Climate Change Science
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Lecture 13
Radiative Transfer in Gases

In this lecture, we examine in greater detail the mechanisms by which gases absorb infrared radiation. Previously, we employed a simplified model in which the absorptivity to solar radiation was taken as approximately 20%, and the emissivity of the atmosphere was assumed to be around 0.95. However, we did not explore how these values are determined. In this session, we delve into the physical principles and complexities of radiative heat transfer in gases, particularly focusing on the roles of major greenhouse gases such as carbon dioxide (CO_2), ozone (O_3), water vapor (H_2O), and methane (CH_4) in absorbing terrestrial infrared radiation.

The starting point for understanding gas absorption is a well-established law of physics often referred to as Beer's Law, which has been known for nearly two centuries. This law states that the change in the intensity of radiation along a given direction, specifically the directional spectral intensity I'_λ (as defined in Lecture 1), is proportional to both the incoming intensity and the distance the radiation travels through the medium. Intuitively, this means that the more photons there are initially, and the greater the distance they travel, the more likely they are to be absorbed or scattered by molecules in the gas.

$$dI'_\lambda = -I'_\lambda k_\lambda dx$$

The proportionality constant in this relation is known as the extinction coefficient, denoted k_λ, which is a property of the gas and has units of inverse meters (m^{-1}). To proceed further, we decompose this extinction coefficient into two components: absorption (a_λ) and scattering (σ_λ), both of which also have units of m^{-1}.

$$k_\lambda = a_\lambda + \sigma_\lambda$$

In this lecture, we focus exclusively on the absorption coefficient and neglect scattering, since in the infrared region, particularly beyond wavelengths of approximately 4-5 microns, scattering effects are minimal.

Scattering is, however, significant in the shortwave or solar spectral region, where it alters the direction of photon travel. When a photon is scattered, it continues to exist but travels in a different direction, whereas an absorbed photon ceases to exist in that form and is converted into heat.

If we integrate Beer's Law without considering scattering, we obtain a familiar exponential attenuation law from first-order differential equations.

$$I'_\lambda(L) = I'_\lambda(0)e^{-a_\lambda L}$$

The solution indicates that the radiation intensity at a distance L from the origin is reduced by a factor of $e^{-a_\lambda L}$, assuming a constant absorption coefficient a_λ.

Using this result, we define the directional spectral absorptivity analogous to what was earlier defined for opaque surfaces as the fraction of radiation absorbed over the path length. This is expressed as

$$\alpha'_\lambda = \frac{I'_\lambda(0) - I'_\lambda(L)}{I'_\lambda(0)} = 1 - e^{-a_\lambda L}$$

According to Kirchhoff's Law, the directional spectral absorptivity (α'_λ) must be equal to the directional spectral emissivity (ε'_λ). Thus, in a gaseous medium, both absorptivity and emissivity are determined by the absorption coefficient a_λ and the path length L. The product $a_\lambda L$ is a non-dimensional quantity that plays a central role in radiative transfer calculations in gases.

If the length of the radiation path is measured in meters, then the absorption coefficient a_λ has units of inverse meters (m^{-1}). However, if we want to incorporate the density of the gas, it becomes more appropriate to express the path length in terms of mass per unit area, specifically in kilograms per square meter (kg/m^2). This quantity is referred to as the mass path length, which represents the amount of gas along the direction of radiation per unit area perpendicular to it.

In this case, the absorption coefficient a_λ must have units of square meters per kilogram (m^2/kg). When expressed this way, it is called the mass absorption coefficient, in contrast to the previously discussed volume absorption coefficient. It's crucial to be attentive when reading textbooks and research papers, as they may define a_λ differently, depending on whether the context involves volume or mass-based definitions.

An advantage of using a_λ in units of m^{-1} is that its reciprocal gives the mean free path of a photon, that is, the average distance a photon travels before being absorbed. This concept is similar to the molecular mean free path in kinetic theory, where it represents the average distance a molecule travels before colliding with another molecule.

