The molecular spectroscopy of the greenhouse effect. An attempt to understand the molecular basis.

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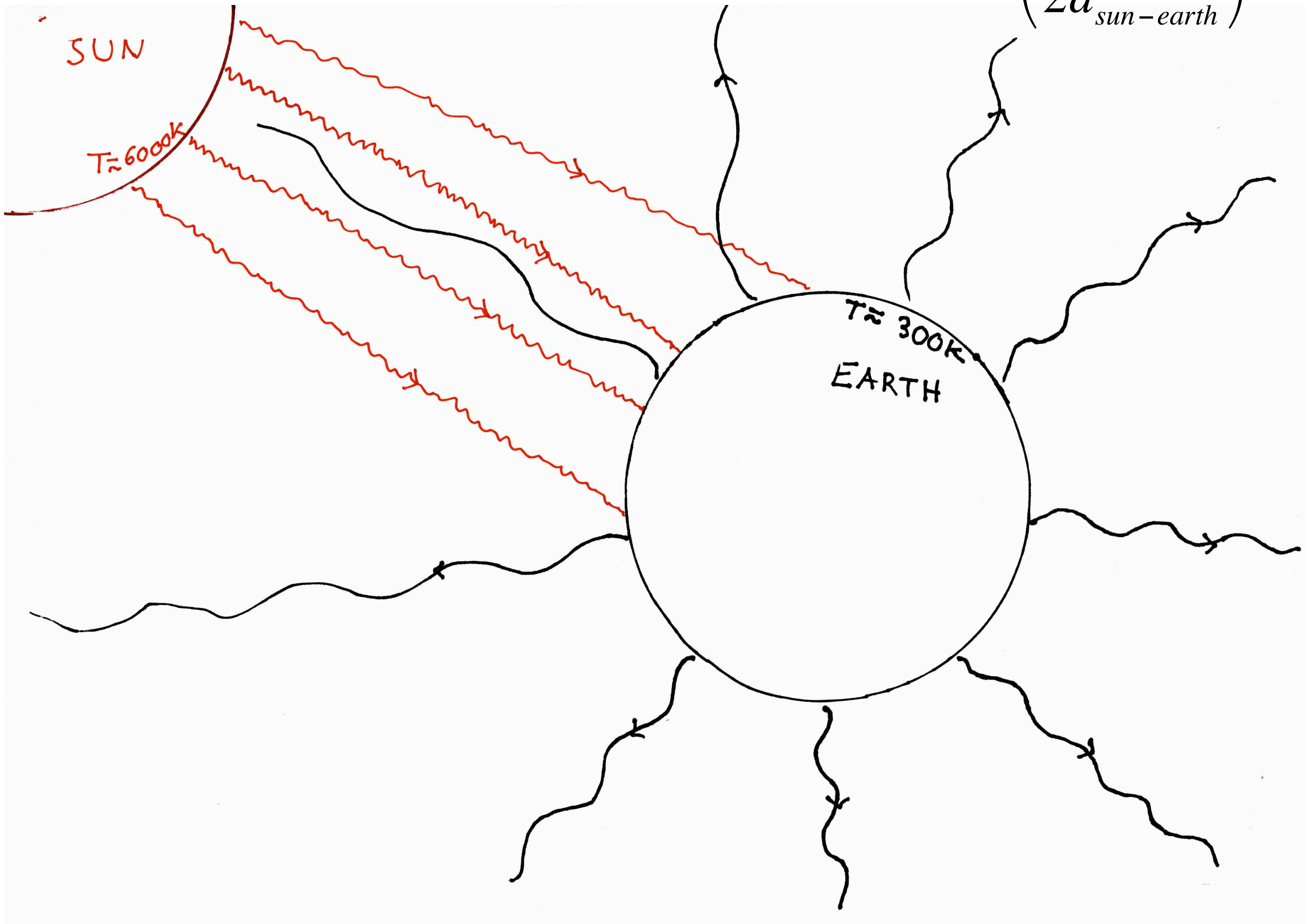
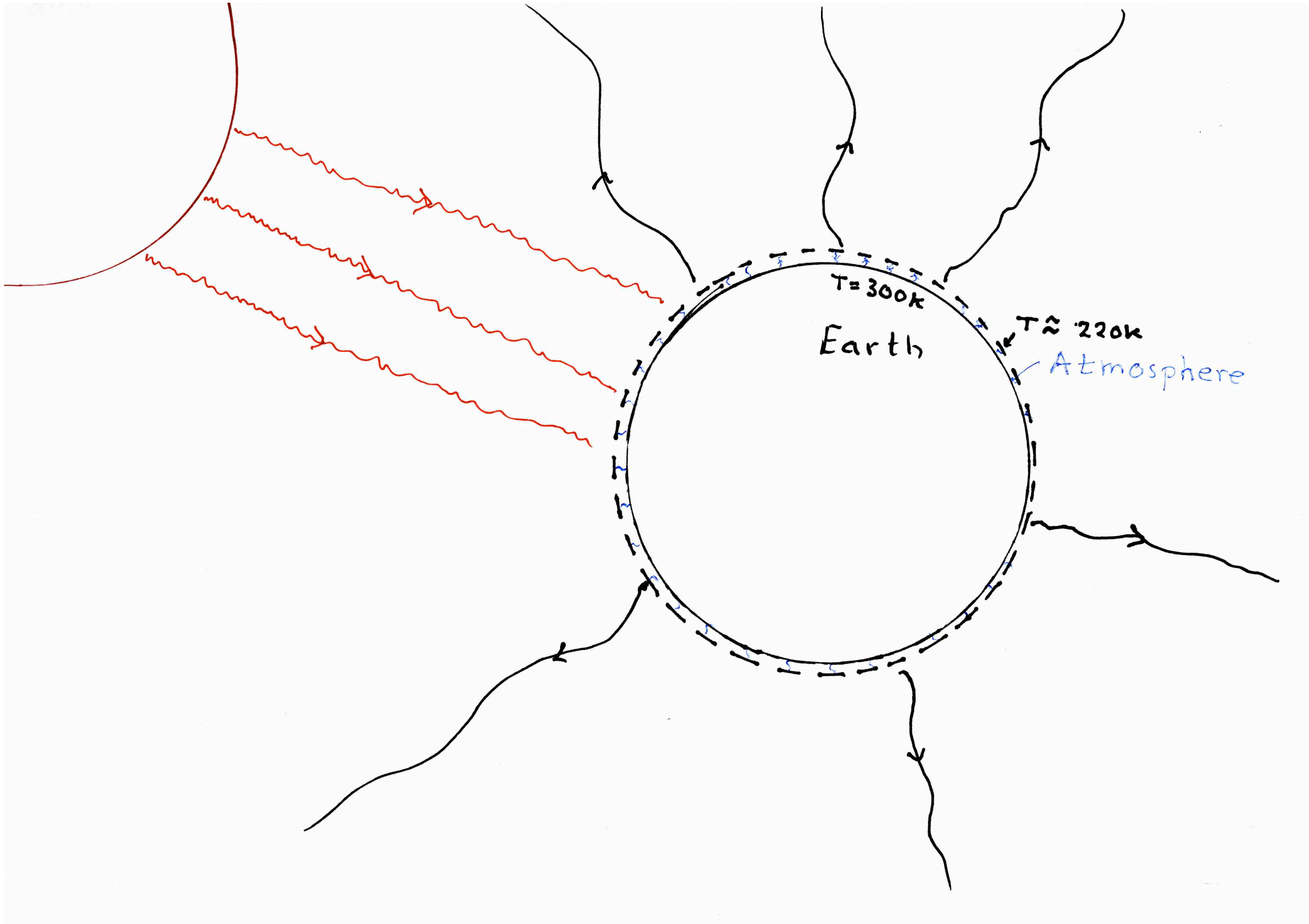
Radiation energy transfer of the earth

