3	**Absorption Spectra** Emission spectrum of hydrogen, vibrational transitions, rotational transitions, vibrational-rotational transitions, transition modes and emission spectra, shape of absorption lines, broadening of spectral lines, absorption spectra of atmospheric gases,.

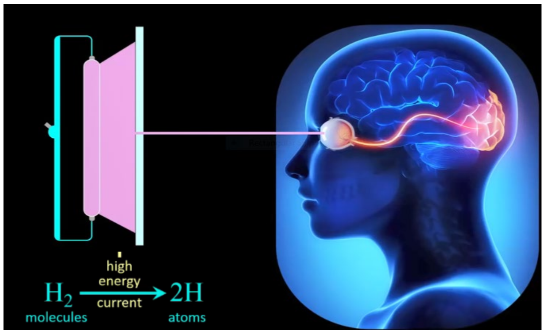
Chapter 3

Absorption Spectra

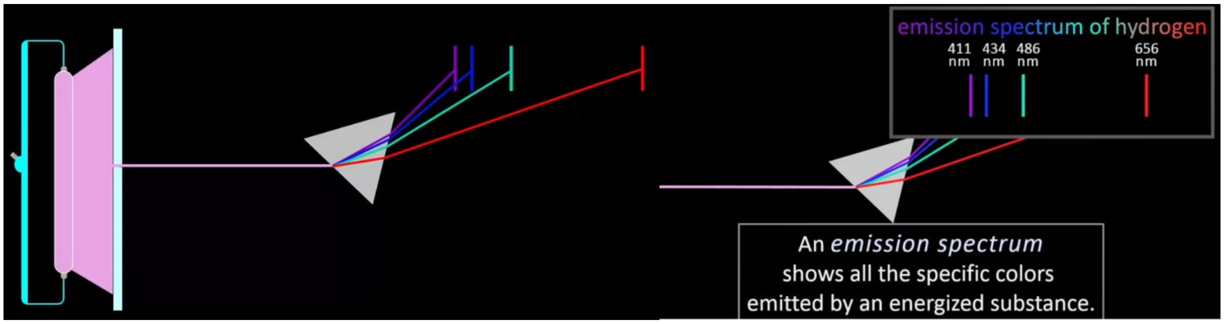
1- Emission spectrum of hydrogen:

In the latter half of the 19th century something remarkable was being noticed by a few scientists. Energized elements (active elements) would emit specific visible colors of light, and the colors were specific to the element, but no one identified, why this was happening? For example, if we energize hydrogen gas with an electric current, the H_2 molecule is split in to hydrogen atoms.

$$(molecules) H_2 \rightarrow 2H\ (atoms)$$



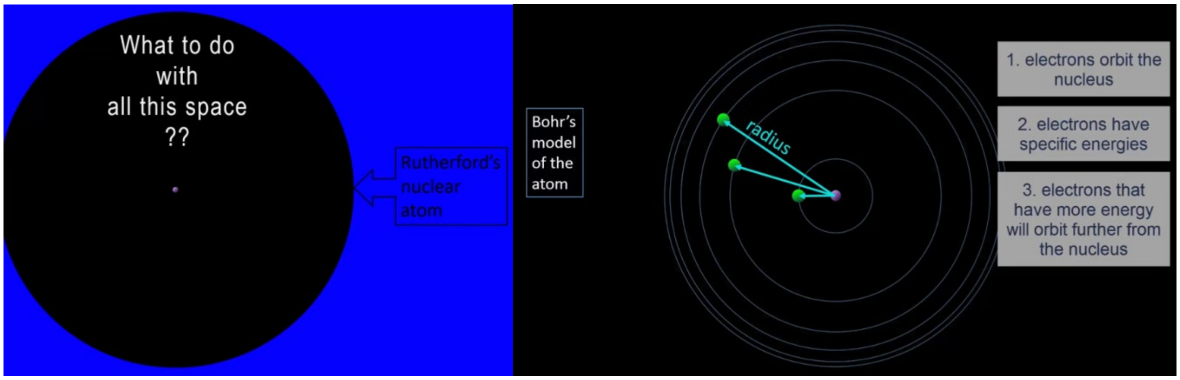
Those energized hydrogen atom emit a specific color spectrum of four colors. Our nervous system however is not able to see the four individual colors, our brain integrates those four colors in to one specific color so that’s the color we use. But when we diffract or split hydrogen’s pale pinkish color, we can then see the colors that are actually being emitted by hydrogen atoms: violet, blue, a sort of **turquoise** and red all at specific wavelengths.



An *emission spectrum* shows all the specific colors emitted by an energized substance.

2. Bohr model:

In 1913 using the atom's vast empty space provided by Ruther ford's nuclear model of the atom. Niels Bohr used these spectral colors to create a model of the atom that explained the existence of the emitted colors and explained the behavior of the electrons in the atom.

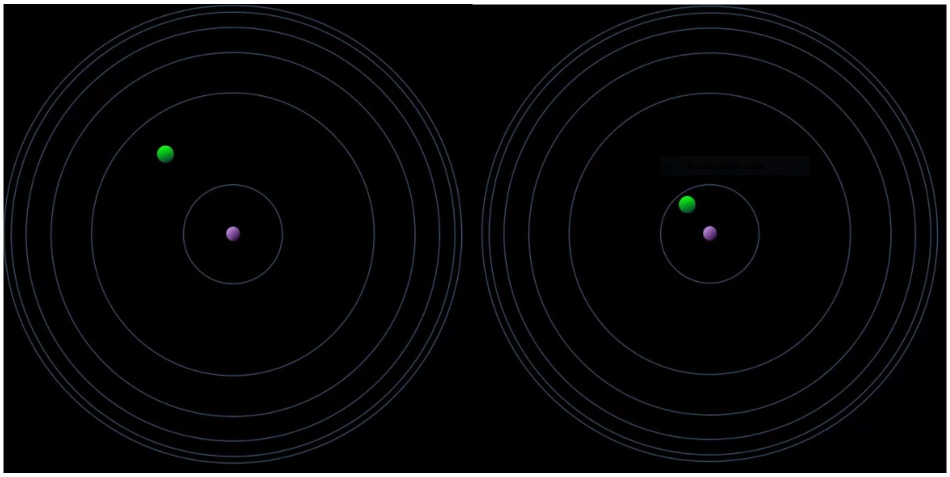


1. electrons orbit the nucleus
2. electrons have specific energies
3. electrons that have more energy will orbit further from the nucleus

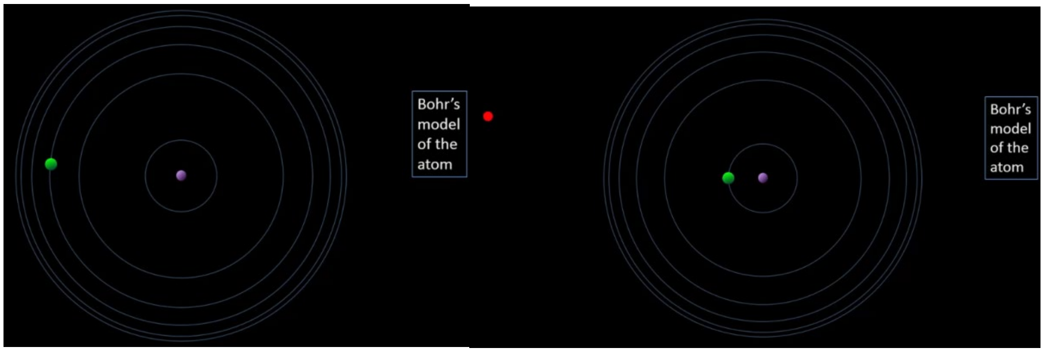
In Boh's atomic model:

1- Electrons orbit the nuleus.
2- The electron have different energized
3- Electrons that have more energy will orbit further from the nucleus.

