From Arrhenius to CO_2 Storage

Part IX: How CO_2 Emits IR Photons

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"Thanks for the lonely night, for the hills, the rush of the darkness and the sea through my heart! This silence murmuring in my ears is the blood of all Nature seething; … the northern lights flare over the heavens to the north. By my immortal soul, I am full of thanks that it is I who am sitting here!"

From 'Pan' by Knut Hamsun (1859–1952), Norwegian winner of the Nobel Prize for Literature in 1920.

Skydive with us into the quantum world, where we provide to those unafraid of molecular energy transfer an answer to the question: what happens to Earth's radiated infrared (IR) photons *after* they are absorbed by IR active CO_2 molecules in the lower atmosphere? Part VIII (*GEO ExPro* Vol. 17, No. 3) showed how CO_2 molecules absorb Earth's IR radiation. Here, we show that the bulk background gases N_2 and O_2 are critical for the greenhouse effect because collisions of CO_2 (and other greenhouse gases) with N_2 or O_2 both take away and add energy to the CO_2 molecules. Every collision that adds energy gives the CO_2 molecule a chance to undergo radiative decay and emit a photon.

Two granite sculptures in the work 'Thoughts for Two', created by the Sami artist Annelise Josefsen. A boy and a girl, sitting under the Northern Lights in remote Tranøy Hamarøy, in northern Norway, where Knut Hamsun spent much of his childhood. The quote above is carved into the smooth rock slopes below them.

Crash Course in Molecular Energy Transfer

First, a brief review of the various mechanisms, definitions, and terms useful in understanding molecular energy transfer. Consider the bimolecular collision in which reactants A in quantum state i and B in quantum state j react to form products A in quantum state l and B in quantum state m,

$$A(i) + B(j) + \Delta E \underset{k_r}{\overset{k_f}{\rightleftarrows}} A(l) + B(m) \qquad (1)$$

Here ΔE is the exchanged energy during the collision process; quantum state 0 corresponds to the ground state. The forward process is described by the right arrow. An increase in the concentration [A(i)] or [B(j)] results in an increase in the rate of reaction. The concentration unit is measured in molecules per cubic centimeters per second. It stands to reason that the reaction rate is proportional to the increase in concentration, so rate = k_f[A(i)][B(j)]. The rate constant k_f is the proportionality constant relating the rate of the reaction to the concentrations of reactants.

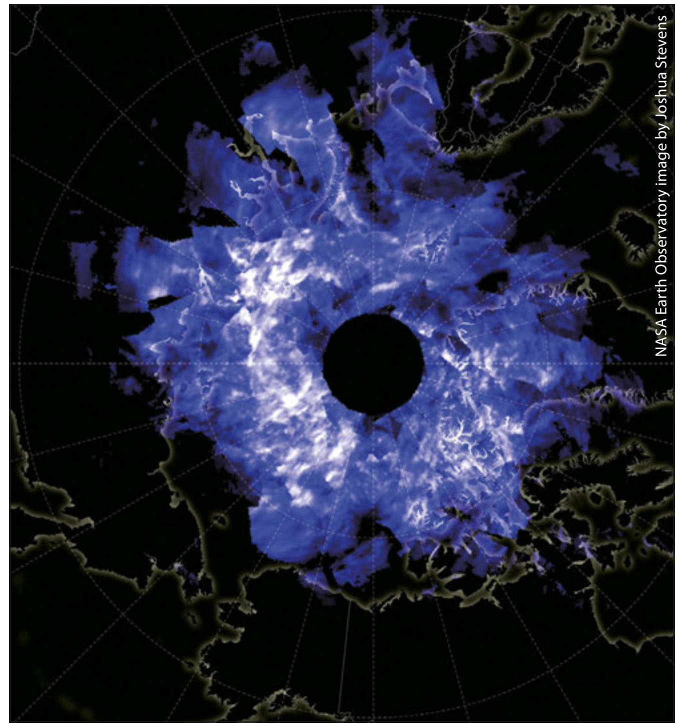
A large k_f means that the reaction is relatively fast, while a small value means that it is relatively slow. Raising the temperature of the reaction usually results in a higher rate of reaction; the particles move faster and faster, resulting in a greater frequency of collisions, so k_f is temperature dependent. The reaction in equation 1 can be shown to have exponential temporal behavior with a 'time constant' $\tau = 1/k[M])$, where M equals A or B and τ is referred to as the relaxation time for the process.