$$T_{earth} \leq T_{sun}\left(\frac{R_{sun}}{2d_{sun-earth}}\right)^{1/2} = 275K$$



Radiation energy balance with atmosphere



Black body radiation

In 1900 Planck derived the density of photon states for a radiation field in a volume V and in equilibrium with the walls at temperature T:

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

A black body emits an energy J per area and time of

$$J = \sigma T^4 \,(W/m^2)$$

For the earth at 300K this is 2.3 10^{17}W, at 210K it is four times less.

$$\sigma \equiv \pi^2 k^4 / (60\hbar^3 c^2) = 5.67 \cdot 10^{-8}\, W m^{-2} K^{-4}$$

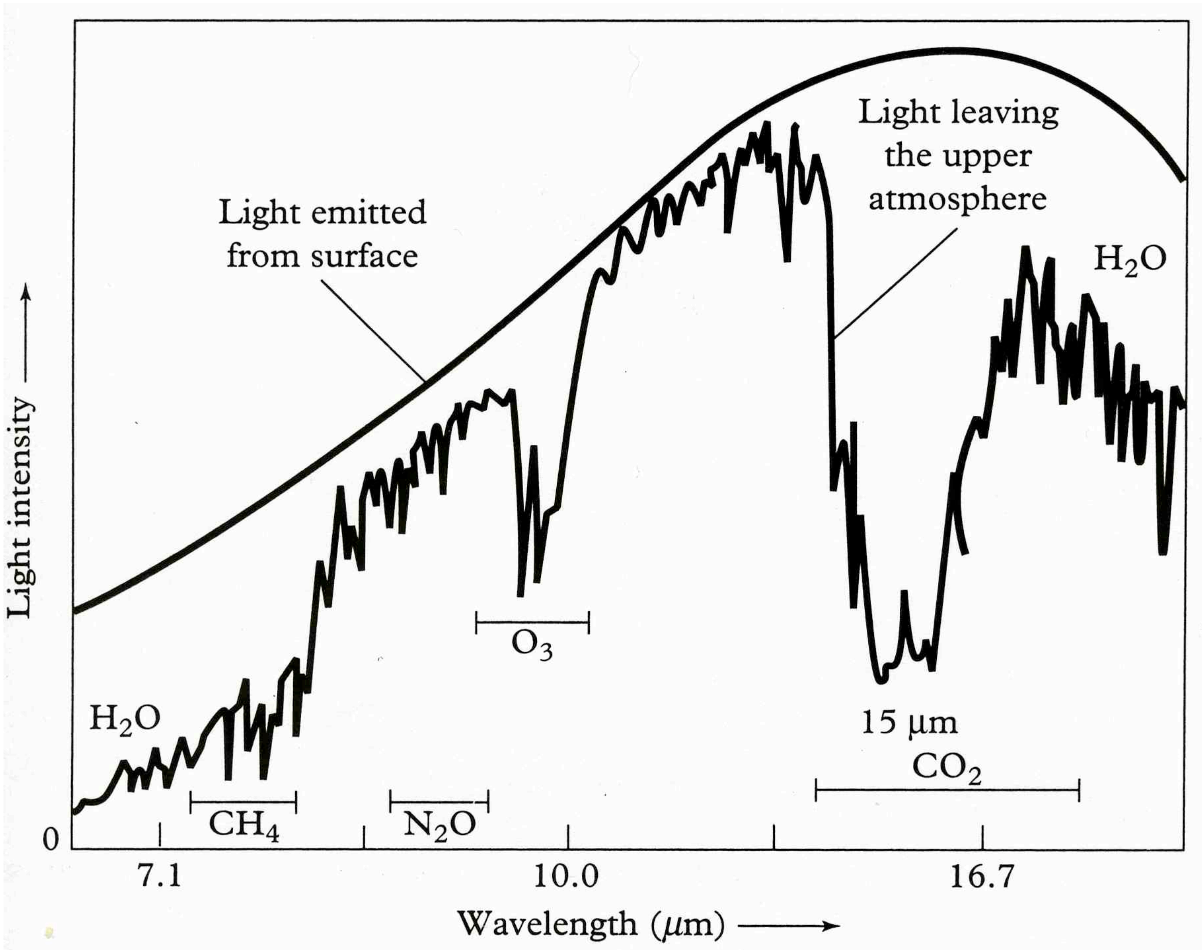
Stefan-Boltzmann constant

The maximum in the energy emission occurs for

$$\hbar\omega / kT = 2.822$$

For solar radiation this corresponds to a frequency in the visible range, while for an object at 300K it corresponds to 585 cm^{-1}, which is in the low infrared region.