This model however presented a very large obstacle for early 20th century physics. It was known that an accelerating charge, which is what these orbiting electrons are will emit energy in the form of light. Constant loss of energy would mean the electron would not be able to maintain an orbit, it would spiral down in to the nucleus due to the strong attractive force of the nucleus. But Bohr said no that would not happen.

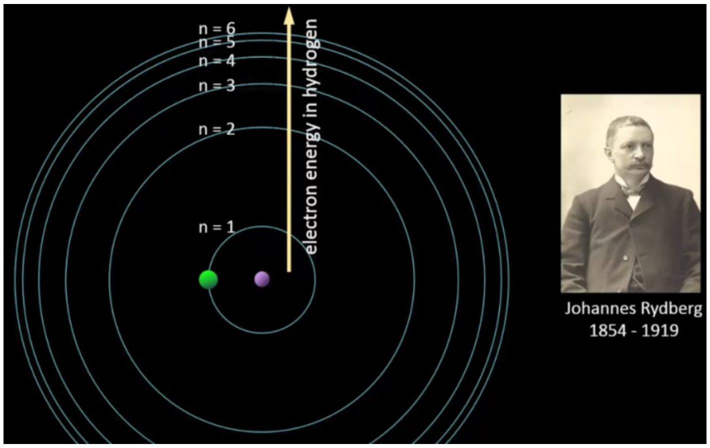


In his model, energy could be absorbed by an electron, putting it in a higher energy orbit, and the electron would only then emit light energy. When the energized electron transitioned from a higher to lower energy change of electron.

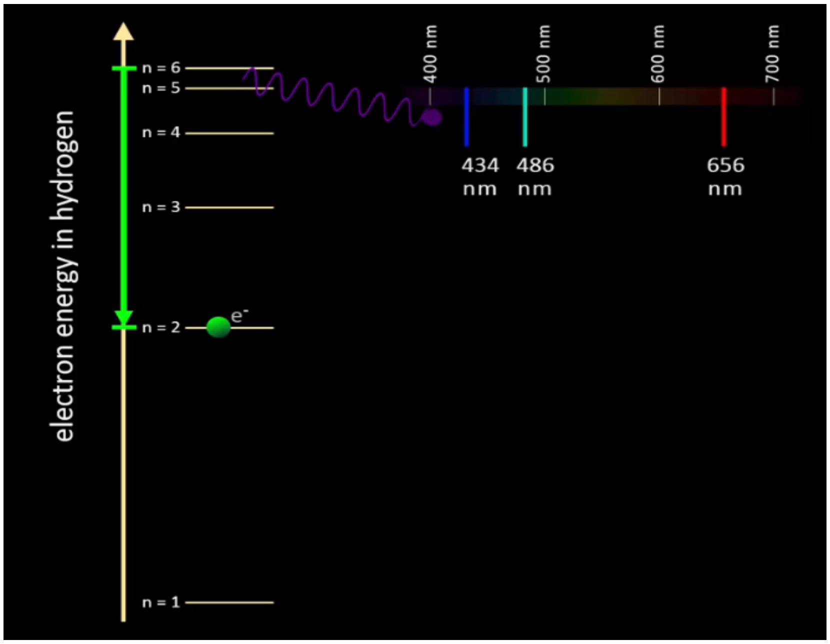


The emission spectrum of any one electron is constant and so Bohr concluded the electrons can only exist at specific discrete energies in order to produce such specific discrete emission spectra. The electron could not exist at energies in between those discrete energies and this is meant by term **quantized electron**. Let'stake a closer look at this last idea, which was a contribution to atomic structure that still holds true in our current quantum mechanical model of the atom.

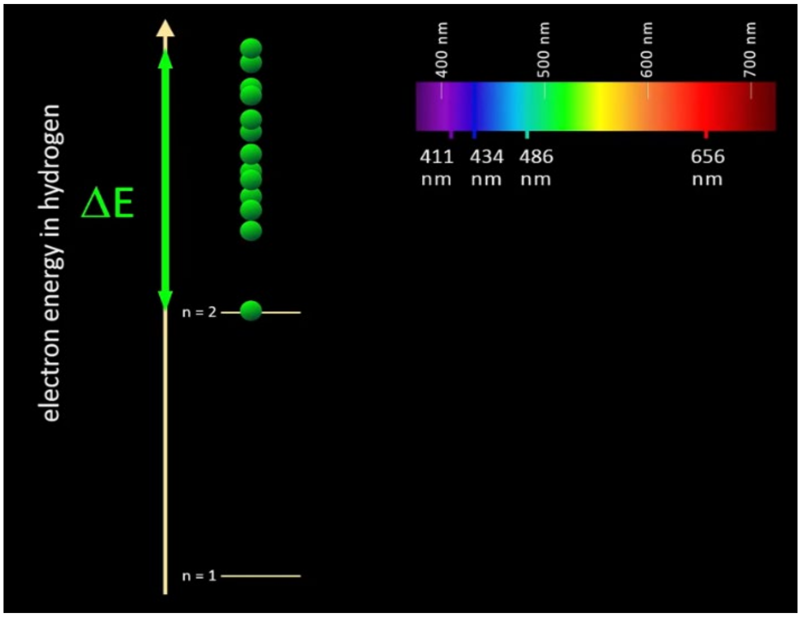
Bohr numbered his orbits with integers, symbolizing each orbit with the letter n, representing the electrons energy. The letter n and the numbering came out of earlier mathematical analyses of alkali metals emission spectra by Johannes Rydberg in 1888 and so using integers is not arbitrary.



They have mathematical significance, which we will see a bit later on. If we focus on a section of the orbits, we get a diagram of the allowed electron energies in hydrogen. Boher found that these energies gives us hydrogens emission spectrum. An electron transitioning from n=3 to n=2 emits a red photon, from 4 to 2 gives a bluish-green color, 5 to 2 gives blue and 6 to 2 gives violet.