Corresponding to the forward process is the reverse process (left arrow) with rate constant k_r. When the rates of the forward and reverse reactions have become equal, the reaction has achieved a state of balance or equilibrium, k_f[A(i)][B(j)] = k_r[A(1)][B(m)], yielding the ratio (Denisov et al. 2003):

$$\frac{k_f}{k_r} = K = \frac{[A(l)]\,[B(m)]}{[A(i)]\,[B(j)]} = \frac{g(l)g(m)}{g(i)g(j)} \exp(-\Delta E/k_B T) \qquad (2)$$

where K is the equilibrium constant, g denotes the degeneracy of the molecular quantum state, and $k_B T$ is the product of the Boltzmann constant and the temperature. The term 'equilibrium' indicates that the different forms of energy (rotational and vibrational) are characterized by one temperature T (energy equilibrium).

There are two kinds of vibrational energy exchange processes during bimolecular collisions: vibration-translation (V-T) and vibration-vibration (V-V). Let us consider a vibrationally excited molecule, A*, where the asterisk denotes one quantum of vibrational excitation. A* collides with a species M, and the vibrational energy is transferred into translational motion. This process may be expressed by the transfer equation:



Satellite view of noctilucent or 'night shining' clouds centered on the North Pole on June 12, 2019. The clouds float 80–85 km high in the atmosphere so that they are still lit by sunlight even after the Sun has dropped below the horizon for people on the ground. As Earth's lower atmosphere warms with spring and summer, the upper atmosphere grows cooler. In the process, ice crystals collect on meteor dust and other particles, creating electric blue wisps on the edge of space.

$$A^* + M \underset{k_f^{VT}}{\overset{k_r^{VT}}{\rightleftarrows}} A + B + \Delta E \qquad (3)$$

where A represents the molecule in its ground state. Equation 3 is the special case of equation 1 when l=1, i=j=m=0, and B=M. In contrast to equation 1, here the left to right process is associated with the reverse rate constant, where the excited reactant A* undergoes vibrational deactivation. The V-T process results in energy transferring from molecular vibrational modes to molecular translation. One molecule loses one quantum while the vibrational state of the other molecule is unaltered. The process associated with the forward rate constant is that where the reactant A acquires enough energy to react by colliding with another molecule M. This process is called vibrational up-pumping.

How CO_2 Relaxes in the Lower Atmosphere

Part VIII told us that the terrestrial radiation follows a blackbody distribution of characteristic temperature of 288K, with 98% of radiative power emitted in the 5–80 μm range. There is only one CO_2 absorption band of importance in this range, at around 15 μm (667 cm^{-1}). This band almost coincides with the spectral maximum of terrestrial radiation and therefore to a large extent determines the interaction of CO_2 molecules with the radiation. CO_2 is responsible for a large gap in the transmissivity of Earth's IR radiation towards space, centered around 15 μm.

The process whereby a CO_2 molecule absorbs an infrared photon of energy 667 cm^{-1} and goes to the vibrationally excited state CO_2*(010) reads:

$$CO_2(000) + 667cm^{-1} \rightarrow CO_2^*(010) \quad (4)$$

The photon transfers its energy to the IR active CO_2 molecule and is removed from the radiation field, while the photon energy raises the CO_2 molecule to a higher vibrational state. But since excited states are energetically unfavorable the molecule wants to return to the ground state by giving up energy. How? We provide the answer by following the respected physics tradition of 'back-of-the-envelope' calculations.