Whether expressed as m^{-1} or m^2/kg, the product $a_\lambda L$ (where L is the path length) is non-dimensional and is known as the optical depth. If the optical depth is much greater than 1, then almost all the radiation is absorbed, and absorptivity approaches 1. Conversely, if the optical depth is very small, the gas absorbs very little radiation. In such a case, the

exponential term in the absorption law can be approximated using a Taylor expansion, and the absorptivity becomes directly proportional to $a_\lambda L$. This is referred to as the optically thin regime.
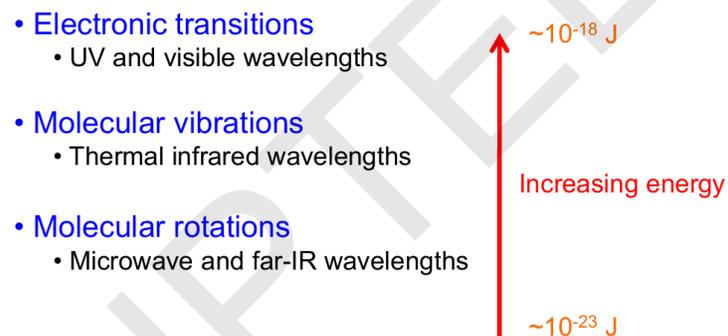
When a gas is optically thick, that is, when $a_\lambda L \gg 1$, the remaining unabsorbed radiation becomes negligible. Absorptivity essentially reaches unity, and saturation is said to occur. Saturation means that in a given wavelength where the gas absorbs strongly, increasing the gas concentration further does not lead to more absorption because nearly all radiation at that wavelength is already absorbed.

However, it is important not to misinterpret this phenomenon. Some people incorrectly argue that because carbon dioxide is already a strong absorber in some wavelengths, further increases in CO_2 concentration do not matter due to saturation. While saturation may occur at certain specific wavelengths, it does not apply to all wavelengths. CO_2 continues to absorb radiation at adjacent wavelengths where it is not yet saturated. Therefore, increases in CO_2 still contribute to enhanced greenhouse effect by filling in absorption in the weaker parts of the spectrum.

This misunderstanding arises because gas absorption is highly wavelength-dependent. A tiny change in wavelength, such as 0.01 microns, can cause the absorption coefficient to shift drastically, say from 100 to 0.01. This extreme spectral variability is a unique characteristic of gases, and it makes analytical expressions for total absorption impractical. While some approximations exist, their validity is limited.

As a result, when we want to compute the total absorptivity over all wavelengths, we must perform a careful and detailed integration over the wavelength domain, accounting for the strong spectral variability of a_λ. In subsequent parts of this course, we will illustrate some of these examples and show why this step is critical for accurate radiative transfer modeling.

Absorption and Emission by Molecules

- Electronic transitions
  - UV and visible wavelengths

~10^{-18} J

- Molecular vibrations
  - Thermal infrared wavelengths

Increasing energy

- Molecular rotations
  - Microwave and far-IR wavelengths

~10^{-23} J

To understand why all this complexity occurs in gas absorption, it's important to grasp the basic physics of absorption. Absorption happens when a photon is absorbed by a molecule, leading to transitions between energy states. This can happen in one of several ways: the photon can excite an electron from the ground state to a higher energy state, known as an electronic transition; it can excite the molecule from the ground vibrational level to a higher vibrational level (a vibrational transition); or it can cause a transition between rotational energy levels of the molecule.

Now, the energy levels in molecules are spaced such that electronic transitions require relatively high-energy photons, typically in the visible or ultraviolet region of the spectrum. This means that solar radiation, which includes visible light, is capable of triggering electronic transitions when photons are absorbed.

