in the upper atmosphere and a vibrational mode around 1050cm⁻¹ contributes to the absorption/reemission. A compound that has attracted much attention is methane. It is present at most altitudes, but degraded slowly at higher altitudes. As shown in Fig 7 it has an absorption peak around 1250cm⁻¹ due to the bending mode. Methane is present at low amounts with a partial pressure of .1-.2 Pa at ground level. However it contributes to the absorption in a frequency range where the atmosphere is largely transparent. It is claimed that addition of methane has strong effect on the energy balance. It is obvious that methane provides only a small contribution to the overall greenhouse effect. However, it can still be very important for the marginal effect related to addition of more of the component to the atmosphere. The oscillator strength is larger for the carbon dioxide than for the methane bending mode, since the dipole derivative is larger in the former case. In addition the carbon dioxide

band is at a frequency range closer to the maximum in the energy distribution. To see how these factors influence the energy balance we now quantitatively analyze the absorption/emission process in an atmosphere of varying pressure and temperature.

From where does the outgoing radiation emanate?

When one considers the radiation from the earth, where there is a temperature and density profile in the atmosphere it becomes a relevant issue to consider from where the emission emanates. Consider first a homogeneous layer with constant temperature and density. Then one can see, as usual, the emission as the reverse of the absorption. It is the surface layer that gives the largest contribution to the radiation. The contribution decreases exponentially as one goes inside the layer. The length-scale is given by $\varepsilon(\omega)/\cos\theta$ so that radiation emitted perpendicular to the layer comes from the deepest sources, while radiation near parallel to the slab emanates nearly exclusively from a surface layer.

In the atmosphere the density decreases with height. The contribution to the emitted radiation from a layer at height z was given in eq.(20) and by taking the derivative with respect to z of this equation we find that if there is a maximum for a certain height it occurs for

$$\frac{\partial \varepsilon(\omega, z)}{\partial z} = -\varepsilon(\omega, z)^2 / \cos\theta \quad (28)$$

Assume, for example, that the absorption coefficient $\varepsilon(\omega, z)$ decreases exponentially with height as was assumed for the density. Then the maximum in radiation comes from a position z_M given by

$$\begin{aligned} \varepsilon(\omega, z) &= \varepsilon(\omega, 0) \exp(-\lambda z) \rightarrow \\ z_M &= \ln[\varepsilon(\omega, 0) / \lambda \cos\theta] / \lambda \end{aligned} \quad (29)$$

This shows that the stronger the absorption at ground level, the more slowly decaying the density and the smaller the angle the further out is the source of the radiation that reaches outside the atmosphere. These conclusions would hold qualitatively for any

other functional form of the monotonic decay of the density. One can note that if $\varepsilon(\omega,0)/(\lambda \cos \theta) \leq 1$ then the maximum occurs for $z=0$ and there is only a small contribution to the “greenhouse” effect at that frequency. However, there is a complication in applying eq.(29) in that not only the density but also the line-shapes of the spectral lines change with pressure and thus with height.

Effects of the lineshape

If one neglects complex formation the absorption of the IR atmosphere can be seen as due to the sum of the absorption from the different IR-active molecules and (see eq.8)

$$\varepsilon(\omega, z) = \sum_i c_i(z) \alpha_i(\omega, z) \quad (30),$$

where $c_i(z)$ is the concentration. For small molecules like carbon dioxide, water and methane in air the vibrational absorption spectrum is due to transitions from a range of thermally populated states for all relevant isotopic species. In addition to the ground state, rotational states are populated up to relatively high rotational quantum numbers. If there are vibrational states with low excitation energies one can also have a sufficient fraction of molecules in the $v=1$ vibrational states that there is a non-negligible contribution to the absorption.

For each compound i the populations P_k^i add to unity and

$$P_k^i = \exp(-\hbar\omega_k/kT) / \sum_m \exp(-\hbar\omega_m/kT) \quad (31).$$

From each state k there are transitions to states l at resonance frequencies ω_{kl} . As long as the transition frequencies are well separated relative to the inverse relaxation times one can assume a Lorentzian shape for each transition. The molecular absorptivity then consists of a sum of all states k , and all transitions k to l

$$\alpha_i(\omega, z) = \sum_k P_k^i \sum_l \left\{ 1 - \exp(-\hbar\omega_{kl}/kT) \right\} \frac{B_{kl}^i \Gamma_{kl}(z) / \pi}{1 + (\omega_{kl} - \omega)^2 \Gamma_{kl}^2(z)} \quad (32),$$

where Γ denotes the relaxation time and we have used eq.(8) to account for the stimulated emission in addition to the absorption. The eqs.(30-32) provide an explicit expression in terms of molecular quantities for the absorption. In addition to the explicit temperature dependent factors in eqs(31,32) the relaxation times Γ are also strongly environment dependent.

The relaxation processes are due to intermolecular collisions/interactions and for gases such processes are usually referred to as pressure broadening. For small molecules at atmospheric pressures the rotational lines of the spectrum are sufficiently separated and the relaxation times sufficiently long that one can consider the individual transitions as independent. It is also reasonable to make the assumption that the dominant relaxation route is through molecular collisions rather than formation of transient complexes. The collision frequency Z can approximately be written as

$$Z = 7\sigma_c^2 p(mkT)^{-1/2} \quad (33),$$

where σ_c is the collision diameter and m the molecular mass. It is a reasonable first approximation to assume that the relaxation time is equal to the angular momentum relaxation time, which in turn can be assumed to be the inverse of the collision frequency Z . It then follows that the relaxation time is inversely proportional to the pressure so that

$$\Gamma_{kl}^i(z) = \Gamma_{kl}^i(0,T)p(0)/p(z) \approx \Gamma_{kl}^i(0,T)\exp(\lambda z) \quad (34).$$

Thus spectral lines will be more narrow at larger heights. It is not sufficient to use the observed absorption spectrum at ground level to describe the spectral properties at all relevant heights. The higher the altitude the more structured is the absorption spectrum and even for the carbon dioxide band one can have spectral regions with low absorption close to peaks of strong absorption. For the case when the concentration is proportional to the pressure

$$c_i(z) = c_i(0)p(z)/p(0) \quad (35),$$

which is approximately true for carbon dioxide and methane, but not for water, there is a cancellation effect between the decrease in concentration and the increase in relaxation time as the altitude changes. Combining eqs.(30-35) we find for the contribution of a single transition k to l of species i

$$\varepsilon_{kl}^i(\omega, z) = c_i(z)\alpha_{kl}^i = P_k^i \left\{ 1 - \exp(-\hbar\omega_{kl}/kT) \right\} \frac{B_{kl}^i \Gamma_{kl}^i(0) c_i(0) / \pi}{1 + (\omega_{kl} - \omega)^2 \Gamma_{kl}^i(0)^2 [p(0)/p(z)]^2} \quad (36).$$

Thus precisely at the resonance frequency there is, in this approximate description, no z-dependence of the absorption, except for temperature effects in the coefficients. Away from resonance, $|(\omega_{kl} - \omega)\Gamma_{kl}^i| > 1$, on the other hand, the absorption coefficient depends quadratically on the pressure and thus also on the concentration. For the case of an exponentially decaying pressure (second equality of eq.34) the condition of eq.(28) yields for the position of maximum radiation z_M

$$z_M = \frac{1}{2\lambda} \ln \left\{ \frac{\varepsilon_{kl}^i(\omega_{kl}, 0)}{2\lambda(\omega - \omega_{kl})^2 \Gamma_{kl}^i(0)^2 \cos \theta} \right\} \quad (37)$$