Finding the Winner

Vibrational energy can be transferred either radiatively by spontaneous or stimulated emission or non-radiatively by collision. Which process is the winner? To find out, one must compare the radiative lifetime of the excited level with the relaxation time of collisions. If the relaxation time is short compared with the average radiative lifetime of the excited level, then the collision process wins.

Radiative lifetime: The photon's energy causes the CO_2 molecule to elevate. The molecule releases this extra energy by emitting the photon, which is identical to the absorbed one, but emits in an arbitrary direction since it, like the drunken sailor, has no memory of its previous steps. Once the emitted photon has left, the molecule returns into its ground state. The radiative lifetime of the (010) molecular vibration is about 1.1s (Cheo, 1971). It is an eternity on a gas kinetic time scale.

Relaxation time by collisions: The collisional relaxation process occurs when the relaxation time can compete with the radiative lifetime of the excited energy levels. Even though the activated CO_2 molecule, at a CO_2 concentration of 400 ppm, is one among around 2,500 other molecules, it is moving very fast and it does not have to move far before it bumps into other molecules – usually N_2 or O_2 – and drops back into its ground state. The freed energy then adds speed to another molecule's motion. When many collisions take place simultaneously, the faster speed of the molecules being bumped into raises the temperature of the gases in the atmosphere, since temperature is proportional to the average kinetic energy of the gas. Since the photon is permanently lost from the radiation field, this is absorption of photons.

How fast does this happen? The collision process for CO_2 deactivation in the temperature range 300–140K against a number of gases has been studied by Siddles et al. (1994). Let M denote either the N_2 or O_2 molecule. The process of vibrational de-excitation from the 667 cm^{-1} level through collision with molecule M can be described by (see equation 3)

Illustration showing an astronaut on Mars, as viewed through the window of a spacecraft. The Martian atmosphere is 96% CO_2 but it is extremely thin (1% of Earth's atmosphere), very dry and located further away from the Sun. This combination makes Mars an incredibly cold place.

$$CO_2^*(010) + M \underset{k_f(v_B)}{\overset{k_r(v_B)}{\rightleftarrows}} CO_2(000) + M + 667cm^{-1} \quad (5)$$

where $k_r(v_B)$ is the V-T rate constant for relaxation of CO_2(010) by M, where the vibrational energy ΔE resident in the CO_2 bending-mode is transferred to M as translational kinetic energy, which is reflected on the macroscopic scale as a temperature increase.

The speed of the process depends on the temperature where the process runs. We select the altitude 3,550m where temperature is 265K (-8°C). The number of molecules per cm^3 in dry air at this height is $[M]=1.79 \times 10^{19}$, with 78% N_2 and 21% O_2. For N_2 and O_2 Siddles et al. (1994) give constants $k_r^{(N_2)} = 2.4 \cdot 10^{-15}$ and $k_r^{(O_2)} = 3.6 \cdot 10^{-15}$ cm^3(molecule s)$^{-1}$. The lifetime of collisional de-excitation for CO_2 (010) in the atmospheric gas bath can be deduced as

$$\tau = 1/(0.78\, k_r^{(N_2)} + 0.21\, k_r^{(O_2)})[M] \approx 21\ \mu s$$

The typical collision time through which a CO_2 (010) molecule can transfer its energy to another gas molecule is about 20 μs in the lower atmosphere at altitude 3.5 km. Collisions take place more often than re-radiation. Therefore, when a CO_2 molecule in air absorbs a photon, it is much more likely – on the order of $1s/20\mu s=0.5 \times 10^5$ times – to heat the surrounding air molecules with the energy it acquired from the absorbed photon than to re-radiate the photon. Statistically, the same CO_2 molecule re-emits the photon energy two out of 100,000 times; but 99,998 times out of 100,000 the excited CO_2 molecule is de-excited by collision. ▶

In physics, thermalization is the process of physical bodies (e.g., molecules) reaching thermal equilibrium through mutual interaction (e.g., collisions). In general, the natural tendency of a system, like the atmosphere, is towards a state of equipartition of energy and uniform temperature. Since the collisional step is fast (about 20 μs at 3.5 km), the photon energy involved at 667 cm^{-1} is rapidly spread out among the surrounding air molecules – or thermalized into the 'heat bath' of the atmospheric gas. CO_2 is then rapidly in thermal equilibrium with the rest of the gas molecules.