In contrast, our focus is primarily on infrared radiation, which carries lower energy per photon (lower $h\nu$). In the infrared region, photons do not have enough energy to cause electronic transitions, but they can cause vibrational or rotational transitions. Among these, vibrational transitions require more energy than rotational ones and typically occur in the 4 to 20 micron wavelength range.

Rotational transitions, which involve even smaller energy differences, occur at much longer wavelengths, typically in the range of around 1500 microns. The energy difference between rotational and electronic transitions is vast, on the order of five magnitudes, or a factor of about 10^5 in Joules.

When there is an electronic transition, the photons involved must be in the visible or ultraviolet region of the spectrum. In contrast, vibrational transitions occur when photons are in the infrared range, typically between 1 micron and 20 microns. Rotational transitions, which require even less energy, take place in the far infrared or microwave regions.

However, it is important to remember that vibrational transitions are almost always accompanied by rotational transitions. This happens because when a photon is absorbed to trigger a vibrational mode in a molecule, it often has slightly more energy than what is

strictly required for just the vibrational transition. This extra energy goes into exciting a rotational mode.

An analogy can help clarify this: imagine giving someone 1 Rupee and 50 Paisa. The 1 Rupee represents the energy needed for the vibrational transition, while the 50 Paisa represents the rotational component. The vibrational change is the major part, while the rotational change is a small addition.

Similarly, electronic transitions, which occur in the visible range, are even more complex. They are usually accompanied by both vibrational and rotational transitions. As a result, the spectrum produced by electronic transitions is highly complicated.

Because of this complexity, the topic of electronic transitions and their spectra in the visible range is beyond the scope of this course and will not be discussed in detail here.

Carbon monoxide, nitrous oxide, water vapor, and ozone exhibit pure rotational spectra because they possess permanent dipole moments. For a rotating molecule to interact with an incoming electromagnetic field, it must have a changing dipole moment during the rotation. For example, as carbon monoxide rotates, its dipole moment fluctuates, allowing it to interact with the electric field of an incoming photon, absorb it, and rotate faster.

In contrast, carbon dioxide and methane do not have permanent dipole moments, and therefore, they do not exhibit pure rotational spectra. However, during vibrational transitions, these molecules undergo distortions that temporarily induce a dipole moment, enabling them to exhibit combined vibration–rotation spectra.

For a molecule to interact effectively with the electric field of radiation, it must possess a permanent electrical or magnetic dipole moment. This requirement explains why the major atmospheric gases like nitrogen (N_2), oxygen (O_2), and argon (Ar) do not absorb or emit radiation in either the visible or infrared spectrum. These gases lack permanent dipole moments, and argon, being a noble gas atom, is monatomic and electrically neutral.

As a result, even though nitrogen, oxygen, and argon together make up 99.9% of the Earth's atmosphere, they do not contribute to atmospheric radiation absorption. This peculiarity makes the atmosphere highly sensitive to trace gases, or minor constituents, such as carbon dioxide, water vapor, ozone, and methane.

These minor gases, though present in very small concentrations - carbon dioxide in hundreds of parts per million (ppm), methane around 1-2 ppm, and ozone and chlorofluorocarbons (CFCs) in parts per billion (ppb) - have disproportionately large effects on Earth's radiation balance and climate. This reality is often misunderstood, with some people assuming that minor gases cannot exert major climatic influence.

Absorption spectra of molecules
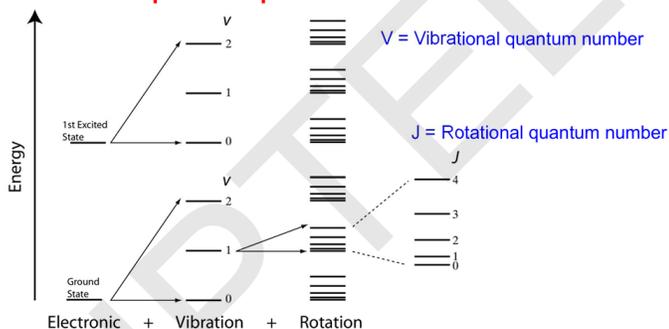
- Electronic, vibrational and rotational energy levels are superimposed
- The absorption spectrum of a molecule is determined by all allowed transitions between pairs of energy levels, and whether the molecule exhibits a sufficiently strong electric or magnetic dipole moment (permanent or otherwise) to interact with the radiation field