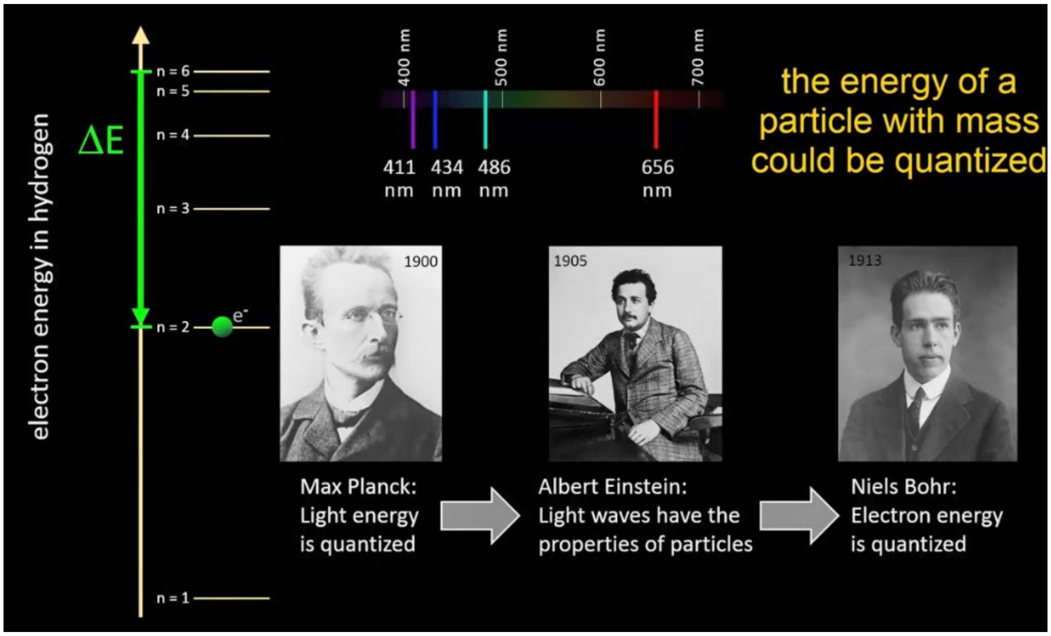


Notice that in the transition the electron does not exist in between those two allowed energies. If electron could exist at any energy, then the changes in electron energy, here represented by delta E, would result in emitting a large spectrum of colors, a continuous rainbow. But only discrete colors are seen, and so the electron must remain at discrete energies.



Again, this is called a quantized electron, an electron that can only exist at discrete energies. Bohr was very bold to tell the world that the electron was quantized but there was the work of two other bold scientist's to support him.

In 1900 in order to solve a problem in the analysis of ultraviolet light Max Planck came up with the idea of quantized light energy. Being that light, in other words electromagnetic waves, cannot have just any energy, they can only exist at discrete energies, which incidentally got him a Nobel Prize. Five years later in 1905, Einstein took that a giant step further with his photoelectric effect. Experimentally showing that light has momentum and momentum is a property derived from mass, but light has no mass, so the quantized light wave was behaving as if it was a particle, which we call a **photon**. So, with the existence of quantized light behaving like a particle with mass. In 1913 Bohr looked at the other side of that coin, and found that a particle with mass, such as the electron, could behave as if was quantized. Yes you guessed it, this got him a Nobel Prize.



the energy of a particle with mass could be quantized

Max Planck: Light energy is quantized

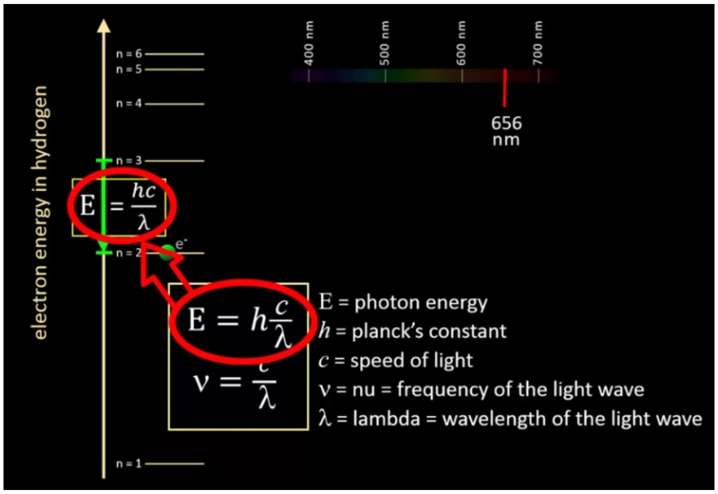
Albert Einstein: Light waves have the properties of particles

Niels Bohr: Electron energy is quantized

Let’s take a more mathematical look at the emission of red light from hydrogen. Let’s mark the energy transition of an electron with an arrow and ΔE.The energy of any electromagnetic wave can be calculated with hc divided by λ, which is a combination of these two equations, by substituting cover lambda for nu.

$$E = hv \ , \qquad E = h\frac{c}{\lambda} \ , \qquad because \quad v = \frac{c}{\lambda}$$

$$E = photo\ energy\ , h = planck's\ constant\ , c = speed\ of\ light\ ,$$
$$v = nu = frequency\ of\ the\ light\ wave\ , \lambda = lambda$$
$$= wavelength\ of\ the\ light\ wave$$



$E = \frac{hc}{\lambda}$

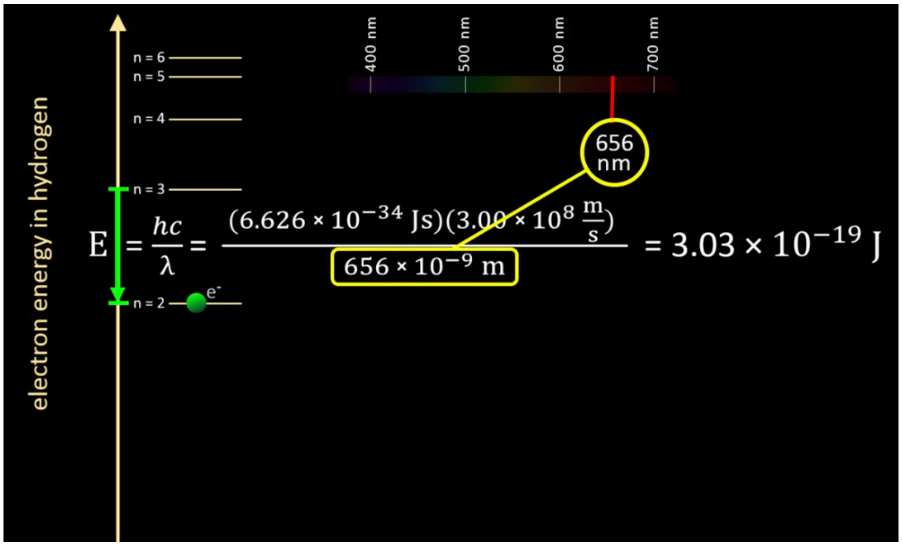
$E = h\frac{c}{\lambda}$

$\nu = \frac{c}{\lambda}$

E = photon energy
h = planck's constant
c = speed of light
ν = nu = frequency of the light wave
λ = lambda = wavelength of the light wave

