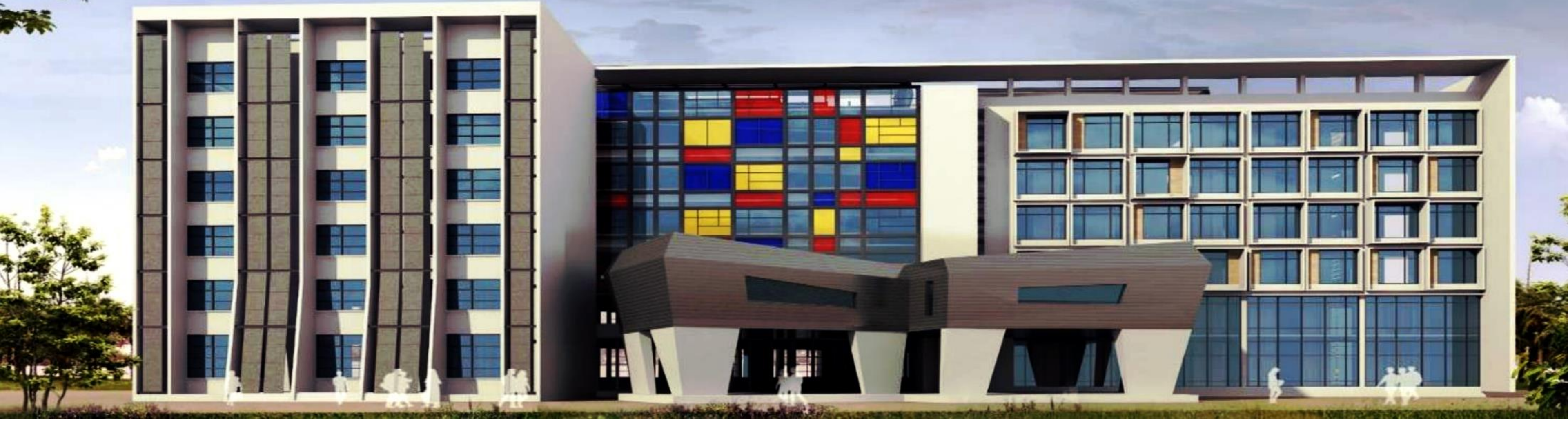


Environmental Chemistry Theory

CY1018

भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

Department of Chemistry

Interaction of EMR with matter

ΔE = E difference between energy levels

$$\Delta E = E_2 - E_1 \qquad E = h\nu = \frac{hc}{\lambda}$$

Absorption Emission

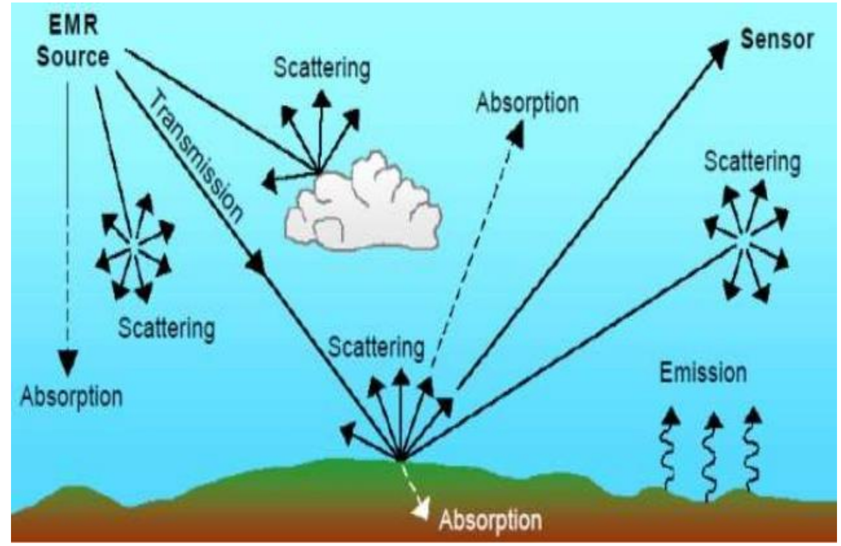


Table 1.1 Electromagnetic spectrum.[a)]

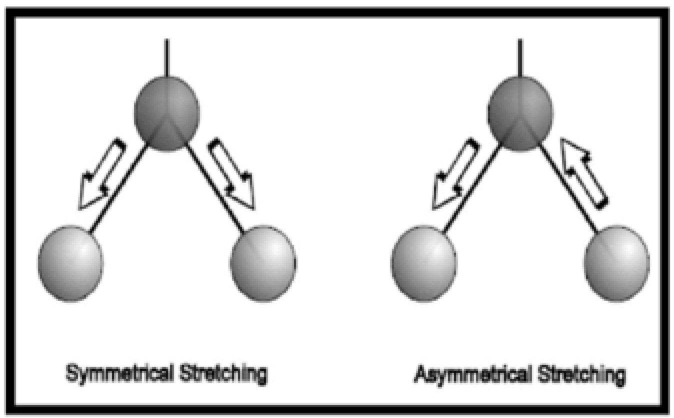
Region	Frequency (s^{-1})	Wavelength	Wavenumber (cm^{-1})	Energy (eV)	Spectroscopy
Radio	$10^6 \rightarrow 3\times10^9$	300 m → 10 cm	$3\times10^{-5} \rightarrow 0.1$	$4.1\times10^{-9} \rightarrow 1.2\times10^{-5}$	Nuclear magnetic resonance
Microwave	$3\times10^9 \rightarrow 3\times10^{12}$	10 cm → 0.1 mm	0.1 → 100	$1.2\times10^{-5} \rightarrow 0.012$	Electron spin resonance and rotational spectroscopy
Infrared	$3\times10^{12} \rightarrow 3\times10^{14}$	0.1 mm → 1 μm	100 → 10 000	0.012 → 1.2	Rotational spectroscopy and vibrational spectroscopy
Visible	$4.3\times10^{14} \rightarrow 7.5\times10^{14}$	700 nm → 400 nm	14 300 → 25 000	1.7 → 3.1	UV –visible
Ultraviolet	$7.5\times10^{14} \rightarrow 3\times10^{16}$	400 nm → 10 nm	$25\,000 \rightarrow 10^6$	3.1 → 120	UV –visible
X-rays	$3\times10^{16} \rightarrow 10^{19}$	100 Å → 0.3 Å	$10^6 \rightarrow 3\times10^8$	$120 \rightarrow 4\times10^4$	Electronic transition (internal electrons)
γ-rays	$10^{19} \rightarrow 10^{22}$	0.3 Å → 0.003 Å	$3\times10^8 \rightarrow 3\times10^{10}$	$10^4 \rightarrow 10^9$	Nuclear transitions