For frequencies clearly off resonance the expression (37) for z_M yields negative values, which simply means that absorption/emission is negligible and it is the background radiation from the ground that dominates. At resonance, on the other hand, the expression for z_M diverges indicating that the emission comes from high altitudes, but also that a more detailed description is needed to avoid the numerical divergence. In contrast to eq.(29) we have here allowed the absorption spectrum to be an explicit function of z. For carbon dioxide the spectral characteristics at atmospheric pressure ($z=0$) are shown in Fig.2. The inset in this figure shows, for example, a discernable peak at 700cm^{-1} . The absorption coefficient at resonance is obtained as

$$\varepsilon_{kl}^i(\omega_{kl}, 0) = \alpha(\omega_{kl})c_{CO_2}(0) \approx 0.09\text{m}^{-1} \quad (38).$$

The relaxation time, at ground level can be estimated from the width at half height and $\Delta\omega_{1/2} \leftrightarrow 0.2\text{cm}^{-1} \rightarrow \Gamma_{kl}^{CO_2}(0) \approx 2 \cdot 10^{-11}\text{s}$. Using eq.(37) we can for this example find the position of maximum emission. This is of interest since there is a gradient in

temperature and the position for the emission reflects the energy of emission. With the relevant parameter values in the example and for a perpendicular orientation

$$z_M(\omega - \omega_{kl}) \approx 3000 \left\{ 4.9 - 2 \ln \left[\left| \omega - \omega_{kl} \right| / \Delta \omega_{1/2} \right] \right\} \quad (39).$$

Thus when $\omega = \omega_{kl} \pm 2\Delta\omega_{1/2}$ the emission emanates from a height of approximately 10km in this example. For larger deviations from resonance the radiation gradually emanates from lower and lower heights with increasingly higher temperatures. For a frequency 0.8cm^{-1} away from resonance the estimated value of z_M is 6km.

The effect of adding a component to the atmosphere

A very important question from a practical point of view is the consequence of adding a component to the atmosphere. One aspect of this question is to what extent a component added to the environment ends up in the atmosphere, rather than in the sea, in the ground or being chemically converted. However, below we concentrate on the question: given a certain increase in concentration of compound j in the atmosphere what is the consequence for the emission of radiation? Adding a compound changes the absorption coefficient in the expression for the emitted energy in eq.(21). When one adds an amount n_j per area of a compound at ground level it takes some time before an equilibrium distribution is established. Due to the existence of the gradient in temperature the maximum effect on the energy balance is typically obtained when the compound has equilibrated in the gravitational field and we consider this case. At equilibrium the fractional increase in concentration is uniform so that

$$\frac{\partial c_j(z)}{\partial n_j} = \frac{c_j(z)}{n_j} \approx \lambda_j \exp(-\lambda_j z) \quad (40)$$

where the second equality is valid for an in general molecular dependent exponentially decaying concentration profile. Using this assumption we have

$$\frac{\partial \varepsilon(\omega, z)}{\partial n_j} = \lambda_j \exp(-\lambda_j z) \alpha_j(\omega, z) \quad (41).$$

By taking the derivative with respect to n_j of eq.(21) we can identify three different contributions to the change in energy emission

$$\begin{aligned}
\frac{1}{2\pi c} \frac{\partial J_{out}(\omega)}{\partial n_j} &= - \int_0^1 e_0(\omega, T_B) \int_0^\infty \lambda_j \exp(-\lambda_j z) \alpha_j(\omega, z) dz \exp[-\Sigma(\omega, 0)/\cos\theta] d\cos\theta \\
&+ \int_0^1 \int_0^\infty e_0(\omega, T(z)) \lambda_j \exp(-\lambda_j z) \alpha_j(\omega, z) \exp[-\Sigma(\omega, z)/\cos\theta] d\cos\theta dz \\
&- \int_0^1 \int_0^\infty e_0(\omega, T(z)) \varepsilon(\omega, z) \int_z^\infty \lambda_j \exp(-\lambda_j z') \alpha_j(\omega, z') dz' \exp[-\Sigma(\omega, z)/\cos\theta] (\cos\theta)^{-1} dz d\cos\theta
\end{aligned} \tag{42}$$

The first term on the rhs represents the decrease in emission from the ground due to the increased absorption (assuming $n_j > 0$). The second term is the increase due to absorption and reemission from the atmosphere and the third term represents the increase due to absorption of the reemitted radiation. When there is no variation in the temperature so that $T(z) = T_B$ the three terms add up to zero as should be the case.

Consider first the special case that the added compound is initially absent in the atmosphere and it has an absorption in a transparent spectral region. This would, for example, approximately apply to part of the bending mode of methane. Thus prior to addition of the compound j we have that $\varepsilon(\omega) \approx 0$ in the relevant frequency range. It is then only the first two terms on the rhs of eq(42) that contribute. Assume that the pressure and the concentration decays with the same characteristic length and neglect the (square root) temperature dependence of the relaxation time we find, using eqs (4),(31) and (36)

$$\frac{\partial J_{out}(\omega)}{\partial n_j} = - \frac{\hbar \omega^3}{2\pi^3 c^2} \sum_{k,l} B'_{kl} \Gamma_{kl}(0) \lambda P_l(T_B) \int_0^\infty \frac{\left\{ 1 - \frac{P_l(T(z))}{P_l(T_B)} \right\}}{[1 + (\omega - \omega_{kl})^2 \Gamma_{kl}^2(0) \exp(2\lambda z)]} dz \tag{43}.$$

Here one see explicitly that when $T(z) = T_B$ there is no effect of the added component on the energy balance. Each transition provides a contribution that is independent of the others. We consider the case where all transitions involve a single vibrational excitation of frequency ω_v combined with different rotational transitions. Thus for all frequencies $\omega_{kl}/\omega_v \approx 1$. An integration over the frequency yields the accumulated effect of the absorption band and

$$\frac{\partial J_{out}}{\partial n_j} = -\frac{\hbar\omega_v^3\lambda}{2\pi^2c^2} \sum_{k,l} B_{kl}' P_l(T_B) \int_0^\infty \left\{ 1 - \frac{P_l(T(z))}{P_l(T_B)} \right\} \exp(-\lambda z) dz \quad (44).$$

In the integral the first factor is increasing with increasing z while the second factor decreases, demonstrating the importance of the temperature gradient for the total effect. One readily calculates the screening effect of the absorption band with knowledge of the spectral characteristics, the decay constant for the pressure and the temperature profile. The rhs of eq.(44) is independent of the concentration and the decrease in emitted radiation is thus depends linearly on added amount in this range as expected. The eq.(44) can be further simplified by neglecting temperature effects in the population of ground states and excited states, respectively. Then the sum of B_{kl}' over k and l can be shown to simply be proportional the total absorption of the vibrational transition (see additional material). Furthermore the integral can be evaluated if one assumes a

constant, reasonably small, gradient $\left\langle \frac{dT}{dz} \right\rangle_{av}$ in temperature and

$$\frac{\partial J_{out}}{\partial n_j} = \frac{\hbar^2\omega_v^4}{2\pi^2c^2\lambda kT_{av}^2} \exp[-\hbar\omega_v/(kT_{av})] \left\langle \frac{dT}{dz} \right\rangle_{av} \int \alpha_v(\omega) d\omega \quad (45)$$

where T_{av} is the average temperature over the relevant interval. The eq.(45) provides a simple relation for the reduction of outgoing radiation energy when one adds a compound with an absorption/emission in a previously transparent spectral region. System parameters that enter are; the temperature profile, the decay length for the pressure decrease with increasing height, the vibrational frequency and the oscillatory strength of the vibrational transition.