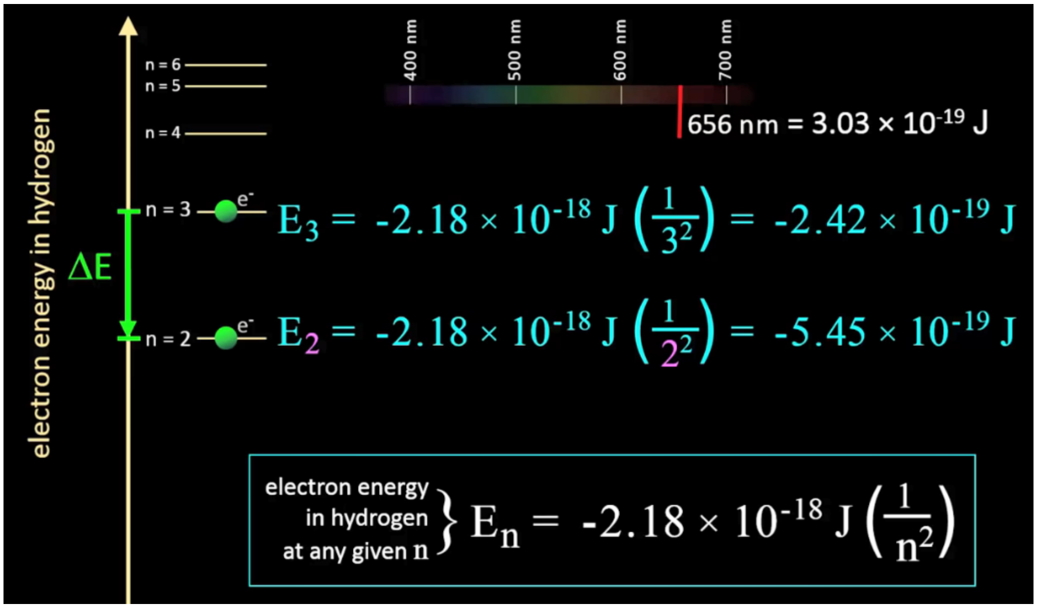
Given that we have the wavelength of the emitted red light, and h and c are constants, we can determine the energy of that red photon. Planck's constant, h , times the speed of light, c , divided by the wavelength expressed in meters to keep units constant, gives a photon energy of $3.03*10^{-19}$ joules.

$$E = \frac{hc}{\lambda} = \frac{(6.626*10^{-34}js)(3*\frac{10^8 m}{s})}{656*10^{-9}m} = 3.03*10^{-19}j$$



$$E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\ \mathrm{Js})(3.00\times10^{8}\ \frac{\mathrm{m}}{\mathrm{s}})}{\boxed{656\times10^{-9}\ \mathrm{m}}} = 3.03\times10^{-19}\ \mathrm{J}$$

In Bohr's model, that would also be the energy difference of the electron transitioning from n=3 energy to n=2 energy. The energy of an electron in hydrogen at any given n can be calculated using this equation derived from **Rydberg's analysis** of atomic emission spectra.



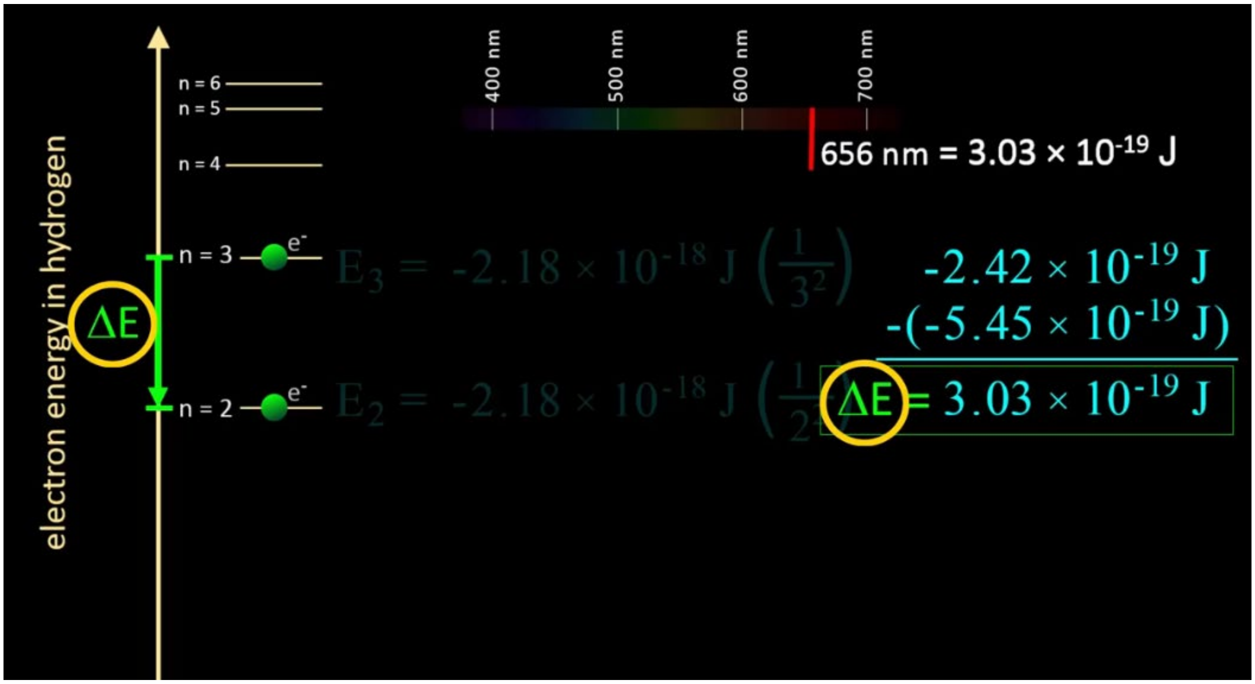
{Electron energy in hydrogen at any given n} E_n= $-2.18*10^{-18}$ j $(1/n^2)$

E_3= $-2.18*10^{-18}$ j $(1/3^2)$ = $-2.42*10^{-19}$j

Let's plug in the two integers from n to find the electron's energy at n=2 and n=3. We may see something interesting. For an electron at n=3, its energy is $-2.42*10^{-19}$joules. For an electron at n=2, its energy is $-5.45*10^{-19}$ joules.

