

Greenhouse gases

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[Quantum mechanics](#) provides the basis for computing the interactions between [molecules](#) and radiation. Most of this interaction occurs when the [frequency](#) of the radiation closely matches that of the [spectral lines](#) of the molecule, determined by the quantization of the modes of vibration and rotation of the molecule. (The electronic excitations are generally not relevant for infrared radiation, as they require energy larger than that in an infrared photon.)

The width of a spectral line is an important element in understanding its importance for the absorption of radiation. In the Earth's atmosphere these spectral widths are primarily determined by "pressure broadening", which is the distortion of the spectrum due to the collision with another molecule. Most of the infrared absorption in the atmosphere can be thought of as occurring while two molecules are colliding. The absorption due to a photon interacting with a lone molecule is relatively small. This three-body aspect of the problem, one photon and two molecules, makes direct quantum mechanical computation for molecules of interest more challenging. Careful laboratory [spectroscopic measurements](#), rather than *ab initio* quantum mechanical computations, provide the basis for most of the radiative transfer calculations used in studies of the atmosphere.

The molecules/atoms that constitute the bulk of the atmosphere; [oxygen](#) (O₂), [nitrogen](#) (N₂) and [argon](#); do not interact with infrared radiation significantly. While the oxygen and nitrogen molecules can vibrate, because of their symmetry these vibrations do not create any transient charge separation. Without such a transient [dipole](#) moment, they can neither absorb nor emit infrared radiation. In the Earth's atmosphere, the dominant infrared absorbing gases are [water vapor](#), [carbon dioxide](#), and [ozone](#) (O₃). The same molecules are also the dominant infrared emitting molecules. CO₂ and O₃ have "floppy" vibrational motions whose quantum states can be excited by collisions at energies encountered in the atmosphere. For example, carbon dioxide is a linear molecule, but it has an important vibrational mode in which the molecule bends with the carbon in the middle moving one way and the oxygens on the ends moving the other way, creating some charge separation, a [dipole moment](#), thus carbon dioxide molecules can absorb IR radiation. Collisions will immediately transfer this energy to heating the surrounding gas. On the other hand, other CO₂ molecules will be vibrationally excited by collisions. Roughly 5% of CO₂ molecules are vibrationally excited at room temperature and it is this 5% that radiates. A substantial part of the greenhouse effect due to carbon dioxide exists because this vibration is easily excited by infrared radiation. CO₂ has two other vibrational modes. The symmetric stretch does not radiate, and the asymmetric stretch is at too high a frequency to be effectively excited by atmospheric temperature collisions, although it does contribute to absorption of IR radiation. The vibrational modes of water are at too high energies to effectively radiate, but do absorb higher frequency IR radiation. Water vapor has a bent shape. It has a permanent dipole moment (the O atom end is electron rich, and the H atoms electron poor) which means that IR light can be emitted and absorbed during rotational transitions, and these transitions can also be produced by collisional energy transfer. Clouds are also very important infrared absorbers. Therefore, water has multiple effects on infrared radiation, through its vapor phase and through its

condensed phases. Other absorbers of significance include [methane](#), [nitrous oxide](#) and the [chlorofluorocarbons](#).

Discussion of the relative importance of different infrared absorbers is confused by the overlap between the spectral lines due to different gases, widened by pressure broadening. As a result, the absorption due to one gas cannot be thought of as independent of the presence of other gases. One convenient approach is to remove the chosen constituent, leaving all other absorbers, and the temperatures, untouched, and monitoring the infrared radiation escaping to space. The reduction in infrared absorption is then a measure of the importance of that constituent. More precisely, define the greenhouse effect (GE) to be the difference between the infrared radiation that the surface would radiate to space if there were no atmosphere and the actual infrared radiation escaping to space. Then compute the percentage reduction in GE when a constituent is removed. The table below is computed by this method, using a particular 1-dimensional model of the atmosphere. More recent 3D computations lead to similar results.

Gas removed	percent reduction in GE
H ₂ O	36%
CO ₂	12%
O ₃	3%

(Source: Ramanathan and Coakley, Rev. Geophys and Space Phys., 16 465 (1978)).[\[3\]](#)

By this particular measure, water vapor can be thought of as providing 36% of the greenhouse effect, and carbon dioxide 12%, but the effect of removal of both of these constituents will be greater than 48%. An additional proviso is that these numbers are computed holding the cloud distribution fixed. But removing water vapor from the atmosphere while holding clouds fixed is not likely to be physically relevant. In addition, the effects of a given gas are typically nonlinear in the amount of that gas, since the absorption by the gas at one level in the atmosphere can remove photons that would otherwise interact with the gas at another altitude. The kinds of estimates presented in the table, while often encountered in the controversies surrounding global warming, must be treated with caution. Different estimates found in different sources typically result from different definitions and do not reflect uncertainties in the underlying radiative transfer.