The above is a pictorial representation of the energy levels in a typical molecule. At the base, we see the ground electronic state, above which lies the excited electronic state. Within each electronic state, there are vibrational modes, and within each vibrational level, there are multiple rotational levels. This hierarchical structure illustrates the layered nature of molecular energy states.

You can observe that the energy difference between vibrational levels is smaller than that of electronic transitions, meaning that vibrational transitions can be excited by infrared (IR) photons. In contrast, electronic transitions require photons in the visible or ultraviolet range because they involve much higher energy differences. Rotational transitions involve even smaller energy differences, requiring far-infrared or microwave radiation to occur.

This provides a basic ordering: rotational transitions occur in the far infrared, vibrational transitions occur in the near to mid-infrared, and electronic transitions occur in the visible and near-ultraviolet parts of the spectrum.

The absorption spectrum of a molecule is determined by all the allowed transitions between these energy levels. However, for a transition to actually result in the absorption of radiation, the molecule must exhibit a sufficiently strong electric or magnetic dipole moment that can interact with the electromagnetic field of the incoming radiation.

Vibrational-rotational transitions
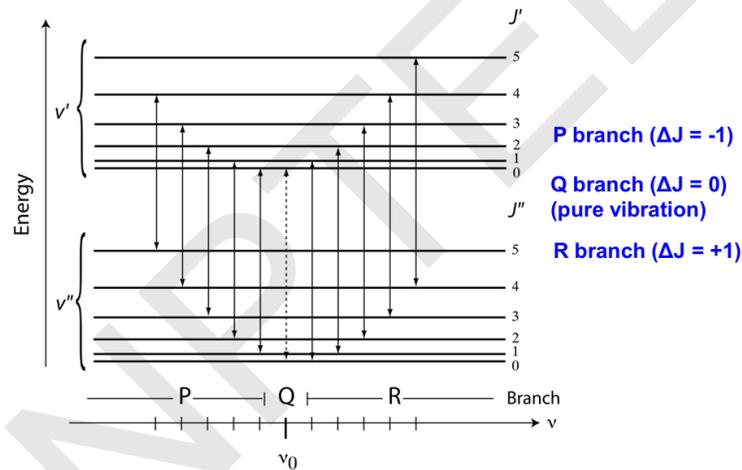
• Relative positions of transitions in the absorption spectrum of a molecule

Now, we are going to focus exclusively on infrared absorption, particularly the vibrational-rotational transitions that occur within molecules. In this context, a molecule starts from a ground vibrational state, and the photon excites it to an upper vibrational state. Within both the ground and upper vibrational states, there are multiple rotational levels, allowing for a variety of combined transitions.

If a transition involves only a change in vibrational state with no change in rotational state, it is called the Q branch. This corresponds to a frequency denoted by ν_0, the central frequency of the vibrational transition. However, due to quantum mechanical selection rules, the Q branch is forbidden in many molecules, and so it may not appear in all absorption spectra. In some cases, though, the Q branch is allowed and can be observed.

When a vibrational transition is accompanied by a decrease in rotational energy (i.e., a transition to a lower rotational level), the resulting frequencies are less than ν_0. These transitions form what is called the P branch. On the other hand, if the rotational energy increases (i.e., the transition is to a higher rotational level), the photon must have a higher frequency than ν_0, and the resulting transitions form the R branch.