Now consider the other extreme where one adds a compound that is already present in such amounts that, in the relevant frequency range, the radiation from the ground is completely screened., so that $\Sigma(\omega,0) > 1$. It is also assumed that in the relevant frequency range the compound j is the dominant absorber/emitter. One can evaluate the induced decrease in emission by explicitly evaluating the second and third terms in the rhs of eq.(44). Here we take a simpler approach. From eqs (28) and (37) we have an explicit expression for the position z_M where the maximum of the radiation emanates. Now

make the simplifying assumption that all the radiation for given frequency and direction comes from this position. Then in analogy with eq.(11)

$$J_{out}(\omega) \approx 2\pi c \int_0^1 e_0(\omega, T[z_M]) \cos\theta d\cos\theta \quad (46)$$

Now the change induced by adding more of compound j is obtained by taking the derivative and

$$\frac{\partial J_{out}(\omega)}{\partial n_j} \approx 2\pi c \int_0^1 \frac{\partial e_0(\omega, T[z_M])}{dz_M} \frac{\partial z_M}{\partial n_j} \cos\theta d\cos\theta = \frac{\pi c}{c_j(0)} \int_0^1 \frac{\partial e_0(\omega, T[z_M])}{dz_M} \cos\theta d\cos\theta \quad (47)$$

where the second equality follows from the simple relation

$$\frac{\partial z_M}{\partial n_j} = \frac{1}{2c_j(0)} \quad (48)$$

obtained from eq.(35). Note that even though z_M depends on the angle theta this doesn't show up in the derivative. The eq.(47), which can also be derived through an explicit integration of the second and third terms of eq.(42) (see additional material), shows that the shift in the position of maximum outgoing radiation is inversely proportional to the concentration at ground level, which in turn implies that the same relation holds for the change in emitted energy. Thus the emitted energy depends logarithmically on the concentration. The eq.(47) also shows that the change in emitted energy is independent of the absorption properties of compound j except for the condition that the absorption is strong enough to screen out the radiation from the ground. Given the temperature profile the integral in eq.(47) is easily evaluated. Use the linear approximation of eq.(22). In the integration over frequency a non-zero contribution is only obtained for the spectral region where the atmosphere is non-transparent. In the frequency dependent factors one can with reasonable approximation replace $\omega \rightarrow \omega_v$. Then from eq.(47) we obtain

$$\frac{\partial J_{out}}{\partial n_j} \approx \frac{(\omega_{max} - \omega_{min})\hbar^2 \omega_v^4}{8\pi^2 c^2 k T_{av}^2} \exp[-\hbar\omega_v / (kT_{av})] \frac{1}{c_j(0)} \left\langle \frac{\partial T}{\partial z} \right\rangle_{av} \quad (49)$$

Here $\omega_{\max}, \omega_{\min}$ denotes the maximum and minimum frequencies where the condition $\Sigma(\omega, 0) > 1$ of non-transparency applies. In eq.(49) the change in energy loss is expressed in terms of readily accessible parameters. The equation provides a clear picture of what factors influence the energy balance for the particular case and it can also serve as a reasonable quantitative estimate of the effect.

Comparing the effects of adding methane and carbon dioxide to the atmosphere.

From eqs.(45) and (49) one can calculate the ratio of the effect of adding a compound M absent in the atmosphere and one, C, already present in such amounts that the total atmosphere is not transparent in a given frequency range.

The ratio is

$$\frac{[\partial J_{out}^v / \partial n_j]_{45}}{[\partial J_{out}^v / \partial n_j]_{49}} = \frac{4\omega_M^4 \exp(-\hbar\omega_M / kT_{av}) c_C(0) \int \alpha_M^v(\omega) d\omega}{\omega_C^4 \exp(-\hbar\omega_C / kT_{av}) \lambda(\omega_{\max} - \omega_{\min})} \quad (50)$$

The ratio is in this example, with a single vibrational frequency for each compound, determined by the respective frequencies of the vibrational transitions, the oscillatory strength of the vibrational transition of compound M, by the pressure decay length, by the concentration at the ground level of compound C and by the frequency span of the non-transparent region for compound C.

Comparison with literature data

Different ipcc reports provide quantitative statements of the effect of adding gases to the atmosphere. It is not easy (for me) to trace back to the original calculations. The key quantity is “radiative forcing”, ΔF (W/m²), which I interpret as the decrease in energy emission caused by an increase in the concentration of the gas. There are different levels of approximations and the treatment presented above should correspond to the simplified one-dimensional model. For carbon dioxide, which is present at a high concentration, the relation is

$$\begin{aligned} \Delta F &= \alpha \ln(C/C_0) \\ \alpha &= 5.35 \end{aligned} \quad (51)$$

Taking the derivative of ΔF we can relate the radiative forcing to the change in J_{em} and

$$\frac{\partial J_{out}}{\partial n_j} = -\lambda \alpha / c(0) \quad (52),$$

where now α is defined in eq.(51). The current concentration of carbon dioxide is given as approximately 350ppm. This probably refers to a per volume basis making the concentration $\approx 1.3 \cdot 10^{-20} m^{-3}$. With a decay constant of $1.7 \cdot 10^{-4} m^{-1}$ the estimated value in the icpp report is

$$\frac{\partial J_{out}}{\partial n_{CO_2}} = -1.2 \cdot 10^{-25} W / molecule$$

If we instead use the estimate calculated in eq.(49) the result is

$$\frac{\partial J_{out}}{\partial n_{CO_2}} = -5.7 \cdot 10^{-25} W / molecule$$

which is a factor of five higher using the values of the parameters shown in the table below. Whether this discrepancy is due to a simple numerical mistake in eq.(49), as for example a factor of 2π , or if it has some real significance is unclear at present. In eq.(49) there is no reduction from interference of water clusters, but that is seemingly not accounted for in eq.(51) either. However, there is a reduction of the emission due to scattering by clouds, which is not accounted for in eq.(49) but presumably in eq.(51).

It is less straightforward to compare the icpp estimate for the effect of methane with the present calculations. The basic reason is that the icpp report considers a more realistic case where methane is already present in sufficient amount to make the assumption of initial transparency questionable. Consequently the report predicts a weaker concentration dependence than the linear one implied for a transparent region. In the absence of interference by N_2O the “radiative forcing” due to methane is given as

$$\Delta F = \alpha \left\{ \sqrt{M} - \sqrt{M_0} \right\} \quad (53)$$

$$\alpha = 0.036 (W / m^2)$$

where M is measured in ppbv. Converted to the effect per added molecule this relation implies

$$\frac{\partial J_{out}}{\partial n_j} = -\frac{\Delta F}{\partial n_j} = -\frac{\partial \Delta F}{\partial M} \frac{\partial M}{\partial c(0)} \frac{\partial c(0)}{\partial n_j} = -\frac{1}{2} \alpha M^{-1/2} 10^9 kT \lambda / p(atm) \quad (54)$$

With M=1500 for methane and p(atm)=1 10⁵Pa and the value of alfa=0.036 from eq.(53) we have the calculated effect of adding methane to the atmosphere of

$$\frac{\partial J_{out}}{\partial n_j} = -3 \cdot 10^{-24} W / molecule$$

according to the ipcc report. If we instead use eq.(45) given above the corresponding value is substantially higher

$$\frac{\partial J_{out}}{\partial n_j} = -7 \cdot 10^{-23} W / molecule$$

This is an overestimate since it is based on the assumption that the existing levels of methane are sufficiently low so that there masking effect is negligible over the whole spectrum. In addition the overlap of the high frequency branch of the methane bending vibration and the low frequency part of the water bending is substantial. To what extent this is accounted for in the ipcc-model is not known to me. Furthermore is the effect of scattering in clouds not taken into account. An additional effect is that for z>12000m the temperature gradient changes sign and for the stronger absorption peaks z_M occurs for these heights (see eq 39) and the contribution to the emitted energy changes sign.