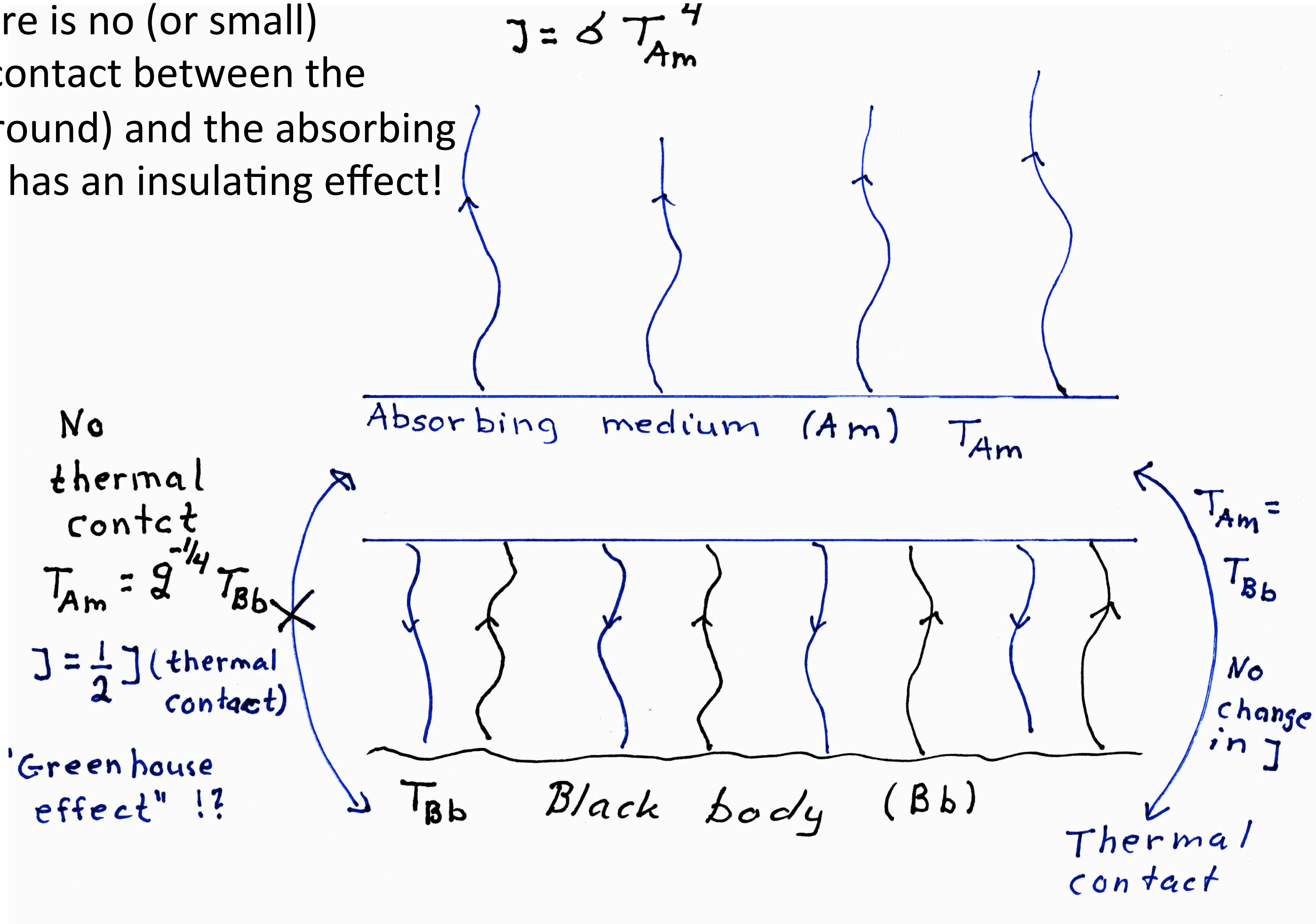
Emission of radiation from the earth



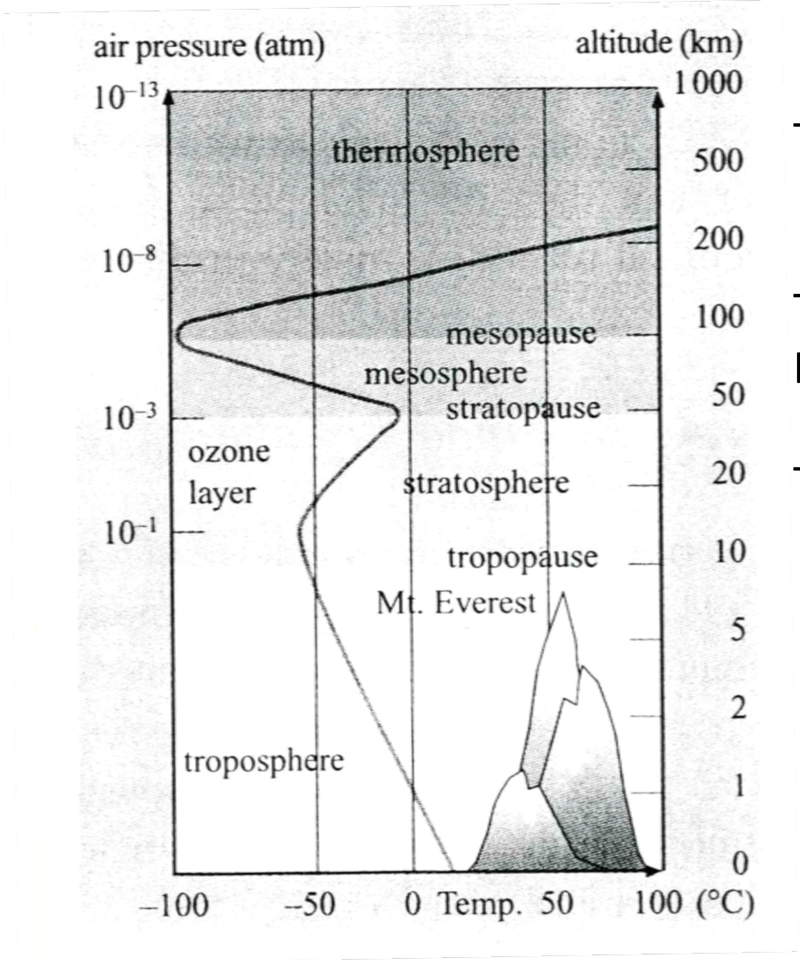
Wave-length (10 micrometer) corresponds to $(10^3\ cm^{-1})^{-1}$

Absorbing/emitting medium above a black body

When there is no (or small) thermal contact between the object (ground) and the absorbing layer this has an insulating effect!



Temperature profile of the atmosphere



The pressure drop can seen as basically due to the gravitational force and the gases distribute basically according to a Boltzmann distribution law.
There is a ground temperature of 290-300K.
It decreases to a minimum value of around 215K at a height of (around) 10-12km.
Then it increases towards 270K with a maximum at around 50km.

The most reasonable explanation of the temperature decrease up to 12km is energy losses due to emission of radiation (greenhouse effect).
The "greenhouse effect" is a real thing. How can we understand it in molecular terms? A clear day we are not surrounded by a black body!

IR-active molecules in the atmosphere

Components of the atmosphere

N_2: Not IR-active	(79%)
O_2: Not IR-active	(19.5%)
H_2O: Stretch and bend modes	(30-100% relative humidity, 3-0.03%)
CO_2: Stretch and bend modes	(350ppm, volume/volume!)
He, Ne, Ar, Xe: Not IR-active	(1%)
CH_4: Stretch and bend modes	(1-2ppm)
O_3: Stretch and bend modes	(<<1ppm, increasing at higher altitudes)
N_2O: Stretch and bend modes	(<1ppm)