Each incoming photon interacts with the molecule based on its frequency. If the energy of the photon matches the energy difference (ΔE) between a specific lower and upper state, satisfying the condition $\Delta E = h\nu$, the photon is absorbed and the transition occurs. This mechanism explains the structure of vibrational-rotational absorption bands seen in the infrared region.
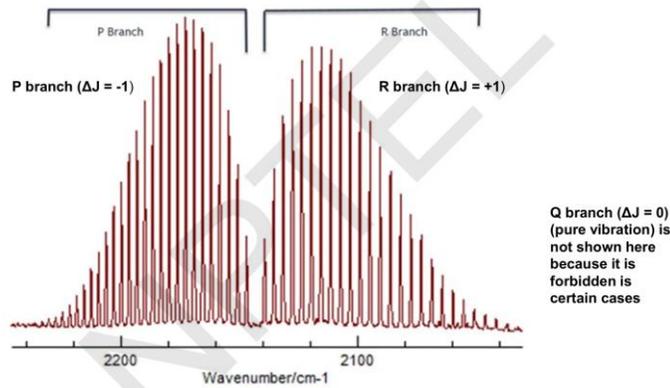
This behavior can be clearly observed in absorption spectra measured in the laboratory as depicted in the above figure. Each spectral line corresponds to a specific photon absorption event by the gas molecules. In such a spectrum, the R branch includes lines at frequencies higher than the central frequency ν_0, while the P branch includes lines at frequencies lower than ν_0. In the example being referred to, there is no Q branch, which aligns with the earlier point that Q branches are often forbidden by quantum mechanical rules for many molecules. This gives the measured spectrum a distinctive structure with two symmetric sets of lines forming R and P branches around a central gap.

However, real-world spectra tend to be more complex than this idealized picture. Take carbon dioxide (CO_2) as an example. The dominant isotope in Earth's atmosphere is made up of carbon-12 and oxygen-16 atoms (i.e., $^{12}C^{16}O_2$). But naturally occurring air samples also contain other isotopes, such as carbon-13 (^{13}C), carbon-14 (^{14}C), oxygen-17 (^{17}O), and oxygen-18 (^{18}O). As a result, you end up with different isotopologues of CO_2, each having slightly different molecular masses.

These differences in mass cause the energy levels to shift slightly, which in turn shifts the spectral lines. For instance, a CO_2 molecule containing ^{12}C and ^{18}O will absorb at a slightly different frequency than one containing ^{12}C and ^{16}O. Therefore, a real CO_2 absorption spectrum appears more crowded or noisy, with many closely spaced lines, due to the presence of these minor isotopologues.

To obtain a simpler and cleaner spectrum, one would need to use a sample of high-purity gas, containing only a single isotopic composition, such as pure $^{12}C^{16}O_2$. While the number of molecules of these minor isotopes is typically small, and hence their overall effect on studies like the greenhouse effect is minimal, their presence can still complicate the appearance of the spectrum.

Therefore, when analyzing experimental spectra, especially if it appears noisy or more complex than expected, it is important to ask whether the gas sample used was isotopically pure or a natural mixture.

From quantum mechanics, we know that the change in rotational quantum number during a photon absorption event follows specific rules depending on the spectral branch. In the P branch, the rotational quantum number decreases by 1 ($\Delta J = -1$); in the R branch, it increases by 1 ($\Delta J = +1$); and in the Q branch, it remains unchanged ($\Delta J = 0$). These transitions occur alongside vibrational changes in molecules and form the structured absorption spectra observed in gases.

The vibrational transitions typically occur in the frequency range of 600 to 1000 cm^{-1} (in terms of wave number), while rotational transitions happen at much lower frequencies, generally between 1 and 500 cm^{-1}. As such, the frequency ranges of rotation and vibration do not overlap. Vibrational transitions require significantly more energy than rotational ones. However, when a vibrational transition occurs, it is usually accompanied by a rotational transition, resulting in a combined vibrational-rotational spectrum. On the other hand, if the incoming photon only has enough energy to cause a rotational transition, it cannot initiate a vibrational transition on its own.