Relative effect of methane and carbon dioxide.

The relative effect of adding methane and carbon dioxide to the atmosphere follows directly from the data given above. From the ipcc report it follows that

$$\frac{\partial [J_{out}^v / \partial n_j]_{Me}}{\partial [J_{out}^v / \partial n_j]_{CO2}} \approx 25$$

while with the estimates given above we have

$$\frac{\partial [J_{out}^v / \partial n_j]_{Me}}{\partial [J_{out}^v / \partial n_j]_{CO2}} \approx 135.$$

This value is a clear overestimate due to the effect of the overlap with the water bending mode and the fact that one can't neglect the effect of the methane already present in the atmosphere. The effect of scattering in clouds has to be analyzed specifically, but one

could possibly think that the effect cancels in the ratio. In reality the problem is more subtle.

Table showing parameter values used in the quantitative estimates (methane absorption intensity from Albert et al 2009):

$$\omega_{Me} = 1311 \text{ cm}^{-1}$$

$$\omega_{CO_2} = 667 \text{ cm}^{-1}$$

$$\int \alpha_{Me}^v d\omega = 5 \cdot 10^{-20} (2\pi c) m^2 s^{-1} (129 \text{ cm}^{-2} \text{ atm}^{-1})$$

$$\lambda = 1.7 \cdot 10^{-4} \text{ m}^{-1}$$

$$c_{CO_2}(0) = 350 \text{ ppm} \leftrightarrow 4.5 \cdot 10^{-4} \text{ kg/m}^3 \leftrightarrow 6 \cdot 10^{21} \text{ m}^{-3}$$

$$\omega_{\max} - \omega_{\min} = 350 \text{ cm}^{-1}$$

$$T_{av} = 260 \text{ K}$$

Conclusions

We have analyzed how the energy emitted from the earth in the infrared region is affected by the presence of an atmosphere containing molecules in the gas phase that can absorb and emit radiation. The basis of the greenhouse effect is that if one has an absorber/emitter that is thermally isolated from the ground it acts to reduce the outgoing radiation energy by cooling the local environment. Since the emitted energy for a black body is proportional to the fourth power of the temperature a reduction in temperature for the emitter has substantial consequences for the energy balance. The main IR absorbers/emitters in the atmosphere are carbon dioxide and water. The bending vibration of carbon dioxide centered at the “frequency” 667 cm^{-1} gives a large contribution to the greenhouse effect in the spectral range 500 to 850 cm^{-1} . For water the situation is more complex. There is a contribution from the bending vibration centered at 1540 cm^{-1} . However, for partial pressures close to saturation water vapor contains dimers, trimers and clusters and these give rise to intermolecular vibrational bands at from 700 cm^{-1} and lower. The net intensity of these absorption transitions depends strongly on the relative humidity and it is not easy to quantify their role in the energy balance. They occur in the lower part of the carbon dioxide vibrational band and could partly mask the effect of this compound. This is particularly relevant at lower altitudes where the concentration of water is much higher than that of carbon dioxide. In the region 850 to 1250 cm^{-1} the atmosphere is nearly transparent and adding compounds

with absorption in this range affects the energy balance strongly. Methane has bending vibrational mode centered at 1310cm^{-1} potentially making it potent “greenhouse gas”.

By making the simplifying assumptions that a) the concentration profile of gases like carbon dioxide and methane, but not water decay exponentially with height with the same characteristic length as the pressure, b) that the widths of the spectral transitions are due to pressure broadening and proportional to the pressure and c) that one can linearize the dependence of temperature on height we have derive explicit analytical expressions for the effect on the energy balance of i) adding a compound to the atmosphere with an absorption in a transparent region and ii) adding a compound already present in such amounts that the atmosphere, as seen from outside, is not transparent in the spectral region of the absorption. In the former case the effect depends linearly on the added amount, while in the second case the dependence is logarithmic. We also find a simple analytical expression in terms of easily accessible parameters for the ratio between the two effects. The calculated cooling effects of carbon dioxide and methane are larger (factors of five and twenty for carbon dioxide and methane, respectively) than implied in the ipcc reports. In the latter case more effects of scattering and other effects are accounted for in amore careful way, which could explain the discrepancy. An additional possibility is that I have made some simple numerical mistake of a factor of two or π or that conversions of units have introduced errors. A virtue with the analysis presented above is that it shows simple analytical forms for the effect in two relevant limits. Analytical expressions are transparent and can serve as a framework for thinking about complications such as scattering/emission of clouds and aerosol particles.