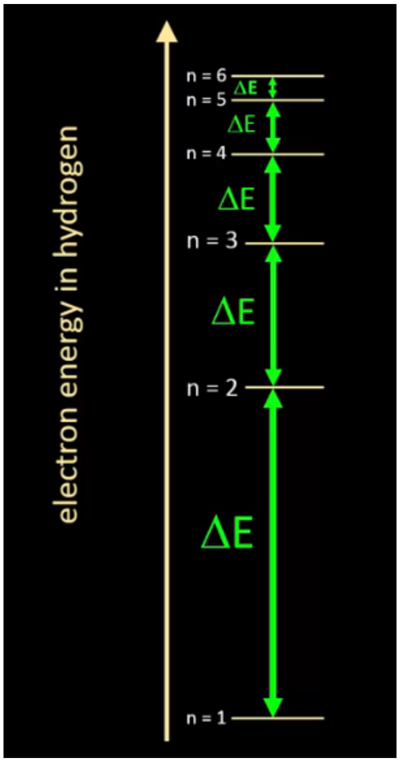
The Difference between these two energies is the energy lost by the electron as it transitions from n=3 to n=2, which would be the energy of the emitted light.

$$\Delta E = [\,-2.42 * 10^{-19}\,J - (-5.45 * 10^{-19} J)] = 3.03 * 10^{-19} J$$



We can see mathematically that the energy lost by an energized electron when transitioning to an allowed energy level is emitted as light. So by determining the energies of emitted light, Bohr was able to work backwards and arrange the allowed energies of electrons by the magnitude of the transitions occurring to produce the observed emission spectrum. Note that the intervals between each succeeding n decreases as electron energy gets higher.

However an electron's most probable distance from the nucleus does increase as the energy of the electron increases and perhaps Bohr's most important contribution to the eventual quantum mechanical model of 13 years later, is that the electron is quantized it can only exist at specific energies so there are a couple of items that you may have been wondering about:


electron energy in hydrogen
n = 6
n = 5
n = 4
n = 3
n = 2
n = 1
ΔE
ΔE
ΔE
ΔE
ΔE

3- Effect of solar light on gas molecules:

3.1 Vibrational

The energy of a molecule can be stored in:
(1) Translational (the gross movement of molecules or atoms through space)
(2) Vibrational
(3) Rotational
(4) Electronic (energy related to the orbit) forms. (See figure below):

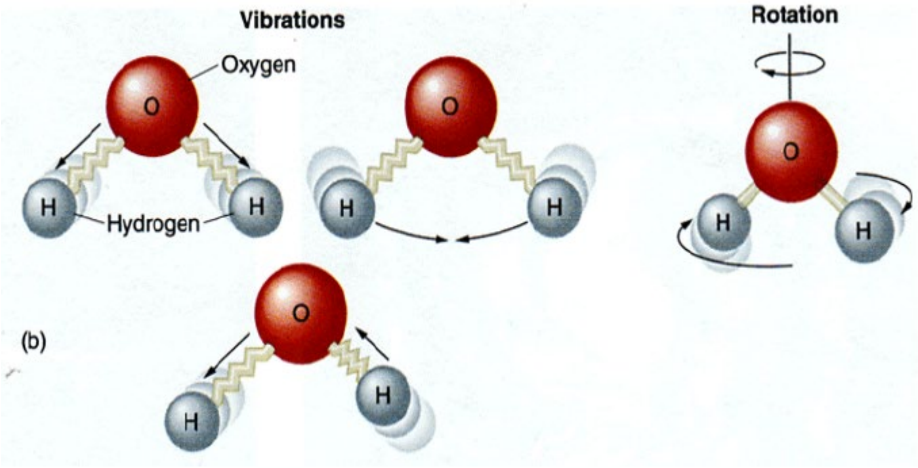


Figure 1: show vibration and rotation in atoms and molecules

Translational energy corresponds to movement of molecules or atoms through space and is not *quantized*. For tiny objects such as molecules in the atmosphere, the energy of rotation is ***quantized*** and can take on only discrete values. Molecular energy can be stored in ***the vibrations*** about the stable bonding of atmos.

In below figure we show effect of the spectrum radiation bands on the molecules and atoms:

- The bond in a molecule produces an equilibrium separation between the atoms. In this equilibrium separation, a molecule can vibrate.
- Excitation of vibrational modes in a molecule requires a photon with wavelength typically shorter than 20 um.
- Excitation of a single mode of a molecule is in general much more intense than excitation of multiple modes, so-called *combination or overtone bands*.
- Examination of the geometry of the molecule can tell us if a molecules gas activated by infrared. for example N_2 and O_2, which not possess dipole do not absorb in the IR.

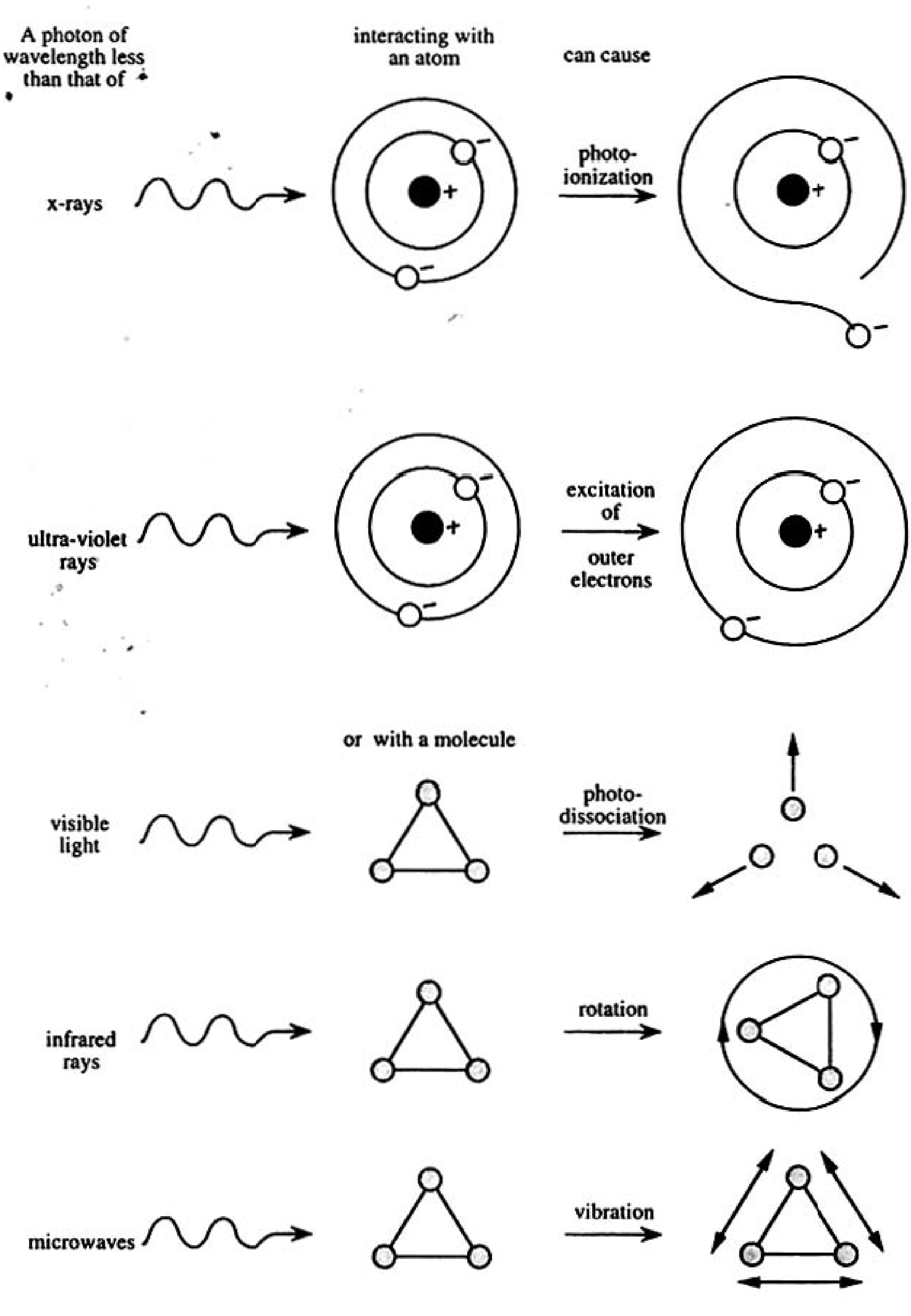


Figure 2: show effect of the spectrum radiation bands on the molecules and atoms

- Overall when two atoms combine to form a molecule, the energy of the molecule is typically lower than the sum of energies of the constituent for each atoms. This is a results of the overlap of the electron densities of the two atoms, which lowers the energy of each electron.