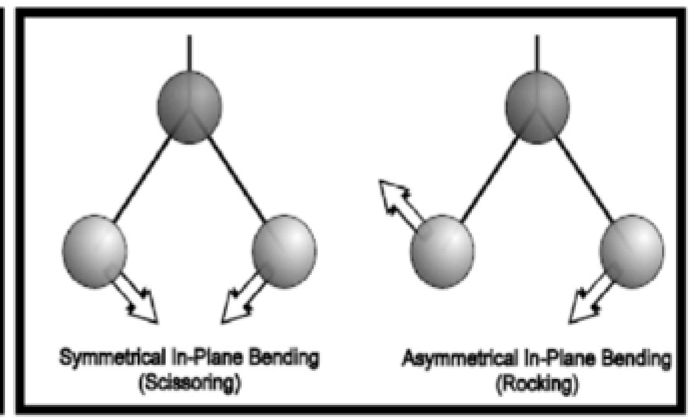
a) Most commonly used spectroscopic units:
Radio frequency radiation: MHz = 10^6 Hz (Hz = s^{-1}). Microwave radiation: GHz = 10^9 Hz.
Infrared radiation: cm^{-1} (wavenumbers). Visible and ultraviolet radiation: nm = 10^{-9} m.
X-ray and γ-ray radiation: nm = 10^{-9} m and Å = 10^{-10} m.

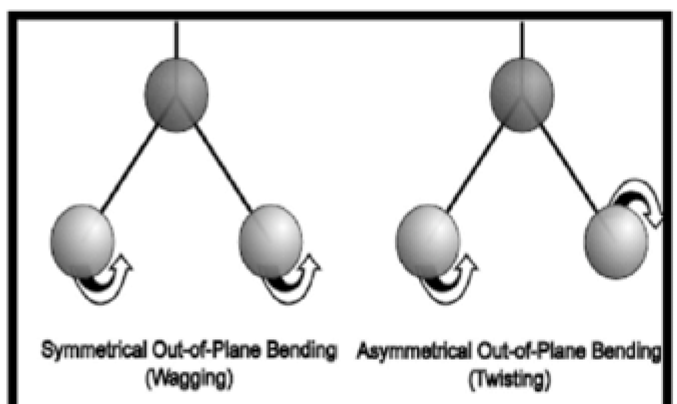
Vibrational (Infrared) Spectroscopy

Photon energies associated with the infrared regime (from 1 to 15 kcal/mole) are not large enough to excite electrons (which need UV-vis region), but may induce **vibrational excitation** of covalently bonded atoms and groups.

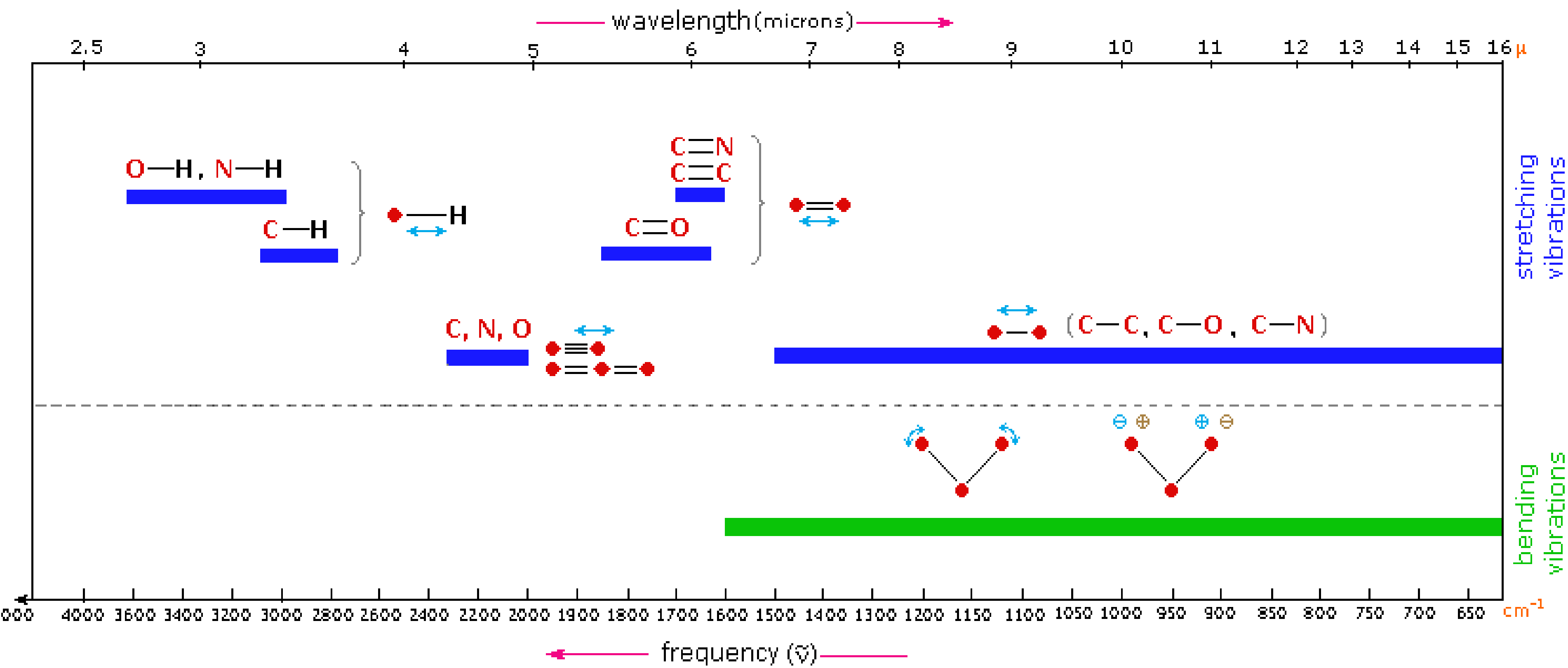
A molecule composed of n-atoms has 3n degrees of freedom, six of which are translations and rotations of the molecule itself. This leaves 3n-6 degrees of vibrational freedom (3n-5 if the molecule is linear).