Håkan Wennerström

Lund 2011 01 10

Figure 1. Energy of IR-light emitted from the earth

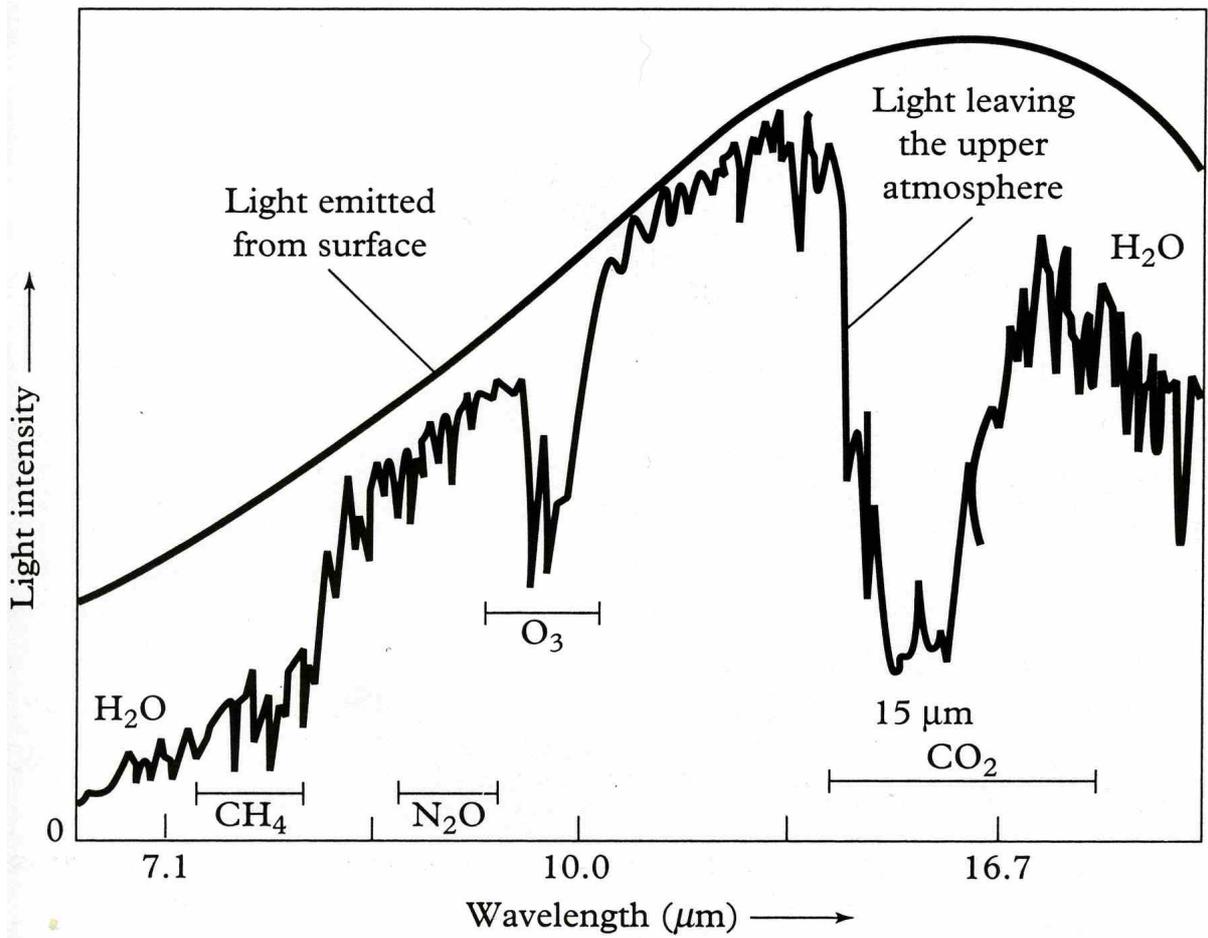


Figure 2

Temperature profile in the atmosphere

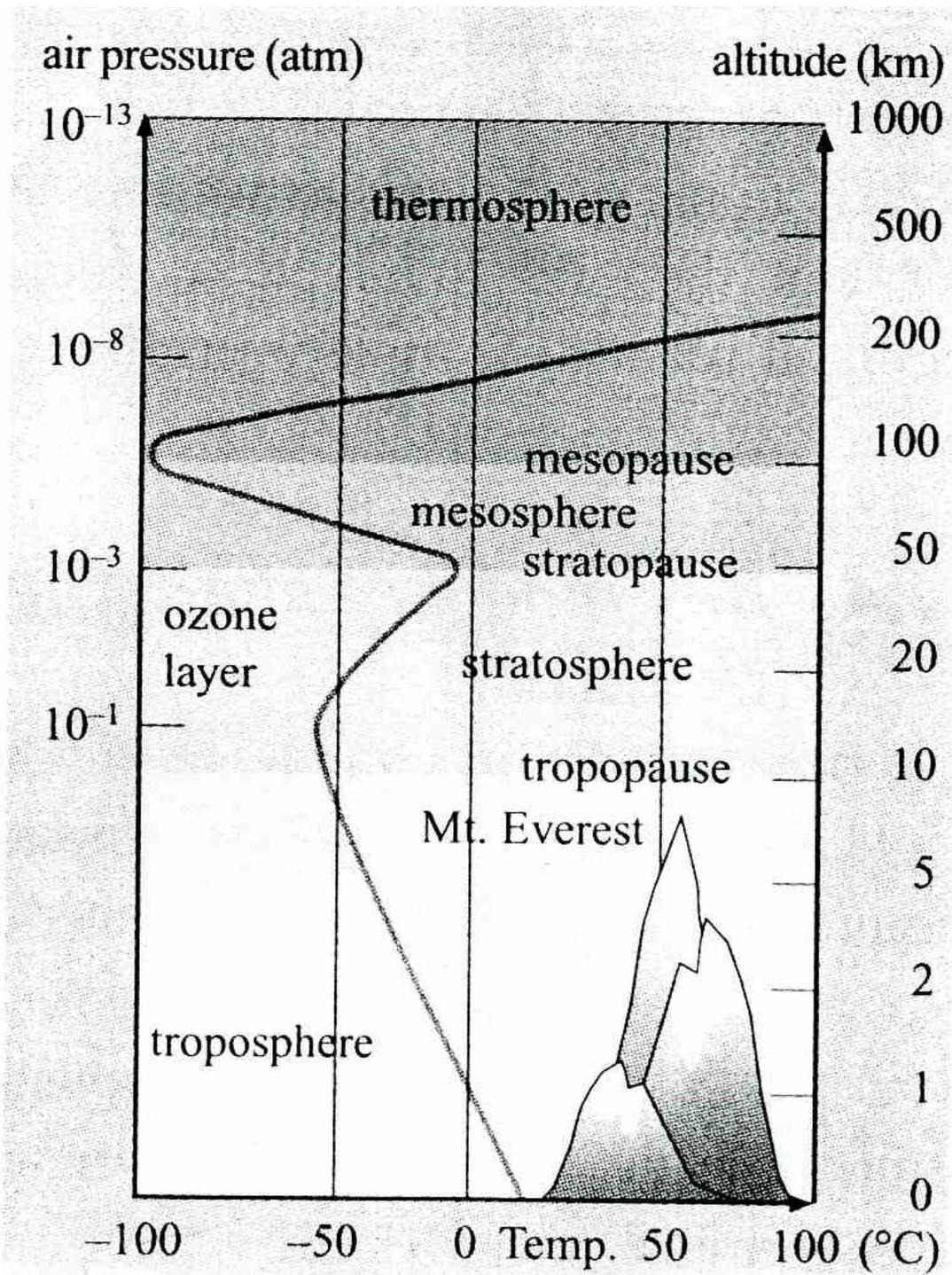


Figure 3 Overview of CO₂ vibrational spectrum. The crucial band is the one to the right.

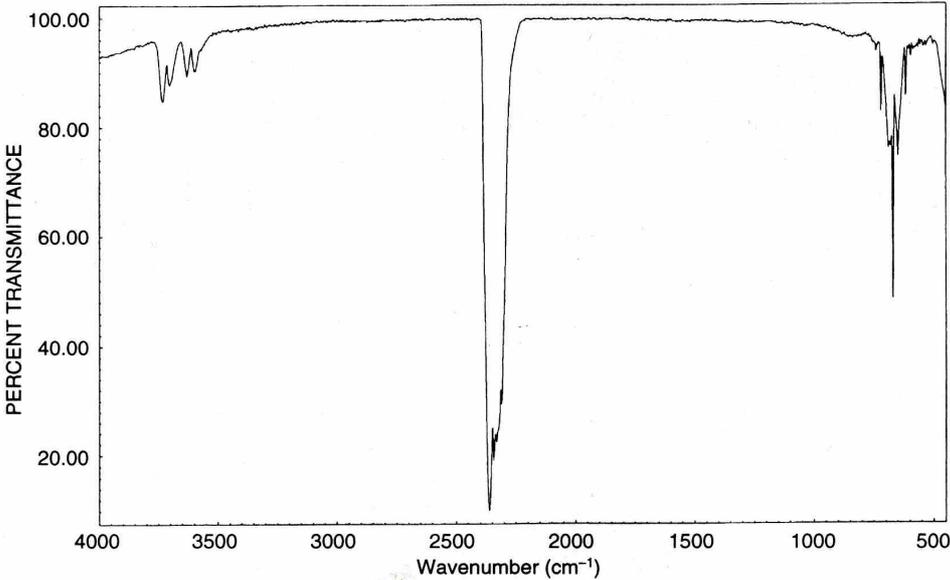


Figure 4 Absorption coefficient for carbon dioxide at $p=1\text{atm}$

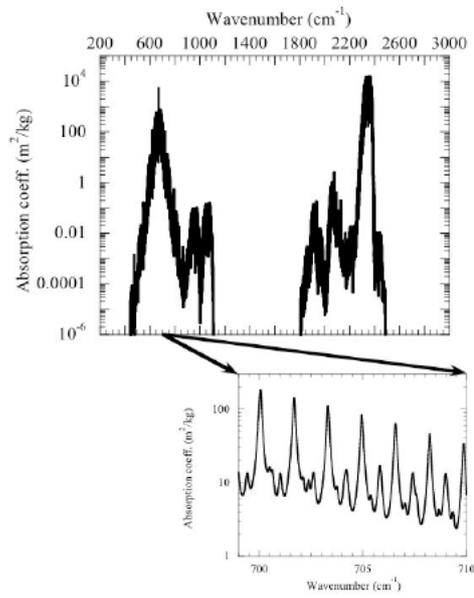


Figure 4.7: The absorption coefficient vs. wavenumber for pure CO_2 at a temperature of $293K$ and pressure of $10^5 Pa$. This graph is not the result of a measurement by a single instrument, but is synthesized from absorption data from a large number of laboratory measurements of spectral features, supplemented by theoretical calculations. The inset shows the detailed wavenumber dependence in a selected spectral region.