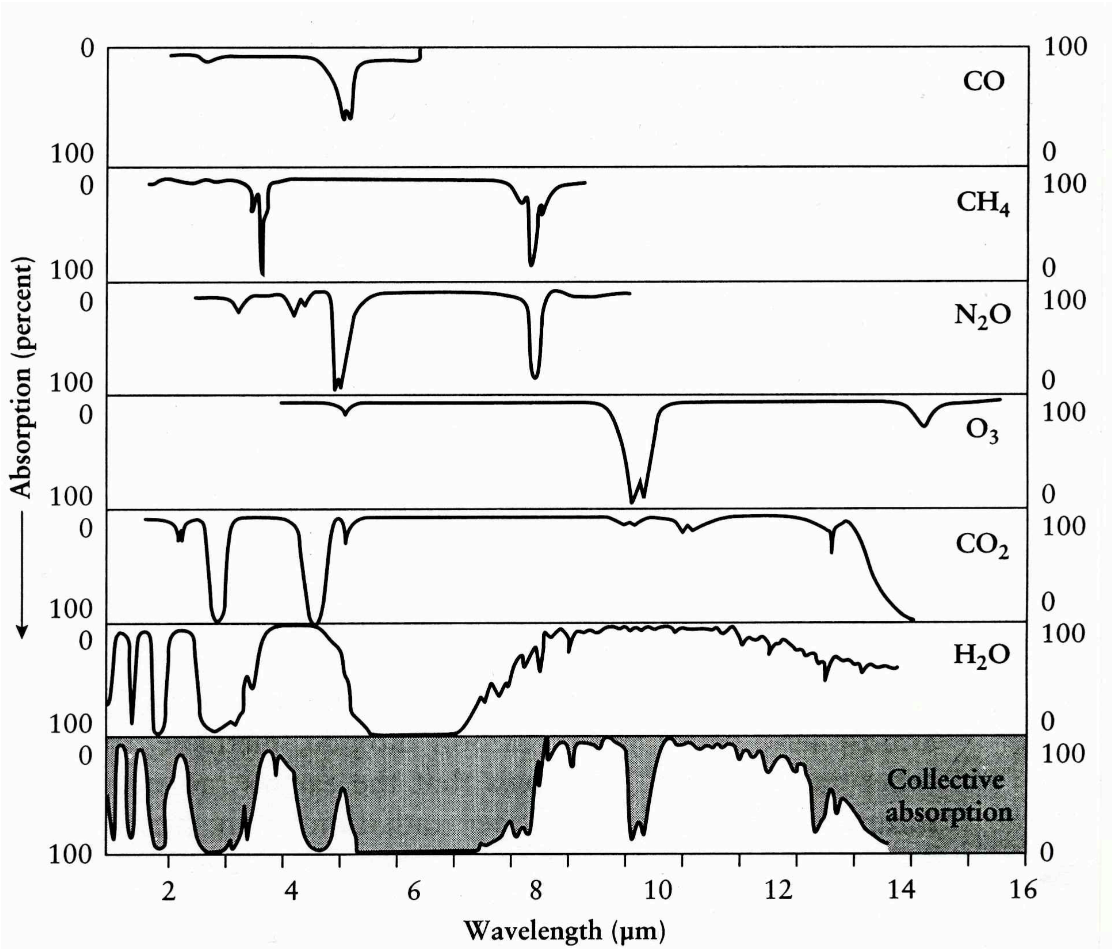
+ pollutants like

NO_x

Hydrocarbons (in addition to methane)

Oxidized unsaturated hydrocarbons.

Absorption properties of the atmosphere

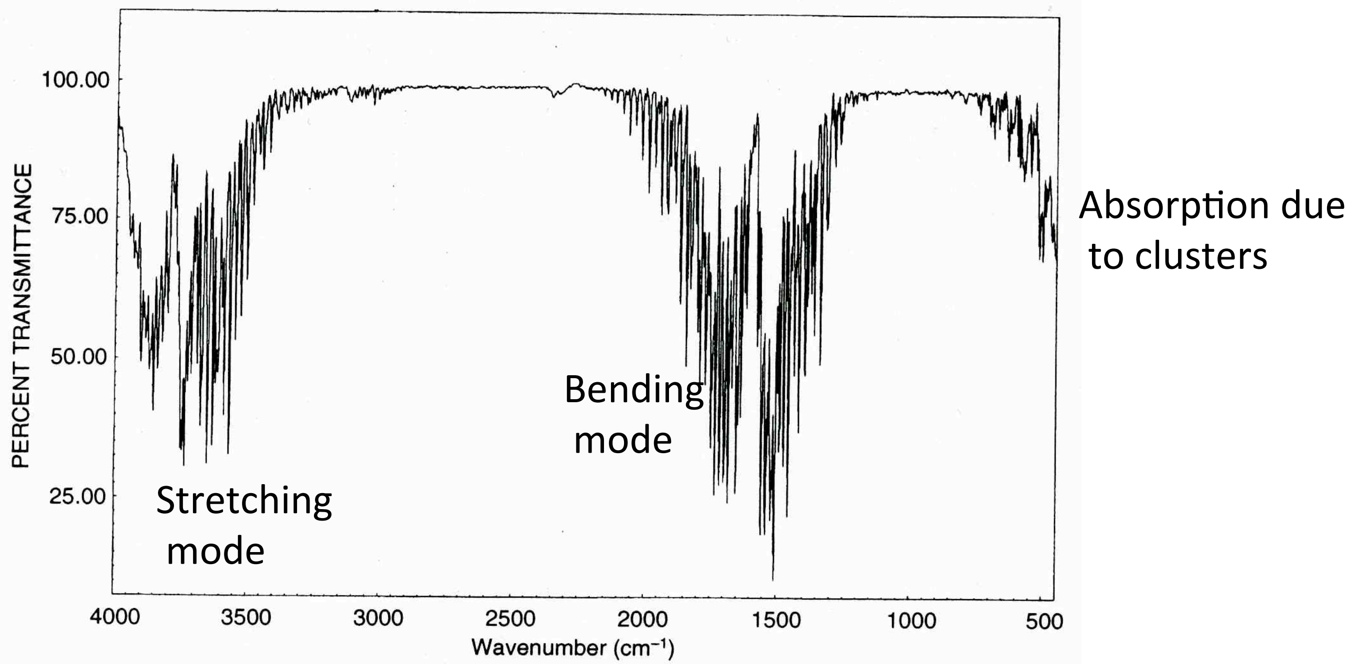


Note the the H_2O spectrum is that of liquid water (textbook error)