3.2 Rotational transitions:

- Rotational energy changes are relatively small, with a minimum on the order of 1 cm^{-1}. For this reason, pure rotational lines occur in the microwave and far-infrared spectra.
- Changes in vibrational energy are generally greater than 600 cm^{-1}, which is much larger than the minimum changes in rotational energy. Thus, vibrational transitions never occur alone but are coupled with simultaneous rotational transitions.
- If the symmetry is broken by having different types of atoms on each side like carbon monoxide and nitrogen oxide (NO) , the molecules begin to have some greenhouse properties
- Because the atoms have different charge in their nuclei, thus one side of molecule will probably have positive charge and other will be slight negative when this charge imbalance this is called ***dipole moment***.
- There is a Changing in electric field of atoms depending on how greenhouse gasses interact with IR light.
- Molecules with three or more atoms have more than one chemical bond, because, single bond never connect more than two atoms. When this molecules vibrated its bonds bend and stretch together as an integrated system not independent of the other.
- CO_2 molecules have shaped in a straight line with carbon in the middle, figure below. Oxygen tends to pull on electrons more tightly than carbon does.

Carbon dioxide

- In CO_2 molecules two modes of vibration can generate an asymmetry in the electric field through bending vibration.
- When CO_2 molecule is bend oxygen carrying negative charges swing from one side of the molecule to the other, CO_2 will be bending and make vibration at absorbs and emit IR light and its consider as infrared active.

- Other method of vibration in gases is asymmetric stretch in which one bond is growing longer and other gets shorter back and forth. There is less IR light absorb in atmosphere thus this mode is less important on earths radiation budget.
- In H_2O molecule oxygen has two electrons hanging off it. Which push the hydrogen toward other side, where each hydrogen has positive charge. The oxygen in water molecule has a dipole moment built in to its resting structure. Rotating H_2O and NO molecules would oscillate the electric field and generate light. Thus there are many modes of vibration of the water molecule including asymmetric stretch and a bend, all these modes are active in IR.

4. Types of Spectra:

Whenever radiation interacts with matter it is absorbed, scattered, or emitted in discrete packets called photons. Each photon contains energy:

$$E = h\,\tilde{v} \qquad (1)$$

Where h is Planck's constant $(6.626 * 10^{34}\ J/\ s)$. Hence, the energy carried by a photon is <u>inversely proportional</u> to the wavelength of the radiation. There are two main types of spectra figure below. They are ***Absorption*** and ***Emission*** Spectra. There is another division no spectra will discussed such as ***(line, band and continum spectrum)***.

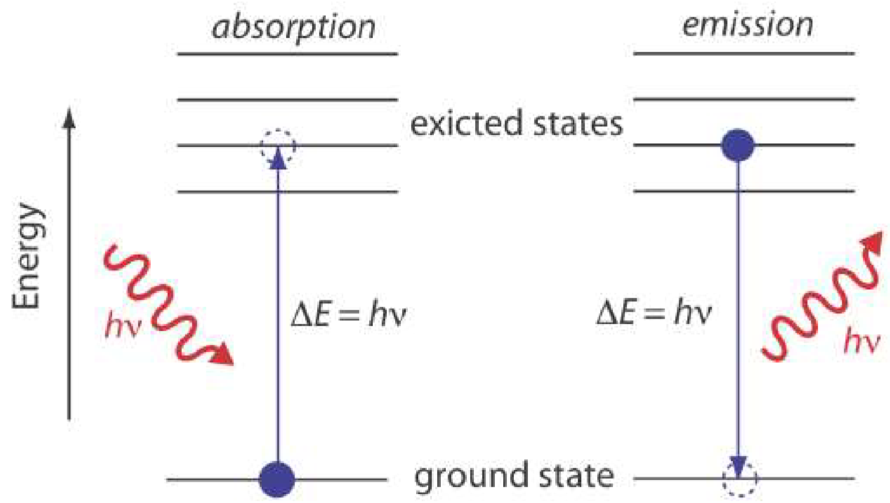


Figure 3: show spectrum of emission and absorption

4.1 Absorption continua

Extreme ultraviolet radiation with wavelengths $\leq 0.1\ um$, emitted by hot gases in the sun's outer atmosphere, is sufficiently energetic to strip electrons from atoms, a process referred to as **photoionization**.

Radiation at wavelengths up to **0.24*um*** is sufficiently energetic to break O_2 molecules apart into oxygen atoms, a process referred to as **photo dissociation**. The oxygen atoms liberated in this reaction are instrumental in the production of ozone O_3. Ozone, in turn, is dissociated by solar radiation with wavelengths extending up to **0.31um**, almost to the threshold of visible wavelengths. This reaction absorbs virtually all of the ~2% of the sun's potentially lethal ultraviolet radiation. The ranges of heights and wavelengths of the primary photoionization and photodissociation reactions in the Earth's atmosphere are shown in **Fig. 4.**