Figure 5 Water in gas phase. The bending mode shows absorption down to 1200 cm^{-1}

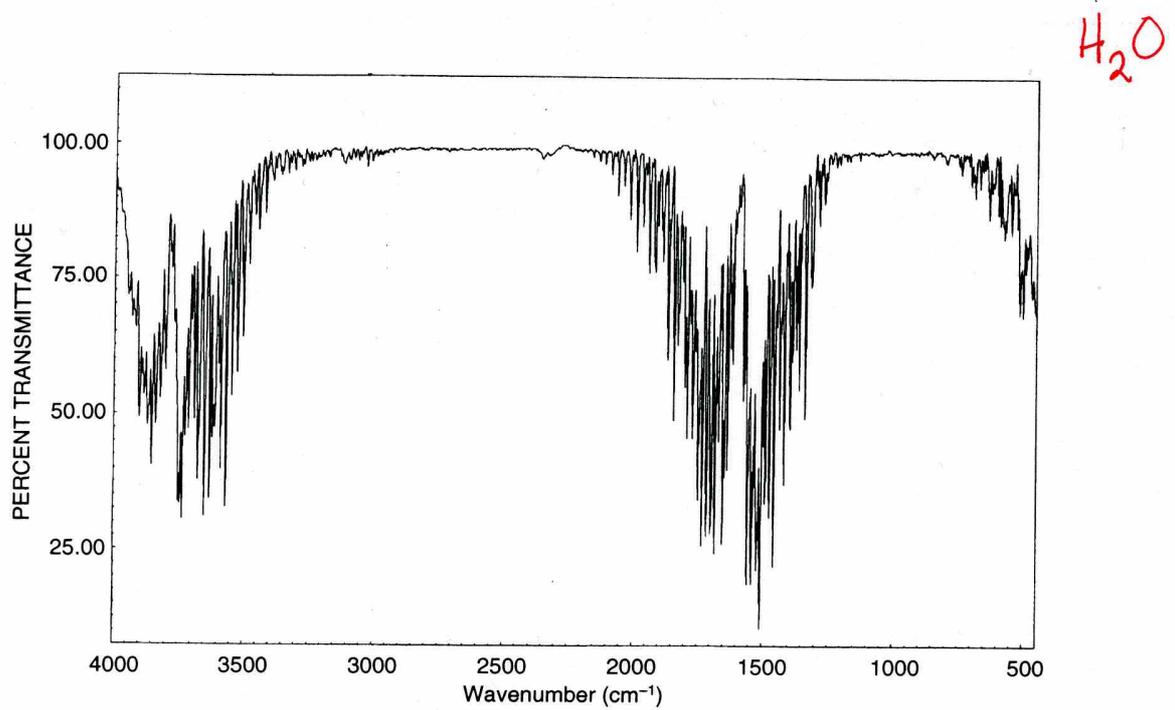
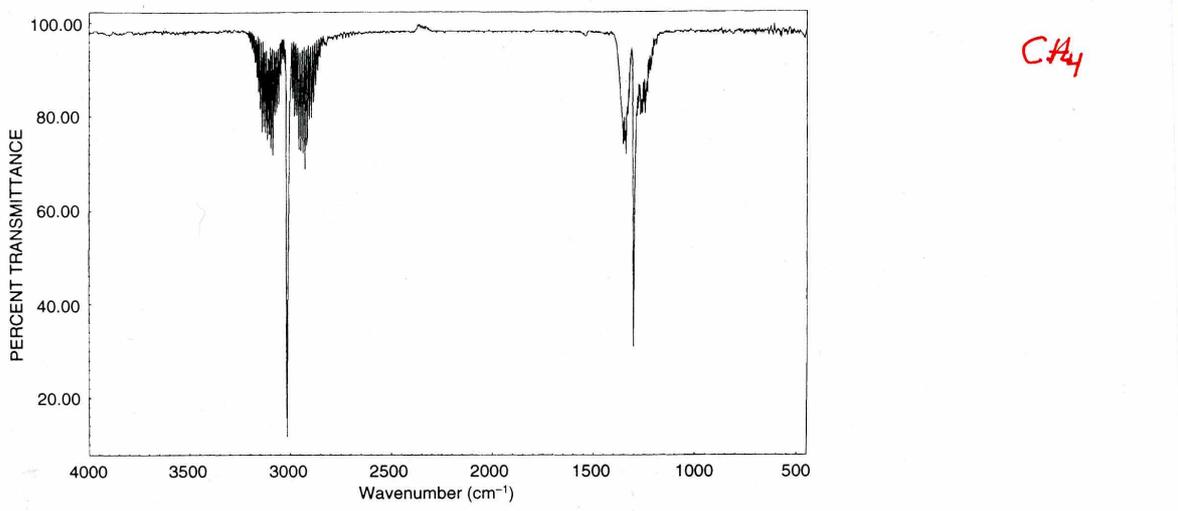


Figure 6. Methane vibrational spectrum with bending mode centered around 1250 cm^{-1}



Greenhouse effect. Supplementary material

Simplification of eq.(44) to yield eq.(45).

Relation between B'_{kl} and transition moments. The Einstein coefficient B_{kl} of eq.(5) is through the Fermi Golden Rule for a dipolar vibrational transition related to the transition dipole moment. For example Atkins (Molecular Quantum Mechanics) gives

$$B_{kl} = \frac{|\mu_{kl}|^2}{6\epsilon_0\hbar^2}. \quad (A1)$$

However this implicitly presupposes a frequency unit of Hertz rather than radians per second as used in the present text. Additionally one has made an isotropic orientational average. Relevant for the present case is thus the slightly modified relation

$$B_{kl}^{\omega} = \frac{\pi|\mu_{kl}(\Omega)|^2}{\epsilon_0\hbar^2} \quad (A2)$$

There is a simple relation between the Einstein coefficient and the line intensity coefficients B'_{kl} in eq.(44) as given in connection with eq.(8). We have

$$B'_{kl} = \hbar\omega_{kl}B_{kl}^{\omega}/c = \frac{\pi\omega_{kl}|\mu_{kl}(\Omega)|^2}{c\epsilon_0\hbar} \quad (A3)$$

Evaluation of transition moment. For vibration rotation transitions the states k and l can be described as combined vibration-rotation states and represented by state vectors

$$|k\rangle = |0\rangle_v |J_k\rangle_R$$

$$|l\rangle = |1\rangle_v |J_l\rangle_R \quad (A4a,b)$$

We have in addition that $\hat{\mu}(\Omega) = \hat{\mu}_{mol} \cos\theta$ and

$$\sum_l |\hat{\mu}(\Omega)|^2 = \sum_l \langle k|\hat{\mu}(\Omega)|l\rangle \langle l|\hat{\mu}(\Omega)|k\rangle = \sum_l \langle 0|\hat{\mu}_{mol}|1\rangle \langle 1|\hat{\mu}_{mol}|0\rangle \langle J_k|\cos\theta|J_l\rangle \langle J_l|\cos\theta|J_k\rangle =$$

$$|\langle 1|\hat{\mu}_{mol}|0\rangle|^2 \sum_l \langle J_k|\cos\theta|J_l\rangle \langle J_l|\cos\theta|J_k\rangle = |\langle 1|\hat{\mu}_{mol}|0\rangle|^2 \langle J_k|\cos^2\theta|J_k\rangle =$$

$$|\langle 1|\hat{\mu}_{mol}|0\rangle|^2 \left\{ \langle J_k|1/3|J_k\rangle + \frac{2}{3} \langle J_k|(3\cos^2\theta - 1)/2|J_k\rangle \right\} = \frac{1}{3} |\langle 1|\hat{\mu}_{mol}|0\rangle|^2 \quad (A5)$$

where the last equality follows from the rotational symmetry of the spherical harmonics functions. This shows that when we sum over initial rotational states we regain the total oscillatory strength of the vibrational transition. The total intensity of the vibrational transition is, if one disregards the stimulated emission, (See for example Atkins)

$$\int \alpha(\omega) d\omega = \frac{\pi\omega_v}{3c\epsilon_0\hbar} |\langle 1|\hat{\mu}_{mol}|0\rangle|^2 = \sum_l B'_{kl} \quad (A6)$$

where the last equality follows from eqs (A3,A5)

Evaluation of the integral over z .