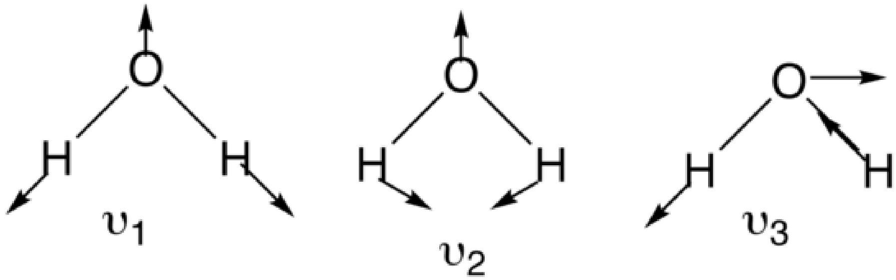
Vibrational (Infrared) Spectroscopy

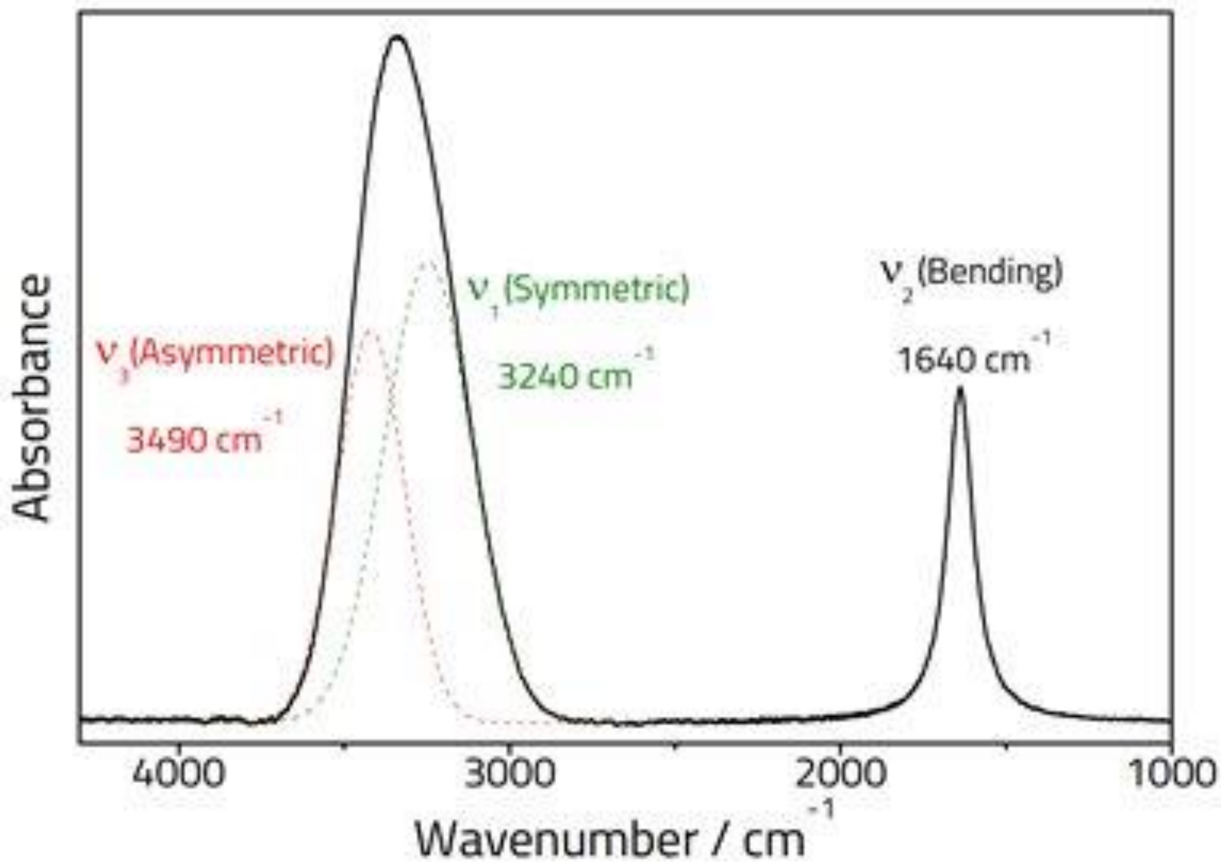


	Stretching Vibrations			Bending Vibrations		
Functional Class	Range (cm^{-1})	Intensity	Assignment	Range (cm^{-1})	Intensity	Assignment
Alkanes	2850-3000	str	CH_3, CH_2 & CH 2 or 3 bands	1350-1470 1370-1390 720-725	med med wk	CH_2 & CH_3 deformation CH_3 deformation CH_2 rocking
Alkenes	3020-3100 1630-1680 1900-2000	med var str	=C-H & =CH_2 (usually sharp) C=C (symmetry reduces intensity) C=C asymmetric stretch	880-995 780-850 675-730	str med med	=C-H & =CH_2 (out-of-plane bending) cis-RCH=CHR
Alkynes	3300 2100-2250	str var	C-H (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
Arenes	3030 1600 & 1500	var med-wk	C-H (may be several bands) C=C (in ring) (2 bands) (3 if conjugated)	690-900	str-med	C-H bending & ring puckering
Alcohols & Phenols	3580-3650 3200-3550 970-1250	var str str	O-H (free), usually sharp O-H (H-bonded), usually broad C-O	1330-1430 650-770	med var-wk	O-H bending (in-plane) O-H bend (out-of-plane)
Amines	3400-3500 (dil. soln.) 3300-3400 (dil. soln.) 1000-1250	wk wk med	N-H (1°-amines), 2 bands N-H (2°-amines) C-N	1550-1650 660-900	med-str var	NH_2 scissoring (1°-amines) NH_2 & N-H wagging (shifts on H-bonding)
Aldehydes & Ketones	2690-2840(2 bands) 1720-1740 1710-1720 1690 1675 1745 1780	med str str str str str str	C-H (aldehyde C-H) C=O (saturated aldehyde) C=O (saturated ketone) aryl ketone α, β-unsaturation cyclopentanone cyclobutanone	 1350-1360 1400-1450 1100	 str str med	 α-CH_3 bending α-CH_2 bending C-C-C bending
Carboxylic Acids & Derivatives	2500-3300 (acids) overlap C-H 1705-1720 (acids) 1210-1320 (acids) 1785-1815 (acyl halides) 1750 & 1820 (anhydrides) 1040-1100 1735-1750 (esters) 1000-1300 1630-1695(amides)	str str med-str str str str str str str	O-H (very broad) C=O (H-bonded) O-C (sometimes 2-peaks) C=O C=O (2-bands) O-C C=O O-C (2-bands) C=O (amide I band)	1395-1440 1590-1650 1500-1560	med med med	C-O-H bending N-H (1¡-amide) II band N-H (2¡-amide) II band
Nitriles	2240-2260	med	C≡N (sharp)			
Isocyanates,Isothiocyanates, Diimides, Azides & Ketenes	2100-2270	med	-N=C=O, -N=C=S -N=C=N-, -N_3, C=C=O			