Water

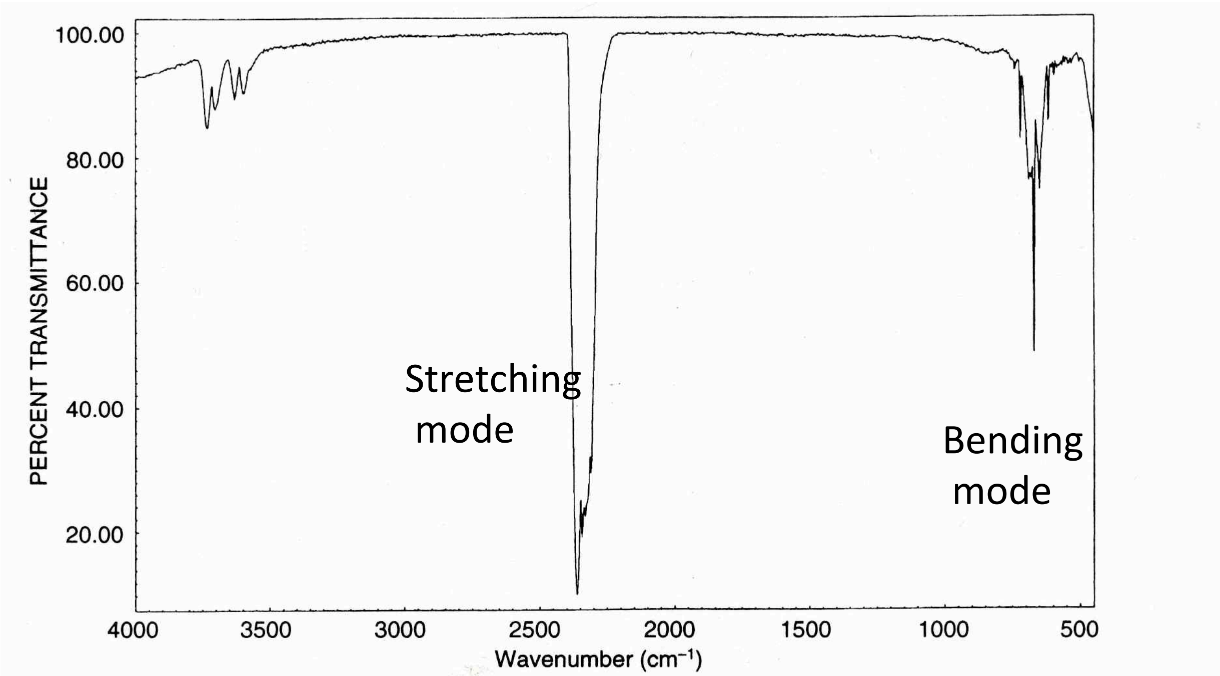
For the isolated water molecule there are two IR-active vibrational modes:
asymmetric stretch at 3757cm^{-1} and a bending mode at 1595cm^{-1}.
The overall width of the rotational band is essentially determined by kT.

IR spectrum for water in the **gas** phase

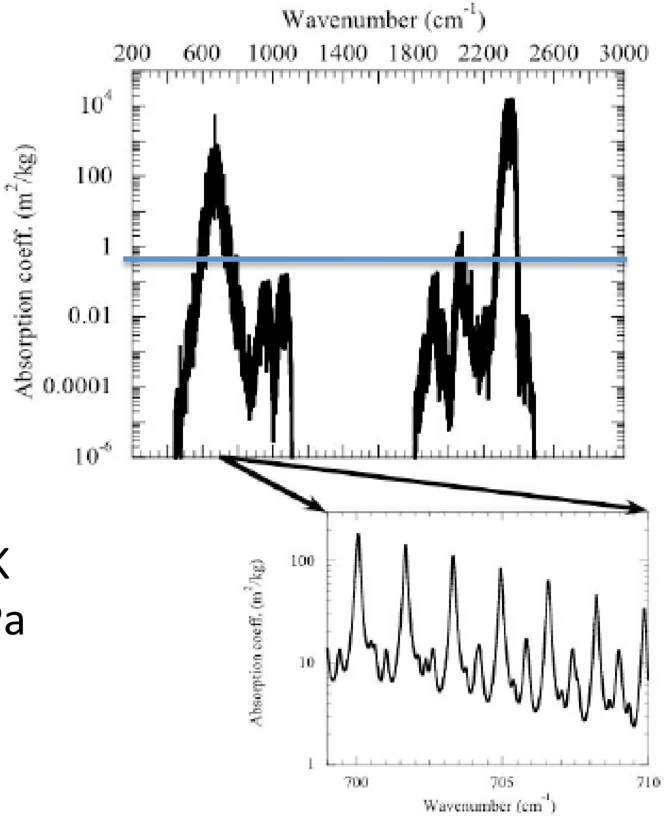


Carbon dioxide

Carbon dioxide is a linear molecule with two IR-active modes. The asymmetric stretch has its basic frequency at 2349cm^{-1} and there is a degenerate bending mode at 667cm^{-1}. The latter is particularly important since at 300K the maximum output energy of a black body is at 585cm^{-1}. For the bending there is a central Q-peak and P and R branches with absorption from different rotational states