For the case when the temperature gradient is limited one can linearize and evaluate the integral over z in eq.(44) Thus

$$\begin{aligned}
& \int_0^{\infty} \left\{ 1 - \frac{P_l(T(z))}{P_l(T_B)} \right\} \exp(-\lambda z) dz \approx \int_0^{\infty} \left\{ 1 - \frac{\exp\{-\hbar\omega_l/kT(z)\}}{\exp\{-\hbar\omega_l/kT_B\}} \right\} \exp(-\lambda z) dz \approx \\
& \int_0^{\infty} (\hbar\omega_l/k) \frac{T_B - T(z)}{T_B T(z)} \exp(-\lambda z) dz \approx -\frac{\hbar\omega_v \langle dT/dz \rangle_{av}}{kT_{av}^2} \int_0^{\infty} z \exp(-\lambda z) dz = \\
& -\frac{\hbar\omega_v \langle dT/dz \rangle_{av}}{kT_{av}^2 \lambda^2} \tag{A7}
\end{aligned}$$

which is independent of l .

Evaluation of the Boltzmann factor $P_l(T_B)$

The probability of occupying a particular vibrationally excited state l is reduced by the fact that there is a large number of rotational states of the ground state vibrational energy. Thus

$$\begin{aligned}
P_l(T_B) &= \frac{\exp(-\hbar\omega_l/kT_B)}{\sum_{k,l} \exp(-\hbar\omega_{k,l}/kT_B)} = \frac{\exp(-\hbar\omega_{k'} /kT_B) \exp(-\hbar\omega_{lk'} /kT_B)}{\sum_{k,l} \exp(-\hbar\omega_{k,l} /kT_B)} \approx \\
& \exp(-\hbar\omega_v /kT_B) \frac{\exp(-\hbar\omega_{k'}(kT_B))}{\sum_k \exp(-\hbar\omega_k /kT_B)} \tag{A8}
\end{aligned}$$

which is also independent of l .

Combination of eqs A6-8.

By combining eqs (A6-8) we now have

$$\begin{aligned}
& \sum_{k,l} B_{kl} P_l(T_B) \int_0^{\infty} \left\{ 1 - \frac{P_l(T(z))}{P_l(T_B)} \right\} \exp(-\lambda z) dz \approx -\frac{\hbar\omega_v \langle dT/dz \rangle_{av}}{kT_{av}^2 \lambda^2} \exp(-\hbar\omega_v /kT_B) \sum_{kl} B_{kl} \frac{\exp(-\hbar\omega_k /kT_B)}{\sum_{k'} \exp(-\hbar\omega_{k'} /kT_B)} = \\
& -\frac{\hbar\omega_v \langle dT/dz \rangle_{av}}{kT_{av}^2 \lambda^2} \exp(-\hbar\omega_v /kT_B) \int \alpha(\omega) d\omega
\end{aligned}$$

(A9), which inserted into eq.(44) gives eq.(45).

Derivation of the temperature profile in an atmosphere without other heat conduction mechanisms.

In eq (13) we found a simple expression for the effect of a perfectly absorbing thermally isolated layer on the temperature and the resulting emission. In an atmosphere there is emission and absorption at all positions and seen as a thin layer it will always be only marginally absorbing and emitting. The integral effect, however, is what we have analyzed taking the observed temperature profile as input. It is a major undertaking to find a realistic model for the energy transport in the atmosphere. In addition to convection there is also water evaporation/condensation/precipitation. Let us consider the extreme case of only radiative energy transfer to elucidate the greenhouse effect also with respect to the temperature profile.

Consider an atmosphere with a uniform density so that the absorbance of a layer of thickness dz is

$$A(\omega, z, \theta) = \rho_0 \alpha dz / \cos \theta \quad (\text{B1}),$$

where we assume that there is no frequency dependence of the absorbance. For a real atmosphere the density decays with increasing height but by using a scaling relation

$$y = \frac{1}{\lambda} \{ \exp(\lambda z) - 1 \} \quad (\text{B2})$$

one can cover also this situation. A thin layer at z of thickness dz will emit (in both directions)

$$J_{em}(z) = 2 \int_0^1 \int_0^\pi 2\pi c e_0(\omega, T(z)) A(\omega, \theta) \cos \theta d \cos \theta d \omega dz = \quad (\text{B3}),$$

$$4\sigma T^4(z) \rho_0 \alpha dz$$

where we have use eqs (B1, 10,12). At steady state this emitted energy is balanced by an absorption of radiation coming from the black body at $z=0$, from the gas between the ground and the layer at z and from the gas above the layer. The combined absorbed energy is

$$J_{abs}(z) = 2\sigma \int_0^1 \{ \cos(\theta) T^4(0) \exp[-z \rho_0 \alpha / \cos(\theta)]$$

$$\int_0^z T^4(z') \rho_0 \alpha \exp[-\rho_0 \alpha (z - z') / \cos(\theta)] dz' + \quad (\text{B4})$$

$$\int_z^\infty T^4(z') \rho_0 \alpha \exp[-\rho_0 \alpha (z' - z) / \cos(\theta)] dz' \} \frac{\rho_0 \alpha}{\cos(\theta)} d \cos(\theta) dz$$

Using scaled variables

$$x \equiv \rho_0 \alpha z, T^4(z) \equiv f_4(x) \quad (\text{B5})$$

and then balancing emitted and absorbed energy gives

$$2f_4(x) = \int_0^1 \{ \cos(\theta) f_4(0) \exp(-x/\cos(\theta)) + \int_0^x f_4(x') \exp[-(x-x')/\cos(\theta)] dx' + \int_x^\infty f_4(x') \exp[-(x'-x)/\cos(\theta)] dx' \} \frac{1}{\cos(\theta)} d\cos(\theta) \quad (\text{B6})$$

This equation can be simplified by partial integration of the last two terms of the rhs. Then one finds that the condition for energy balance is

$$\int_0^1 \left\{ \int_0^x f_4'(x') \exp[-(x-x')/\cos(\theta)] dx - \int_x^\infty f_4'(x') \exp[-(x'-x)/\cos(\theta)] dx \right\} d\cos(\theta) = 0 \quad (\text{B7})$$

This is an integral equation for the derivative of the T^4 temperature profile. To define a solution one has to add a boundary condition in addition to the one for $z=0$. Clearly if the temperature far away is also $T(0)$ the equation is satisfied when the derivative is zero and one has a constant temperature as expected. If the temperature is low far out and if $x \gg 1$ the two integrals cancel for a constant value of $f_4'(x)$. This case corresponds to the model discussed on p6 with a sequence of black body layers. A constant derivative of $f_4(x)$ implies a temperature profile

$$T(z) = T(0) \left(1 + \frac{C\rho_0\alpha z}{T(0)^4} \right)^{1/4} \quad (\text{B8}).$$

For a more weakly absorbing system the integral equation (B7) has to be solved numerically.