Example: Water

(3n-6 = 3)
degrees of vibrational freedom





Why do we see the Sky in blue ?

Rayleigh Scattering (molecular scattering)

- Scattering by molecules and particles whose diameters are << wavelength

- Primarily due to oxygen and nitrogen molecules

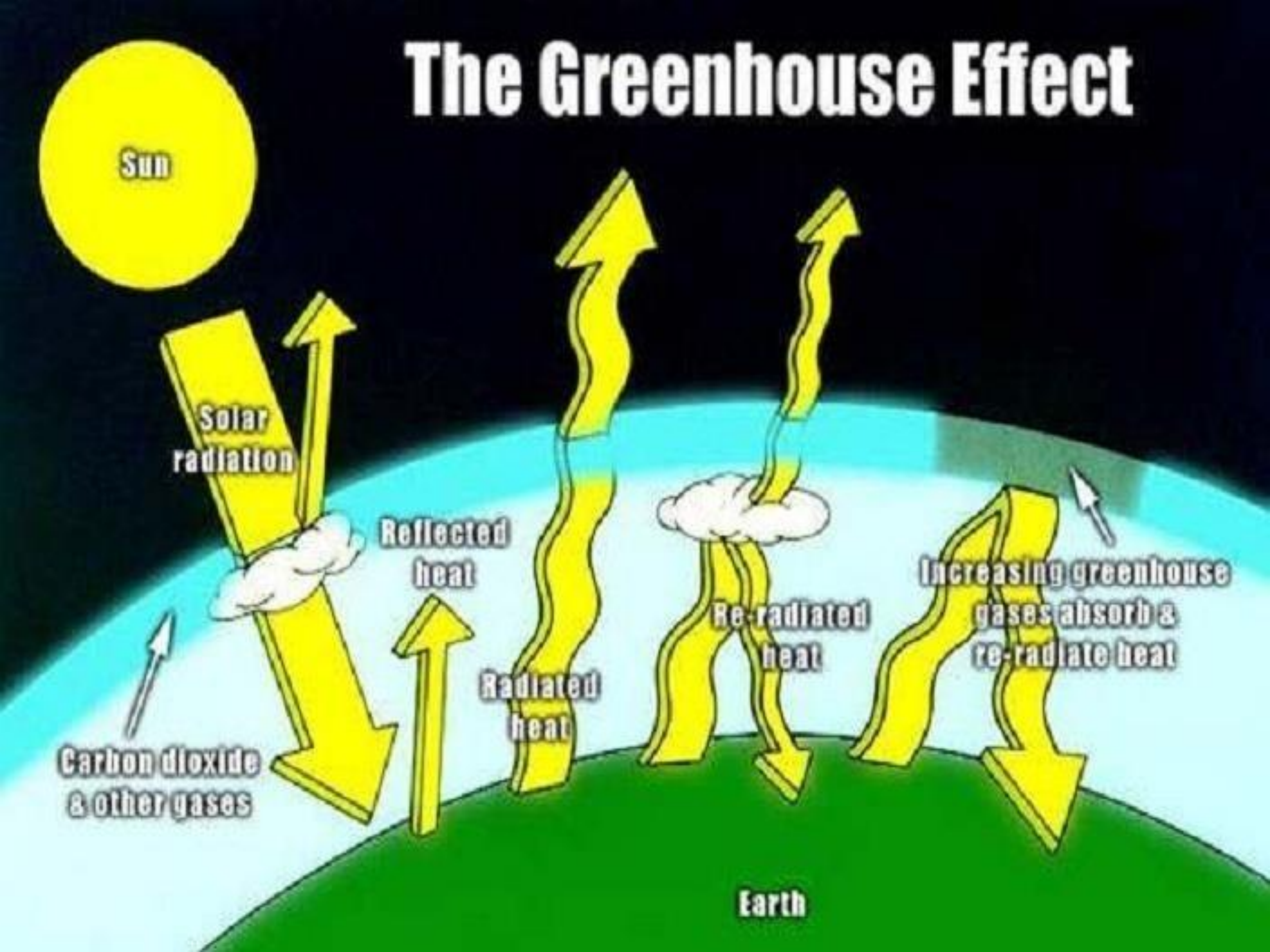
- Scattering intensity is proportional to λ^{-4}

Blue radiation (λ = 0.46)

Red radiation (λ = 0.66)