Quantitative absorption coefficient CO_2

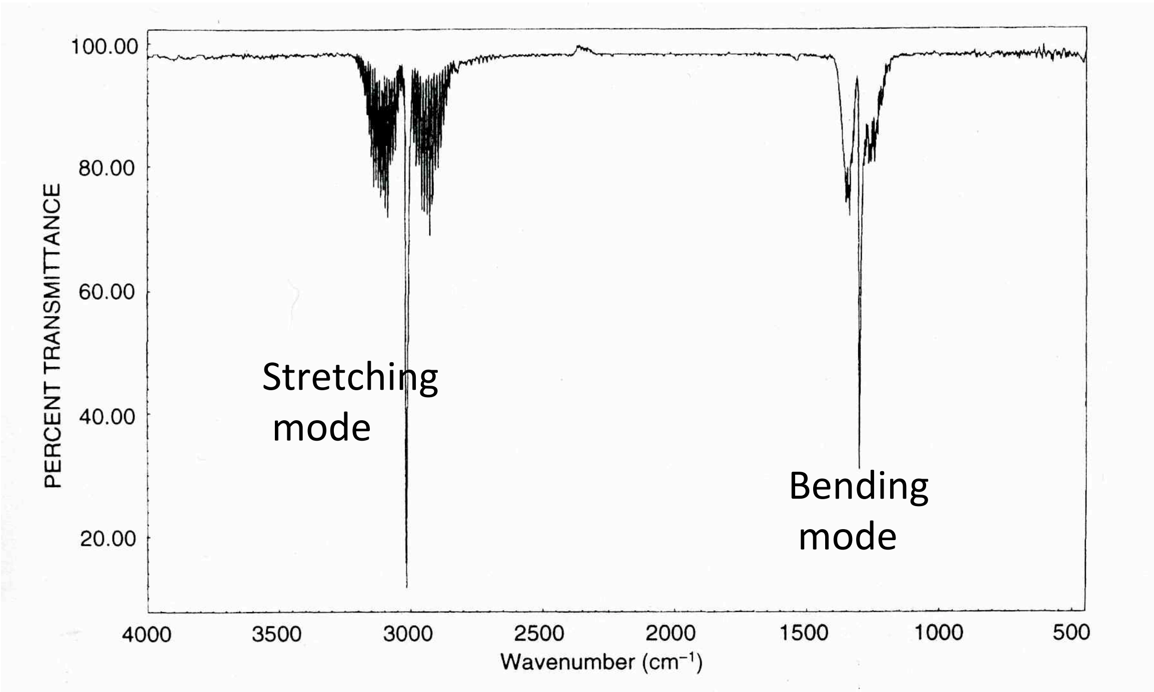


Current CO_2 content in the atmosphere is ≈350ppm (V/V)
Using Beer's law the atmosphere is non-transparent in the ranges 500-850cm^{-1} and 2200-2500 due to CO_2 absorption

T=293K
P=10^5Pa

Rotational fine structure

Methane



Methane has a pressure of 0.1-0.2Pa at ground level. (Corresponds to1-2ppm). The bending mode vibration at 1311cm^{-1} is in a region where the atmosphere is relatively transparent. Methane is said to be a potent greenhouse trace gas.

Spectral variations with temperature and pressure

At pressure= 1 atm (10^5Pa) the rotational peaks of the IR –spectrum are resolved for small molecules, but not for larger hydrocarbons.

The width of the peaks are determined by intermolecular interactions.

In the simplest case the width is inversely proportional to the collision frequency and thus proportional to the pressure (and the square root of the temperature).

The width can also be influenced by the formation of transient complexes (with H_2O), which is pressure and temperature dependent.

The overall width of the rotational spectrum is proportional to the temperature.

The lower the temperature the smaller is the influence of vibrationally excited states. For the CO_2 bending vibration there is a change from 8% to 2% between T=300K and T=210K.

QUESTION: Experimental data base or experiment combined with theory for interpolation?

Quantitative expressions for the insulating effect of greenhouse gases

A molecule that has an IR-transition in a spectral region where the atmosphere is otherwise transparent has an effect proportional to the concentration (HW):