Evaluation of eq.49 through direct integration.

For the case of a strongly absorbing compound we can neglect the radiation from the ground so that I is only the second and third terms of the rhs of eq. (42) that are of interest. Make the assumptions that we only need to consider absorption of one compound in the frequency range of interest. The integral over z' in the third term can be simplified

$$\int_z^\infty \alpha_j(\omega, z') \exp(-\lambda z') dz' = \frac{1}{c_j(0)} \int_z^\infty c_j(0) \alpha_j(\omega, z') \exp(-\lambda z') dz' \quad (C1)$$

$$\frac{1}{c_j(0)} \int_z^\infty \varepsilon(\omega, z') dz' = \frac{1}{c_j(0)} \Sigma(\omega, z)$$

using his result we can now make a partial integration of the third term and

$$\int_0^1 \Sigma(\omega, z) \exp[-\Sigma(\omega, z)/\cos(\theta)] / \cos(\theta) d \cos(\theta) = \quad (C2)$$

$$\exp[-\Sigma(\omega, z)] - \int_0^1 \exp[-\Sigma(\omega, z)/\cos(\theta)] d \cos(\theta)$$

The two terms, called T_2 and T_3 , can now be summed and

$$T_2 + T_3 = -\frac{\lambda}{c_j(0)} \left\{ \int_0^\infty e_0(\omega, T(z)) \varepsilon(\omega, z) \exp[-\Sigma(\omega, z)] dz - \right. \quad (C3)$$

$$\left. -2 \int_0^\infty e_0(\omega, T(z)) \varepsilon(\omega, z) \int_0^1 \exp[-\Sigma(\omega, z)/\cos(\theta)] d \cos(\theta) dz \right\}$$

This can be brought to a form more suitable for explicit evaluation through a partial integration and

$$T_2 + T_3 \cong -\frac{\lambda}{c_j(0)} \left\{ \int_0^\infty \frac{\partial e_0(\omega, T(z))}{\partial z} \exp[-\Sigma(\omega, z)] dz - \right. \quad (C4)$$

$$\left. -2 \int_0^\infty \frac{\partial e_0(\omega, T(z))}{\partial z} \int_0^1 \exp[-\Sigma(\omega, z)/\cos(\theta)] \cos(\theta) d \cos(\theta) dz \right\}$$

Note that if there is no gradient in temperature there is no net effect of the gas. If we now make the assumption the the absorption is due to a sum of Lorentzian with a line-width that decreases exponentially with increasing height we have that

$$\Sigma(\omega, z) = \int_z^\infty \varepsilon(\omega, z') dz' = \sum_{kl} \varepsilon_{kl}^j(\omega_{kl}, 0) \int_z^\infty 1/[1 + (\omega - \omega_{kl})^2 \Gamma_{kl}^2(0) \exp(2\lambda z')] dz' = \quad (C5)$$

$$\sum_{kl} \frac{\varepsilon_{kl}^j(\omega, 0)}{2\lambda} \ln \{ 1 + 1/[(\omega - \omega_{kl})^2 \Gamma_{kl}^2 \exp(2\lambda z)] \}$$

Thus we can write

$$\begin{aligned} \exp(-\Sigma(\omega, z)) &= \prod_{kl} \left\{ 1 + \frac{1}{(\omega - \omega_{kl})^2 \Gamma_{kl}^2(0) \exp(2\lambda z)} \right\}^{-\varepsilon_{kl}^j(0)/2\lambda}, \\ \exp[-\Sigma(\omega, z)/\cos(\theta)] &= \prod_{kl} \left\{ 1 + \frac{1}{(\omega - \omega_{kl})^2 \Gamma_{kl}^2(0) \exp(2\lambda z)} \right\}^{-\varepsilon_{kl}^j(0)/(2\lambda \cos(\theta))}, \end{aligned} \quad (C6)$$

When this is inserted into eq(42) we obtain

$$\frac{\partial e_0[\omega, T(z)]}{\partial z} \left\{ 1 + \frac{1}{(\omega - \omega_{kl}) \Gamma_{kl}^2(0) \exp(2\lambda z)} \right\} \quad (C7).$$

To evaluate the total contribution this expression has to be integrated over all frequencies in the relevant range. If we assume that we can neglect overlap between peaks the product terms in eq (C7) are different from unity only over a small frequency range $\pm \Delta\omega/2$ around each resonance frequency. The decrease in energy output is then

$$\begin{aligned} (2\pi c)^{-1} \frac{\partial J_{out}}{\partial n_j} &\approx -\frac{2\lambda}{c_j(0)} \sum_{kl} \int_{z_{min}}^{\infty} \int_{\omega_{min}}^{\Delta\omega/2} \frac{\partial e_0[\omega, T(z)]}{\partial z} \left\{ 1 + \frac{1}{\omega^2 \Gamma_{kl}^2(0) \exp(2\lambda z)} \right\}^{-\varepsilon_{kl}^j/2\lambda} dz d\omega + \\ &\frac{4\lambda}{c_j(0)} \sum_{kl} \int_{z_{min}}^{\infty} \int_{\omega_{min}}^{\Delta\omega/2} \int_0^1 \frac{\partial e_0[\omega, T(z)]}{\partial z} \left\{ 1 + \frac{1}{\omega^2 \Gamma_{kl}^2(0) \exp(2\lambda z)} \right\}^{-\varepsilon_{kl}^j/(2\lambda \cos(\theta))} d\cos(\theta) d\omega dz \end{aligned} \quad (C8)$$

Here the integration has been limited to the frequency range where the frequency dependent factor in the integrand has been reduced to $1/2$. Furthermore it is then not consistent to integrate for z-values that are small than when the frequency range goes to zero. This condition defines z_{min} so that

$$\begin{aligned} \omega_{min} &= [\varepsilon_{kl}^j / \lambda 2 \ln 2]^{1/2} \Gamma_{kl}^{-1} \exp(\lambda z) \\ \omega_{min}(\cos(\theta)) &= [\varepsilon_{kl}^j / \lambda \cos(\theta) 2 \ln 2]^{1/2} \Gamma_{kl}^{-1} \exp(\lambda z) \\ z_{min} &= \lambda^{-1} \ln[(2\varepsilon_{kl}^j / \lambda \ln 2)^{1/2} / \Delta\omega \Gamma_{kl}] \\ z_{min}(\cos(\theta)) &= \lambda^{-1} \ln[(2\varepsilon_{kl}^j / \lambda \cos(\theta) \ln 2)^{1/2} / \Delta\omega \Gamma_{kl}] \end{aligned} \quad (C9)$$

It is still problematic to solve the integrals. First we replace the gradient in e_0 by the average value as done in the main text. Then we series expand the remaining factor in the integrand and

$$\left\{ 1 + \frac{1}{\omega^2 \Gamma^2 \exp(2\lambda z)} \right\}^\gamma \approx 1 - \frac{\gamma}{\Gamma^2 \exp(2\lambda z)} \frac{1}{\omega^2} \quad (C10)$$

With this simplification is the integration over frequency straightforward. The interation over z involves several terms but they add nicely up to the simple result that for each transition kl there is a contribution to the decrease in emission of magnitude

$$(2\pi c)^{-1} \left(\frac{\partial J_{out}}{\partial n_j} \right)_{kl} \approx - \left\{ \frac{\partial e_0(\omega, T)}{\partial z} \right\}_{av} \frac{\Delta\omega}{c_j(0)} \quad (C11)$$

Summing over all transitions cover, by definition, the frequency width of the whole vibrational peak and we regain eq.(49). (However this is a factor of four larger than previously obtained. I haven't gone through carefully to see if this is due to a simple error in the calculations presented above)