The Life Events of CO_2 Molecules

The atmospheric bath receives an inflow of energy from Earth's IR radiation where CO_2 absorbs photons in the 667 cm^{-1}-centered band but seemingly only negligibly emits photons. The gas bath increases its temperature, but a gas cannot easily increase its emissivity (Robitaille, 2014). As Earth continuously sends IR energy upwards, CO_2 photon absorption would make the air get really hot … unless there is a process that is able to pass the received energy on. The gas needs to cool, and the question is how? This process must involve the creation of additional photons that can become the energy carriers for radiation.

Of course, in steady state, under the assumption of local thermodynamic equilibrium, the reverse process to that we have considered is also ongoing, at equal rate, all the time (see equation 5). Therefore, collisions of ground-state CO_2 molecules with air molecules may excite the former and cause them to radiate. The rate constant $k_f(\nu_B)$ for vibrational up-pumping at gas temperature 265K, where $k_B T$ = 184.2 cm^{-1}, can be found from $k_f(\nu_B)$ by using equation 2:

$$k_f/k_r = 2\ \exp(-667/184.2) = 0.0535$$

The number 2 in this equation arises because of CO_2 (010) being doubly degenerate; the two bending mode vibrations in CO_2 have equal energy. Repeating the calculations as above with a new rate constant, the relaxation time for the reaction is found to be around 20 μs/0.0535 or about 400 μs.

Recall that the radiative lifetime of CO_2 de-excitation is around 1.1s. Since the collisional processes are much faster, a CO_2*(010) molecule can de-excite in 20 μs and excite back to the (010) state in 400 μs. It is quite a pace! One trip back and forth takes 420 μs so that during 1.1s the number of possible trips is 1.1s/420 μs = 2,620. When 100,000 CO_2*(010) molecules are available for de-excitation, it is likely that two of these will be reserved for radiation of a photon; the remaining 99,998 are back after 420 μs to offer 2/100,000 of these to radiate a photon while the rest de-excites through collisions. During a time interval of 1.1s, a back-of-the-envelope calculation indicates that a little less than 2,620 x 2 = 5,240 CO_2*(010) are likely to participate in the photon radiation process. This is around 5% of the CO_2*(010) molecules. We may thus conclude that around 5% of the CO_2 molecules which absorb IR radiation from Earth's surface tend to radiate IR photons (at altitude 3.5 km). The rest are busily colliding with N_2 and O_2 molecules.

The process of photon absorption and emission can be defined as follows: The photons in the band around 667 cm^{-1} from Earth's surface are absorbed by CO_2 molecules. Only a very small percentage re-radiate photons in a random direction and the rest lose that energy to the surrounding bath of atmospheric molecules. In turn, the atmospheric molecules collide with CO_2 molecules so that they get excited to the (010) state. A very small percentage radiates new photons, again in a random direction, and the rest lose the energy by collision. It is a stressful life! The process repeats forth and back rapidly, so that in the timeframe of about a second, around 5% of the CO_2 molecules radiate. Close to the surface the percentage is slightly higher since the temperature is elevated, while higher in the troposphere it is slightly less since the temperature is lower.

On Mars it gets cold enough to freeze carbon dioxide out of the atmosphere during the winter. This slab of ice is a few meters thick and is penetrated by the flat-floored pits shown here. The quasi-circular pits in the center of the scene are about 60m across. The distinct color of the pit walls may be due to dust mixed into the ice.

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