Furthermore, it's important to note that molecules in the lowest vibrational state are not necessarily in the lowest rotational state. Even when the molecule is in its ground vibrational level, it can occupy higher rotational states, such as rotational level 4 or beyond. This is a common condition in nature and contributes to the diversity of rotational transitions observed in vibrational-rotational spectra.

The rotational energy levels of a molecule are quantized and described by a formula derived from quantum mechanics. The energy E_J at a given rotational level J is given by:

$$E_J = \frac{J(J+1)\left(\frac{h}{2\pi}\right)^2}{2I}$$

Here, J is the rotational quantum number, h is Planck's constant, and I is the moment of inertia of the molecule. The moment of inertia depends on the mass of the atoms in the molecule and their distance from the axis of rotation. For example, in the case of a carbon monoxide (CO) molecule rotating about a vertical axis, the moment of inertia must be calculated using the positions and masses of the carbon and oxygen atoms relative to the center of mass.

When there is a change in the rotational quantum number (ΔJ), there is a corresponding change in energy, which results in the absorption or emission of a photon. The frequency ν of the photon associated with such a transition is given by:

$$\nu = 2B(J+1) \qquad B = \frac{h}{8\pi^2 cI}$$

Here, B is the rotational constant, which is a function of Planck's constant, the speed of light, and the moment of inertia of the molecule. The rotational constant B determines the spacing between the rotational energy levels and hence directly controls the frequency of radiation absorbed or emitted in a rotational transition.

The units of B are typically expressed in wave number (cm^{-1}), although it can also be given in terms of frequency (Hz). Understanding this relationship between molecular structure and energy level transitions is crucial in interpreting rotational spectra of gases.

In vibrational transitions, molecules absorb photons that excite them from one vibrational energy level to another. Each molecule can exhibit multiple vibrational modes, depending on its structure. For example, carbon dioxide (CO_2) exhibits three fundamental vibrational modes: symmetric stretching, asymmetric stretching, and bending.

In the symmetric stretching mode, both oxygen atoms move in and out simultaneously along the axis of the carbon atom in the center. This mode absorbs radiation at around 7.2 microns, but it is relatively weak in terms of infrared activity. The second mode, asymmetric stretching, involves the two oxygen atoms moving in opposite directions while one moves toward the carbon atom, the other moves away. This asymmetry makes the mode much more infrared-active, and it shows a strong absorption band at 4.3 microns. However, since this wavelength is not near the peak of the Earth's thermal emission spectrum, it contributes less to the greenhouse effect.

The third and most important vibrational mode is the bending mode, in which the CO_2 molecule bends rather than stretches. This mode strongly absorbs radiation at around 15 microns, which is close to the peak wavelength of Earth's blackbody emission. Therefore, the 15-micron bending mode is the most significant contributor to the greenhouse effect from CO_2. It is important to note that vibrational transitions are always accompanied by rotational transitions, leading to a combined vibration-rotation spectrum.

For each vibrational transition, the frequency of the absorbed photon depends on molecular properties, governed by the equation:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Here, k is the bond force constant (which describes the strength of the bond, like the stiffness of a spring), and μ is the reduced mass of the system, calculated from the masses m_1 and m_2 of the atoms involved using:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

A vibrating molecule is analogous to a spring-mass oscillator where the atoms oscillate like masses on a spring. The quantum mechanical nature of these oscillators means the molecules can only absorb photons with very specific energies those that match the gap between quantized vibrational energy levels. It is given by

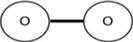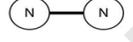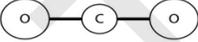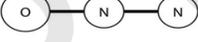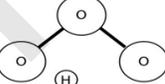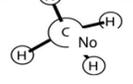$$E_n = h\nu = (n + 1/2)\frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

From basic spectroscopic data, values such as the bond force constant (k) and the reduced mass (μ) of the vibrating atoms can be determined. These parameters are extensively tabulated in standard spectroscopy references and textbooks, and are well-established through experimental and theoretical studies. With these known values, the vibrational frequency of a molecule can be calculated.