$(0.66/0.46)^4 = 4.24$

Blue is scattered 4 x more than red radiation



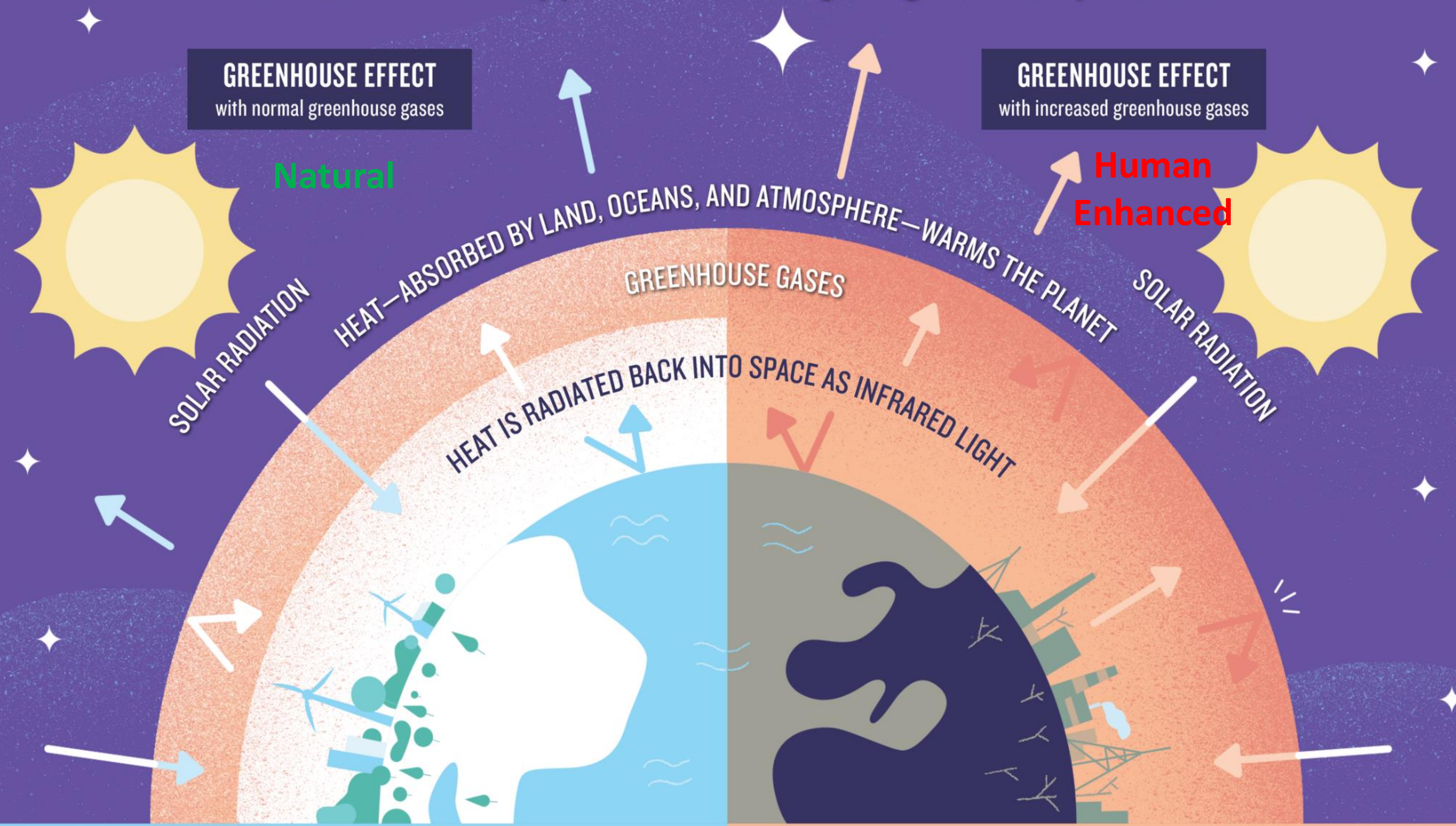
The Greenhouse Effect
Sun
Solar radiation
Reflected heat
Radiated heat
Re-radiated heat
Increasing greenhouse gases absorb & re-radiate heat
Carbon dioxide & other gases
Earth

What is the Greenhouse Effect?

"The greenhouse effect is a good thing. It warms the planet to its comfortable average of 59 degrees Fahrenheit (15 degrees Celsius) and keeps life on earth, well, livable. Without it the world would be a frozen, uninhabitable place, more like Mars. The problem is, mankind's voracious burning of fossil fuels for energy is artificially amping up the natural greenhouse effect. The result? An increase in global warming that is altering the planet's climate systems in countless ways."

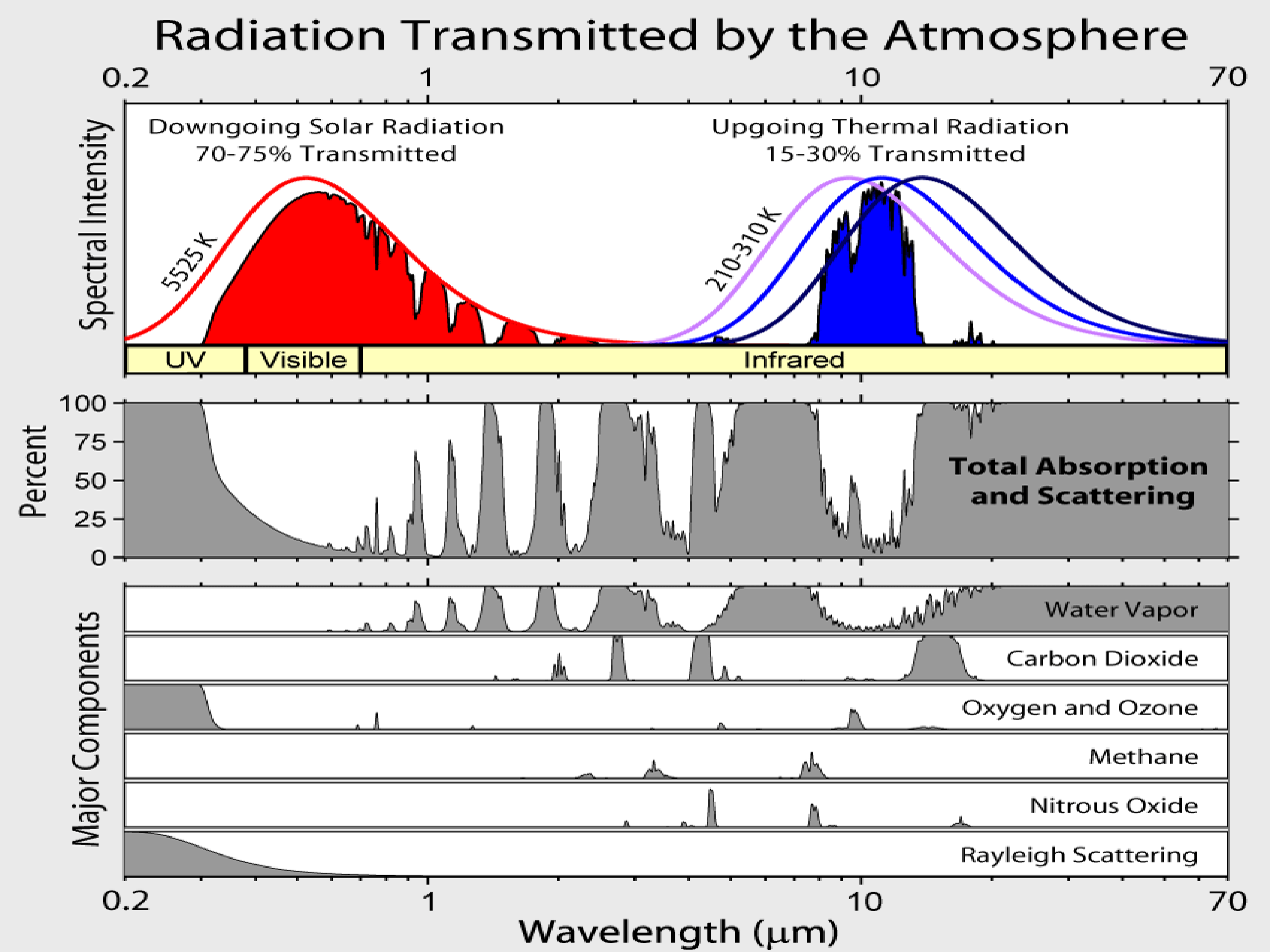
"Identified by scientists as far back as 1896, the greenhouse effect is the natural warming of the earth that results when gases in the atmosphere trap heat from the sun that would otherwise escape into space."