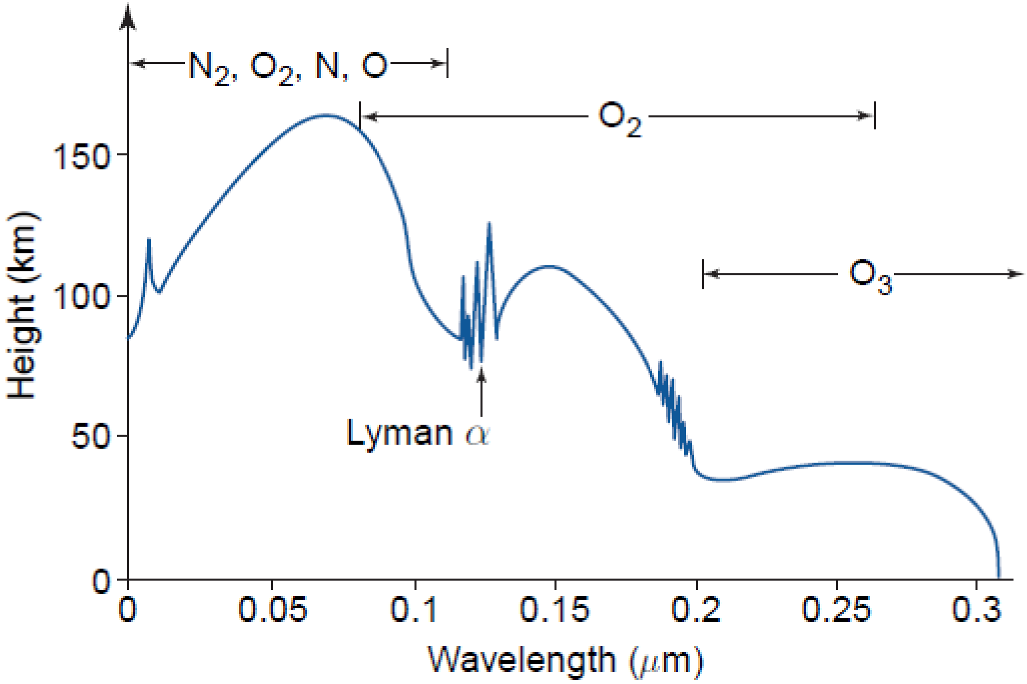


Figure 4: Depth of penetration of solar ultraviolet radiation in the Earth's atmosphere for overhead sun and an average ozone profile.

Photons that carry sufficient energy to produce these reactions are absorbed, and any excess energy is imparted to the kinetic energy of the molecules, raising the temperature of the gas. Since the energy required to liberate electrons and/or break molecular bonds is very large, **the so-called absorption continua** associated with these reactions are confined to the **x-ray** and ultraviolet regions of the spectrum. Most of the solar radiation with wavelengths longer than **0.31 um** penetrates to the Earth's surface.

4.2 Absorption lines

Radiation at visible and infrared wavelengths does not possess sufficient energy to produce ***photoionization*** or ***photo-dissociation***, but under certain conditions appreciable absorption can occur. To understand the processes that are responsible for absorption at these longer wavelengths, it is necessary to consider other kinds of changes in the state of a gas molecule. The internal energy of a gas molecule can be written in the form:

$$E = E_0 + E_v + E_r + E_t \qquad (2)$$

Where E_o is the energy level of the orbits of the electrons in the atoms, E_v and E_r refer to the energy levels corresponding to the vibrational and rotational state of the molecule, and E_t is the translational energy associated with the random molecular motions.

Quantum mechanics predicts that only certain configurations of electron orbits are permitted within each atom, and only certain vibrational frequencies and only certain rotation rates are permitted for a given molecular species. Each possible combination of electron orbits, vibration, and rotation is characterized by its own energy level, which represents the sum of the three kinds of energy.

A molecule may undergo a transition to a higher energy level by absorbing electromagnetic radiation and it may drop to a lower level by emitting radiation. Absorption and emission can occur only in association with discrete changes in energy level E. The frequency of the absorbed or emitted radiation is related to the change in energy level through the relation:

$$\Delta E = E2 - E1 = h\tilde{v} \qquad (3)$$

Absorptivity at visible and longer wavelengths can be described in terms of a ***line spectrum*** consisting of extremely narrow absorption lines separated by much wider gaps in which the gas is virtually transparent to incident radiation.

The changes in state of molecules that give rise to these absorption lines may involve orbital, vibrational, or rotational transitions or combinations. Orbital transitions are associated with absorption lines in the ultraviolet and visible part of the spectrum; vibrational changes with near-infrared and infrared wavelengths; and rotational lines, which involve the smallest changes in energy, with infrared and microwave radiation.

The absorption spectra of the species O_2 and N_2 exhibit a sparse of absorption lines because these molecular species do not possess an electric dipole, even when they are vibrating. In contrast with the so-called "greenhouse gases" (notably H_2O, CO_2, O_3, and trace species such as CH_4, N_2O, CO, and the chlorofluorocarbons) exhibit varieties of closely spaced absorption lines in the infrared region of the spectrum that are due to pure rotational or simultaneous vibrational– rotational transitions.

4.3 Broadening of absorption lines

The absorption lines of molecules are of finite width due to quantizing their energy levels, but this "natural broadening absorption lines" is in consequential to the broadening, attributable to the motions and collisions of the gas molecules such as:

- **Doppler broadening**: The Doppler shifting in the gas molecules experience at incident radiation and from random motions toward or away from the source of the radiation.

- **Pressure broadening:** (also referred to as collision broadening) associated with molecular collisions.

The absorption spectra in the vicinity of pressure and Doppler-broadened absorption lines can be represented by:

$$k_v = Sf(v - v_0) \dots\dots\dots\dots\dots\dots\dots\dots\dots . (4)$$

Where

$k_v = absorption\ \ spectra\ \ by\ doppler\ and\ pressure\ broadened$

$v_0 =$ is the wave number on which the line is centered

$f\ =$ is the so – called shape factor.

$S\ =$ Is the line intensity

$$S = \int_0^\infty k_v\, dv$$

The shape factor for Doppler broadening is inferred from the Maxwell–Boltzmann distribution of the velocity of the molecules in a gas, which has the shape of the familiar Gaussian probability distribution, It is have the form:

$$f = \frac{1}{\alpha\sqrt{\pi}} \exp[-\left(\frac{v - v_0}{\alpha}\right)^2] \qquad (6)$$

where

$$\alpha = \frac{v_0}{c^*} \left(\frac{2kT}{m}\right)^{1/2} \qquad (7)$$

In this expression the so-called half-width of the line (i.e., the distance between the center of the line and the points at which the amplitude is equal to half the peak amplitude) is, $\alpha\sqrt{ln2}$, m is the mass of the molecule and k is the Boltzmann's constant (1.381*10^{-23} J/K. molecules), and $c^*$is the speed of light, T is temperature of molecules absorption line.

The shape factor for pressure broadening, commonly referred to as the *Lorentz line shape*, is given by:

$$f = \frac{\alpha}{\pi[(v - v_0) + \alpha^2]} \dots\dots\dots\dots\dots\dots\dots\dots\dots. (8)$$

In this expression the half-width of the line is determine by:

$$\alpha \propto \frac{p}{T^N} \qquad (9)$$

Which is proportional to the frequency of molecular collision p . The exponent N ranges from 1/2 to 1 depending on the molecular species.

Shapes of absorption lines of the same strength and half-width, but broadened by these two distinctly different processes, are constracted in **Fig. 5**. The "wings" of the absorption lines shaped by pressure broadening extend out farther from the center of the line than those shaped by Doppler broadening.

For a water vapor line at 400 cm^{-1} and a temperature of 300 K, the Doppler line width is 7*10^{-4} cm^{-1}. A typical water vapor line width for air at the same temperature at the Earth's surface is ~100 times wider due to the presence of pressure broadening. Below ~20 km, pressure broadening is the dominant factor in determining the width of absorption lines, whereas above 50 km, where molecular collisions are much less frequent, Doppler broadening is the dominant factor.

In the intermediate layer between 20 and 50 km, the line shape is a convolution of the Doppler and Lorentz shapes.