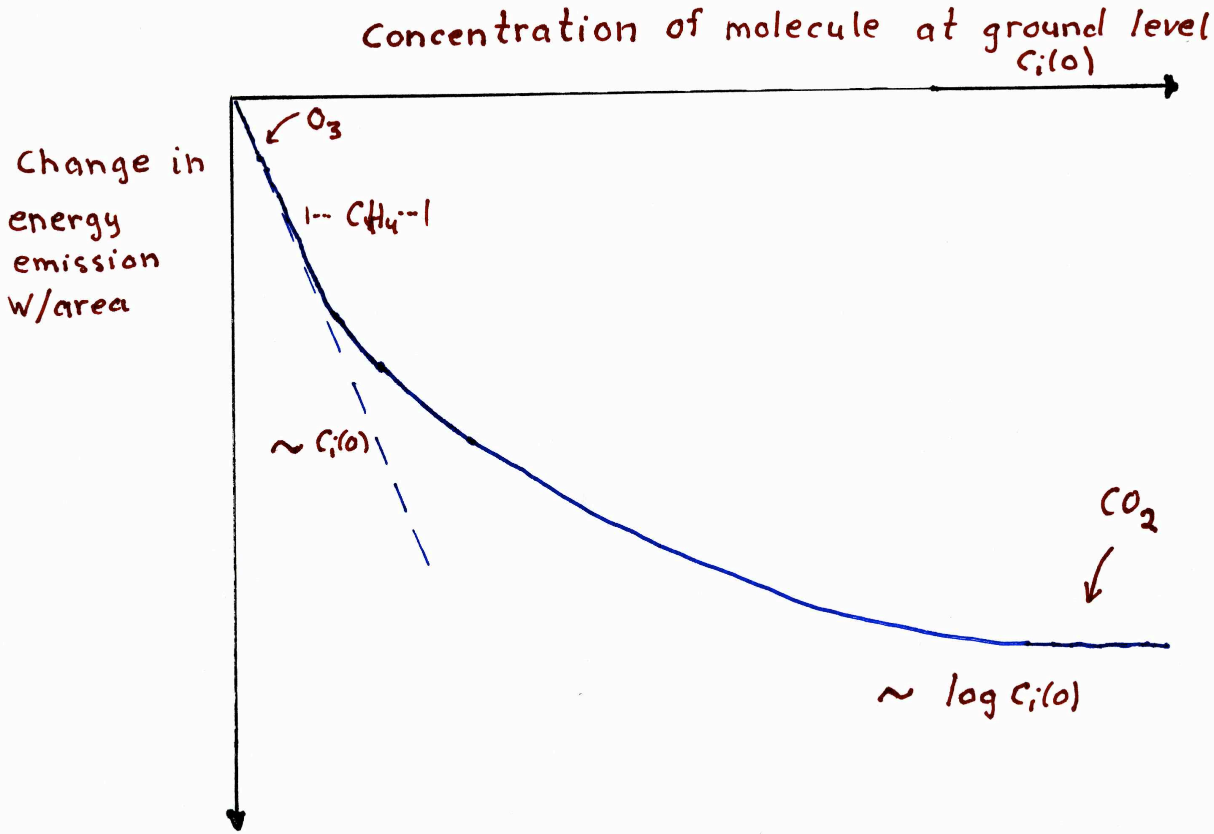
$$J_{out} \approx c_j(0)\frac{2(\hbar\omega_v/kT_{av})^2(\omega_v/2\pi c)^2}{\lambda^2}\exp[-\hbar\omega_v/kT_{av}]\left\langle\frac{dkT}{dz}\right\rangle_{av}\int\alpha_v(\omega)d\omega$$

For a molecule that is present in such amounts that the atmosphere is non-transparent the effect on the emission depends on the logarithm of the concentration.

$$J_{out} \approx \log(c_j(0))\frac{(\omega_{\max}-\omega_{\min})(\hbar\omega_v/kT_{av})^2(\omega_v/2\pi c)^2}{2\lambda}\exp[-\hbar\omega_v/(kT_{av})]\left\langle\frac{\partial kT}{\partial z}\right\rangle_{av}$$

Full manuscript at
http://www.physchem.lu.se/people/seniors/wennerstrom/

Illustration of how the cooling effect depends on the concentration of the "greenhouse" gas



Relative effect of carbon dioxide and methane

Adding a molecule like CO_2 to an atmosphere where the molecule is already abundant has a smaller effect on the energy emission than adding a molecule with an absorption in a region where the where the atmosphere is transparent.

Ratio methane to carbon dioxide molecule/molecule for effect on energy emission.

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

Estimate based on figures in iccp-report

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

Estimate based on the simplified equations given above
Overestimate due to neglect of effect of overlap with water bending mode and neglect of effect of methane already present in the atmosphere.

Note that if increase is counted on a relative basis carbon dioxide is still more important than methane since it 200 times more abundant.

Open spectroscopic issues

- Effect of clouds! They will scatter IR-radiation (and increase the optical path length). Water spectrum in liquid (and solid) state has a strong low frequency (libration) branch. Pollutants can accumulate in the drops increasing the IR-absorption/emission.
- Water cluster formation close to saturation. Gives IR-activity overlapping with that of carbon dioxide.
- Effect of aerosol particles. These will both scatter and absorb/emit.
- Effect of decreasing peak width at higher altitudes. Emission at frequencies close to resonance can occur at heights above 12km, where the temperature gradient changes sign.

Conclusions

- The "greenhouse effect" is caused by the IR absorption/ emission of carbon dioxide, water, methane and some other trace or pollutant gases.
- The (negative) temperature gradient in the atmosphere is caused by the IR absorption/emission and with no temperature gradient no insulating effect.
- Carbon dioxide and water are the most important molecules for the effect. There is little overlap of the spectra, except for water clusters.
- Methane is the most important trace gas
- There are unclear issues connected to peak widths when one goes to quantitative modeling.