In the last century, human activities such as burning fossil fuels and deforestation have caused a jump in the concentration of greenhouse gases in the atmosphere. The result: extra trapped heat and higher global temperatures.

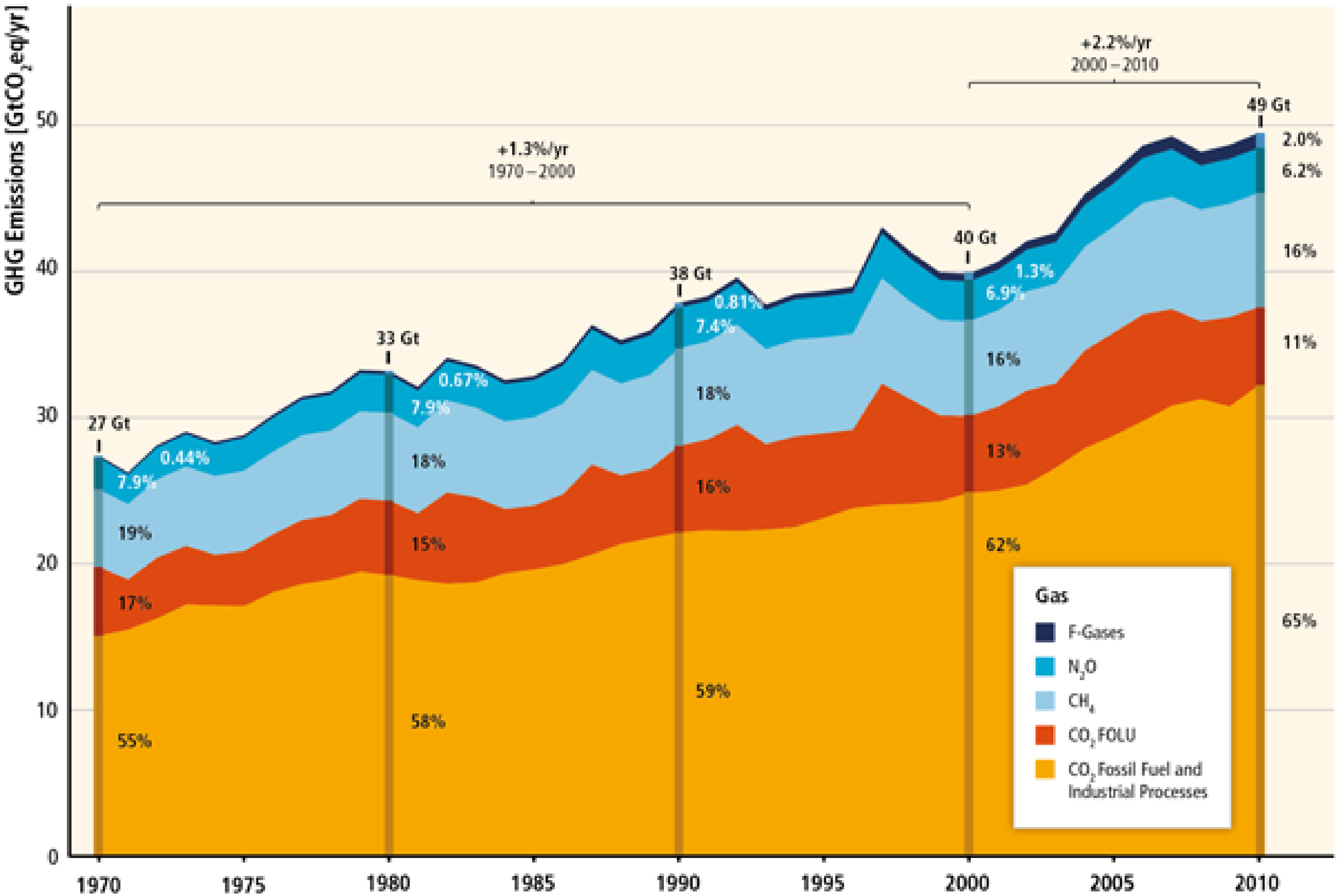


Some heat continues into space while the rest, trapped by greenhouse gases, help maintain the planet's relatively comfortable temperatures. Less gas = less heat trapped in the atmosphere.

Increased greenhouse gases means less heat escapes. Between preindustrial times and now, the earth's average temperature has risen 1.8 °F (1.0 °C).