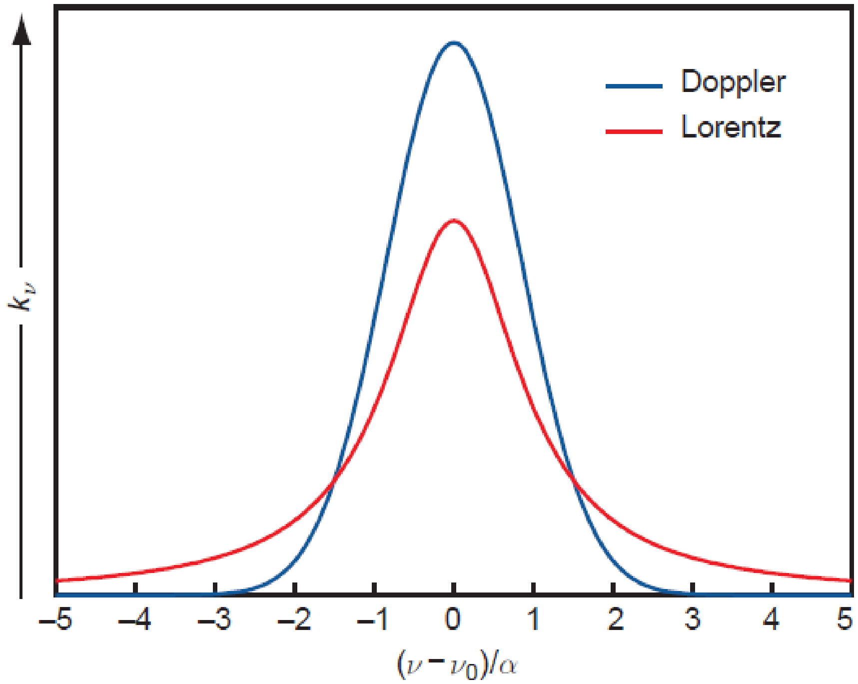


Figure 5: contrasting absorption line shapes associated with Doppler broadening and pressure broadening. Areas under the two profiles, indicative of the line intensity, S, are the same.

Laboratory measurements of absorption spectra exist for only a very limited sampling of pressures and temperatures. However, through the use of theoretically derived absorption line information, adjusted empirically to improve the fit with existing measurements, atmospheric physicists and climate modelers are able to calculate the absorption spectra for each of the radiatively important atmospheric gases for any specified thermodynamic conditions.

An example showing the excellent agreement between observed and theoretically derived absorption spectra is shown in Fig. 6. Note the narrowness of the lines, even when the effects of Doppler and pressure broadening are taken into account. The greatest uncertainties in theoretically derived absorption spectra are in the so-called "continua," where the superposition of the outermost parts of the wings of many different lines in nearby line clusters produces weak but in some cases significant absorption.

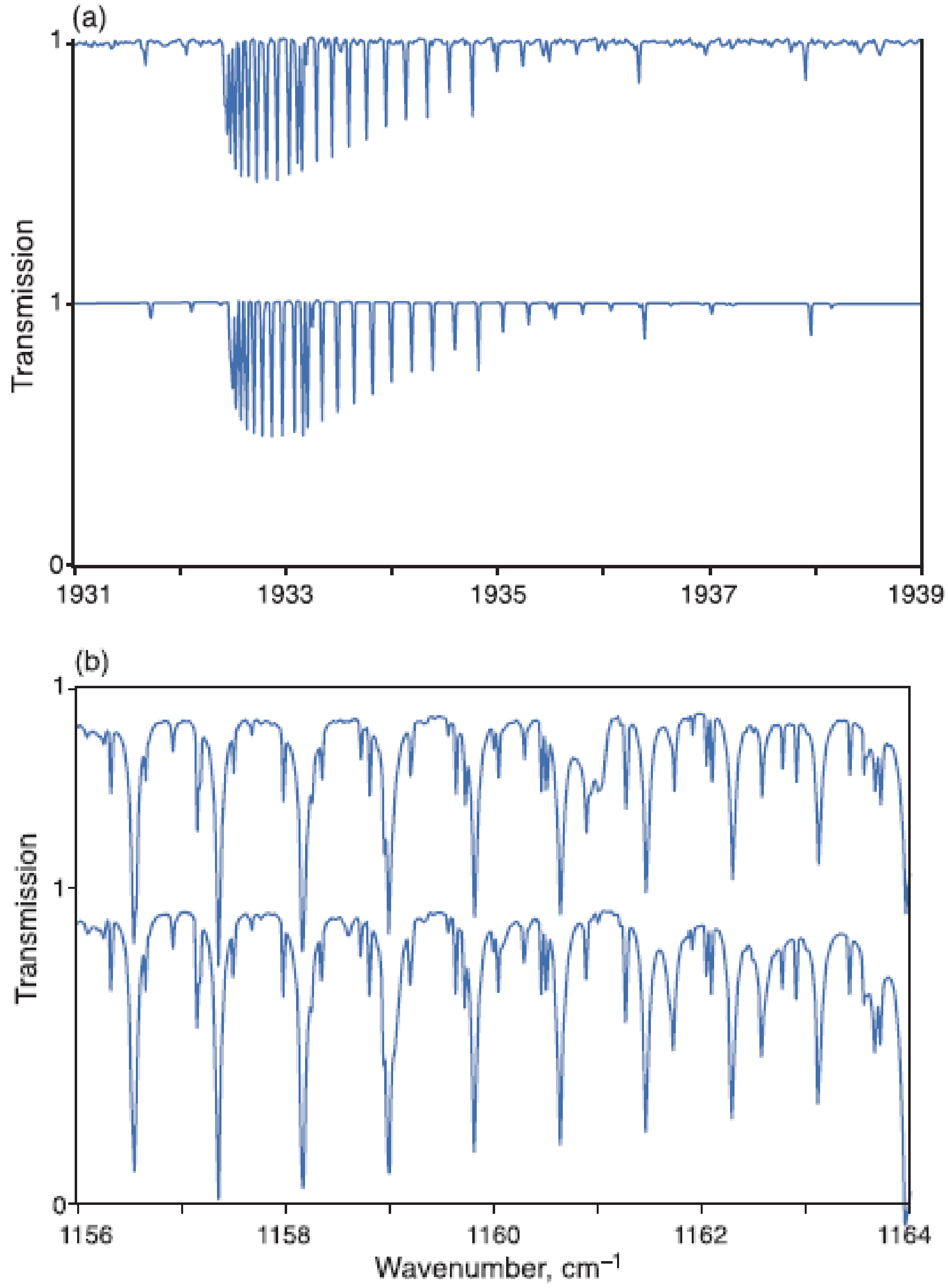


Fig. 6: Comparisons of observed and calculated transmissivity spectra. (a) Spectral range 1931 to 1939 cm^{-1} for carbon dioxide and (b) Spectral range 1156 to 1164 cm^{-1} for ozone and nitrous oxide. The upper plot in each panel is the observed spectrum and the lower plot is the calculated spectrum.