Vibrational transitions involve greater energy changes than pure rotational transitions. Both stretching and bending motions within a molecule can lead to absorption of infrared radiation, but stretching typically occurs at higher frequencies compared to bending.

Molecules such as oxygen (O_2) and nitrogen (N_2), despite being the most abundant in Earth's atmosphere, do not possess a permanent electric dipole moment. As a result, they do not absorb infrared radiation through vibrational or rotational transitions. While they exhibit weak magnetic dipole interactions, these are too minor to contribute to the greenhouse effect and are only relevant in specialized contexts like remote sensing.

In contrast, molecules like carbon monoxide (CO) are asymmetric and have a permanent dipole moment, making them active in the infrared. Carbon dioxide (CO_2), although a symmetric linear molecule with no permanent dipole, can still absorb infrared radiation due to momentary asymmetries introduced during vibrational-rotational transitions. Nitrous oxide (N_2O), being inherently asymmetric due to unequal masses on either side of the nitrogen atom, possesses a permanent dipole moment and is infrared active.

Water vapor (H_2O) and ozone (O_3) are asymmetric top molecules with permanent dipole moments. They exhibit multiple vibrational modes, leading to strong absorption features in the infrared. Methane (CH_4), though symmetric in structure, can become infrared active when vibrations distort the molecule enough to temporarily create a dipole. These properties explain why relatively minor constituents of the atmosphere, such as CO_2, H_2O, O_3, N_2O, and CH_4, play a disproportionately large role in the Earth's greenhouse effect.

| Molecule	Structure		Permanent Electirc Dipole Moment?
Oxygen	O—O	linear	No (magnetic dipole)
Nitrogen	N—N	linear	No
Carbon Monoxide	O—C	linear	Yes
Carbon Dioxide	O—C—O	linear	No
Nitrous Oxide	O—N—N	linear	Yes
Water	O with H, H	asymmetric top	Yes
Ozone	O with O, O	asymmetric top	Yes
Methane	C with H, H, H, H	spherical top	Yes

Methane (CH$_4$)

- Spherical top
- 5 atoms, $3(5) - 6 = 9$ fundamental modes of vibration
- Due to symmetry of molecule, 5 modes are degenerate, only v_3 and v_4 fundamentals are IR active
- No permanent dipole moment   =>   No pure rotational spectrum

- Fundamental modes

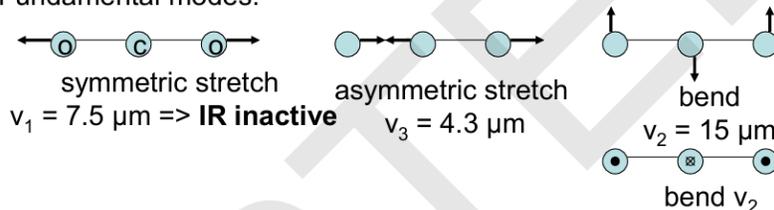v_1 v_2 $v_3 = 3.3$ μm $v_4 = 7.7$ μm
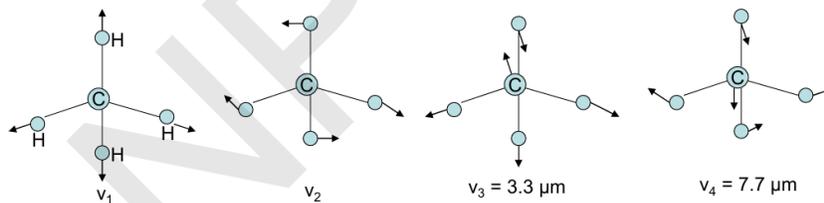
Ozone (O$_3$)