Radiation Transmitted by the Atmosphere
0.2
1
10
70
Spectral Intensity
Downgoing Solar Radiation
70-75% Transmitted
Upgoing Thermal Radiation
15-30% Transmitted
5525 K
210-310 K
UV
Visible
Infrared
Percent
100
75
50
25
0
Total Absorption
and Scattering
Major Components
Water Vapor
Carbon Dioxide
Oxygen and Ozone
Methane
Nitrous Oxide
Rayleigh Scattering
Wavelength (μm)

- Water vapor
- Carbon dioxide (CO_2)
- Methane (CH_4)
- Nitrous oxide (N_2O)
- CFCs
- Others



GHG Emissions [GtCO2eq/yr]
+1.3%/yr
1970 – 2000
+2.2%/yr
2000 – 2010
27 Gt
33 Gt
38 Gt
40 Gt
49 Gt
0.44%
7.9%
19%
17%
55%
0.67%
7.9%
18%
15%
58%
0.81%
7.4%
18%
16%
59%
1.3%
6.9%
16%
13%
62%
2.0%
6.2%
16%
11%
65%
Gas
F-Gases
N2O
CH4
CO2 FOLU
CO2 Fossil Fuel and Industrial Processes
1970
1975
1980
1985
1990
1995
2000
2005
2010
0
10
20
30
40
50

"**Carbon dioxide (CO_2)** *is by far the most important greenhouse gas. Analysis of ice cores from Greenland and Antarctica shows that pre-industrial levels of carbon dioxide in the atmosphere were about 280 ppmv (parts per million by volume). The level in 2016 was about 44 percent higher, 403 ppm. The rate of increase amounts to 1–2 ppm per year.*

Global carbon dioxide emissions from fossil fuel combustion, cement production and other industrial processes are the major source of global greenhouse gas emissions. Currently, they account for about 68 per cent of total global greenhouse gas emissions, and were estimated to be 36.2 $GtCO_2$ in 2015. Once released from fossil storage, carbon dioxide remains in the atmosphere for a very long time and can affect the climate long into the future.

Changes in land use (mainly deforestation) also contribute to carbon dioxide emissions. They represent slightly less than a fifth of the total emissions of carbon dioxide. In recent years, there has been a decline in carbon dioxide emissions from land use, largely due to a lower pace of deforestation and increased afforestation."

"***Methane(CH_4)*** *is formed naturally by* *<u>the bacterial decomposition of organic matter under oxygen-free conditions</u>. Because of various types of human activity, emissions of methane have roughly doubled. <u>Rice cultivation, cattle breeding, emissions from coal mines and the leakage of fossil gas</u> represent significant anthropogenic sources around the world, as do the treatment of wastewater and organic waste.*

The pre-industrial concentration of methane is estimated to have been 0.7 ppm. Today's level is more than twice as high, about 1.8 ppm. The life of methane in the atmosphere is relatively short, <u>on the average 10–15 years</u>."

“**Nitrous Oxide(N_2O) :** *Our knowledge of the extent of emissions and the factors that control them is incomplete, but denitrification is the main source of nitrous oxide in the atmosphere. This process, which is carried out by micro-organisms, occurs naturally in the soil. However, the more nitrogen is made available to plants by adding it in the form of fertilizer or through the deposition of airborne nitrogen, the more nitrous oxide is formed. Another source of nitrous oxide emissions is all sorts of combustion. During the combustion process, small amounts of N_2O are formed in addition to the “ordinary” nitrogen oxides (NO and NO_2). This amount depends largely on the combustion conditions.*
Nitrous oxide is a greenhouse gas whose pre-industrial level is estimated to have been 270 ppb (parts per billion). The level in 2011 was 324 parts per billion, an increase of 20 percent. About a third of the nitrous oxide emitted today are caused by humans.
Nitrous oxide has a long residence time in the atmosphere, an average of about 120 years.”

“**Fluorine compounds :** *The greenhouse gases described so far occur naturally in the atmosphere. This does not apply to the group of synthetic fluorine compounds, which in many cases are very long-lived and potent greenhouse gases. Their large heating effect, per molecular weight, is due to their ability to absorb radiation in a previous fully transmissive part of the infrared spectrum.*

The most familiar substances in this group are the chlorofluorocarbons (CFC gases, known as CFCs), which have mainly attracted attention because of their ability to break down the stratospheric ozone. CFC gases are also powerful greenhouse gases. Measured per molecule, some of them are tens of thousands of times more effective than carbon dioxide. CFC gases are however being phased out globally.

Other substances in this group are so-called f-gases, which have significant greenhouse effects and include:

HFCs, which are similar to CFCs but do not contain chlorine and therefore do not affect the ozone layer. Used as a replacement for CFCs in many applications. They are not as long-lived in the atmosphere as CFCs and not as powerful in their greenhouse effect.

Sulphur hexafluoride (SF6), used in the electronics industry, for example.

PFCs (also called fluorocarbons, FCs) emitted during aluminium production, but also used in the electronics industry.

Since the released amounts of these substances are small, their contribution to the greenhouse effect is so far only a few percent, calculated over a hundred-year period. However, global emissions are increasing rather sharply, particularly of HFCs, and several of them have effects that last for a very long time – the mean residence time of SF6 in the atmosphere is estimated at 3,200 years.”

Ozone as a greenhouse gas

Although ozone was present at ground level before the Industrial Revolution, peak concentrations are now far higher than the pre-industrial levels, and even background concentrations well away from sources of pollution are substantially higher. Ozone acts as a greenhouse gas, absorbing some of the infrared energy emitted by the earth. Quantifying the greenhouse gas potency of ozone is difficult because it is not present in uniform concentrations across the globe. However, the most widely accepted scientific assessments relating to climate change (e.g. the Intergovernmental Panel on Climate Change Third Assessment Report) suggest that the radiative forcing of tropospheric ozone is about 25% that of carbon dioxide.
The annual global warming potential of tropospheric ozone is between 918–1022 tons carbon dioxide equivalent/tons tropospheric ozone. This means on a per-molecule basis, ozone in the troposphere has a radiative forcing effect roughly 1,000 times as strong as carbon dioxide. However, tropospheric ozone is a short-lived greenhouse gas, which decays in the atmosphere much more quickly than carbon dioxide. This means that over a 20-year span, the global warming potential of tropospheric ozone is much less, roughly 62 to 69 tons carbon dioxide equivalent / ton tropospheric ozone.
Because of its short-lived nature, tropospheric ozone does not have strong global effects, but has very strong radiative forcing effects on regional scales. In fact, there are regions of the world where tropospheric ozone has a radiative forcing up to 150% of carbon dioxide.

"**Particles** *in the atmosphere also affect the radiation balance. Sulphate particles reflect incoming sunlight and hence reduce the amount of solar energy that reaches the Earth's surface. Sulphate particles originate from sulphur dioxide emissions.*

There are also carbon particles ("black carbon") in the air. These can both absorb heat and reflect incoming light. Their net effect on climate is therefore difficult to assess. Particles of black carbon can both absorb heat and reflect incident light. Particles also have an effect on the environment by forming condensation nuclei for water vapour in the atmosphere, which can affect cloud formation and precipitation. Unlike greenhouse gases, the residence time of particles in the air is short, about two weeks.

The net effect of particles is difficult to assess and contributes to a high degree of uncertainty, but has been estimated by the IPCC to be somewhere between -0.1°C and -1.9°C."

The relative contributions

To evaluate the effect of different greenhouse emissions on the climate you need to know the volume of the emission, its ability to absorb heat radiation in different wavelength bands, its lifetime in the atmosphere and possible secondary effects.
In order to compare the contributions of the various greenhouse gases, it is necessary to calculate how much carbon dioxide would be required to achieve the same effect on the earth's radiation balance; the quantity is GWP (global warming potential), and the unit is a carbon dioxide equivalent.

Gas	GWP	Lifetime (Y)
Carbon dioxide (CO_2)	1	Variable
Methane (CH_4)	25	12.2
Nitrous oxide (N_2O)	298	120
Hydrofluorocarbons (HFCs)	12-14,800	1.5-264
Perfluorocarbons (PFCs)	7,390-12,200	3200-50000
Sulphur hexafluoride (SF_6)	22,800	3200

With a shorter perspective, gases with short residence time, such as methane, will have a greater relative importance, while the importance of very long-lived gases increases if you take a long-term perspective.

Solutions

Slowing Climate Disruption

Prevention

Cut fossil fuel use (especially coal)

Shift from coal to natural gas

Improve energy efficiency

Shift to renewable energy resources

Transfer energy efficiency and renewable energy technologies to developing countries

Reduce deforestation

Use more sustainable agriculture and forestry

Put a price on greenhouse gas emissions

Reduce poverty

Slow population growth

Cleanup

Remove CO_2 from smokestack and vehicle emissions

Store (sequester) CO_2 by planting trees

Sequester CO_2 in soil by using no-till cultivation and taking cropland out of production

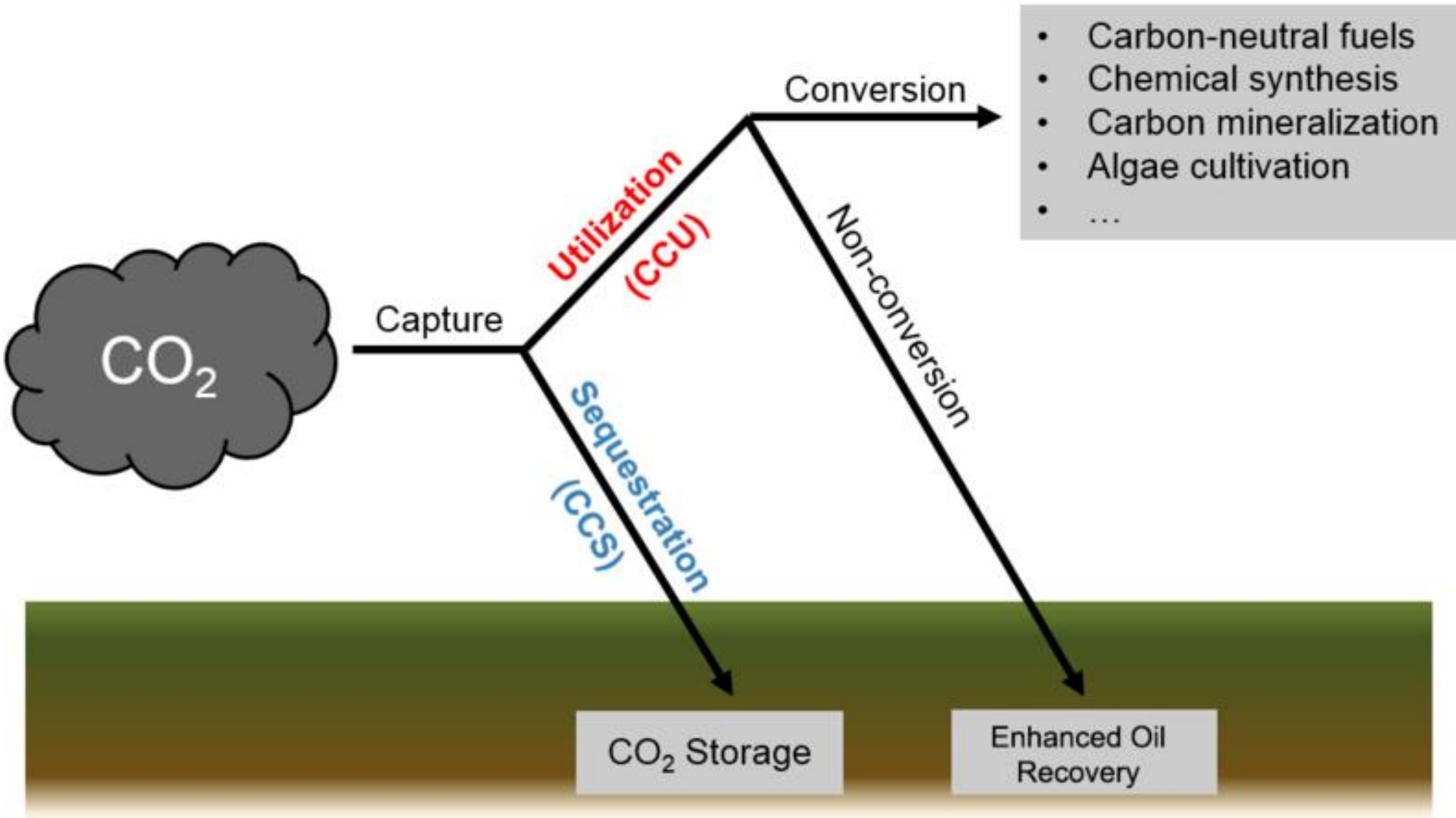
Sequester CO_2 deep underground (with no leaks allowed)

Sequester CO_2 in the deep ocean (with no leaks allowed)

Repair leaky natural gas pipelines and facilities

Use animal feeds that reduce CH_4 emissions from cows (belching)

1. Energy Efficiency
2. Energy Conservation
3. Fuel Switching
4. Carbon Capture and Sequestration (CCS)



CO_2
Capture
Utilization
(CCU)
Conversion
Carbon-neutral fuels
Chemical synthesis
Carbon mineralization
Algae cultivation
…
Non-conversion
Sequestration
(CCS)
CO_2 Storage
Enhanced Oil Recovery