- Ozone is primarily present in the stratosphere except anthropogenic ozone pollution which exists in the troposphere
- Asymmetric top → similar absorption spectrum to H$_2$O due to similar configuration (nonlinear, triatomic)
- Strong rotational spectrum of random spaced lines
- Fundamental vibrational modes

symmetric stretch
v_1 = 9.01 µm

bend
v_2 = 14.3 µm

asymmetric stretch
v_3 = 9.6 µm
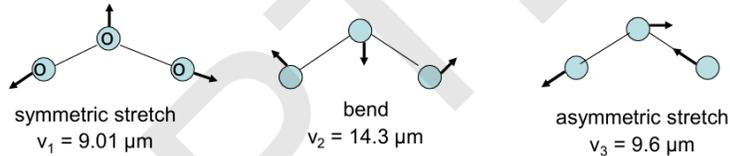
- 14.3 µm band masked by CO$_2$ 15 µm band
- Strong v_3 band and moderately strong v_1 band are close in frequency, often seen as one band at 9.6 µm
- 9.6 µm band sits in middle of 8-12 µm H$_2$O window and near peak of terrestrial Planck function
- Strong 4.7 µm band but near edge of Planck functions

Carbon dioxide (CO$_2$)

- Linear → no permanent dipole moment, no pure rotational spectrum
- Fundamental modes:

symmetric stretch
v_1 = 7.5 µm => **IR inactive**

asymmetric stretch
v_3 = 4.3 µm

bend
v_2 = 15 µm

bend v_2

- The v_3 vibration is a parallel band (dipole moment oscillates parallel to symmetric axis), transition ΔJ = 0 is forbidden, no Q branch, greater total intensity than v_2 fundamental
- The v_2 vibration is perpendicular band, has P, Q, and R branch
- The v_3 fundamental is the strongest vibrational band, but the v_2 fundamental is most effective due to "matching" of vibrational frequencies with terrestrial Planck emission function
- [13]C isotope (1% of C in atmosphere) and [17/18]O isotope (0.2%) cause a weak splitting of rotational and vibrational lines in the CO$_2$ spectrum

Water vapor (H$_2$O)

- Most important IR absorber
- Asymmetric top → Nonlinear, triatomic molecule has complex line structure, no simple pattern
- 3 vibrational fundamental modes

symmetric stretch
v_1 = 2.74 μm

bend
v_2 = 6.25 μm

asymmetric stretch
v_3 = 2.66 μm
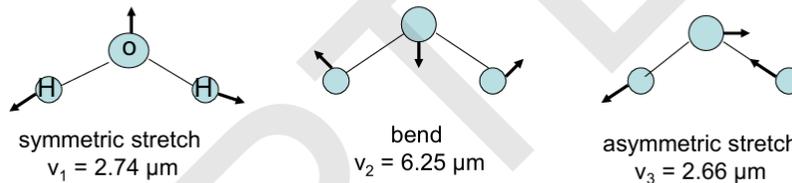
- Higher order vibrational transitions (Δv >1) give weak absorption bands at shorter wavelengths in the shortwave bands
- ^{2}H isotope (0.03% in atmosphere) and ^{18}O (0.2%) adds new (weak) lines to vibrational spectrum
- 3 rotational modes (J_1, J_2, J_3)
- Overtones and combinations of rotational and vibrational transitions lead to several more weak absorption bands in the NIR

Nitrous oxide (N$_2$O)

- Linear, asymmetric molecule (has permanent dipole moment)
- Has rotational spectrum and 3 fundamentals
- Absorption band at 7.8 μm broadens and strengthens methane's 7.6 μm band.
- 4.5 μm band less significant as it is at the edge of the Planck function.

- Fundamental modes:

symmetric stretch
v_1 = 7.8 μm

asymmetric stretch
v_3 = 4.5 μm

bend
v_2 = 17.0 μm

bend v_2