Agenda

Summary so far:

Solar influx $S(\nu, \lambda)$ is known (Stefan-Boltzmann Law, Sun cycles)

Earth' albedo is measured by satellites

Earth surface temperature is measured → t dependence

Atmospheric composition, density and temperature profiles are measured and modeled in detail

Interaction of elm Radiation With Matter

Task: Explain $T(t)$

Model radiative forcings due to specific components (CO_2, CH_4,…)

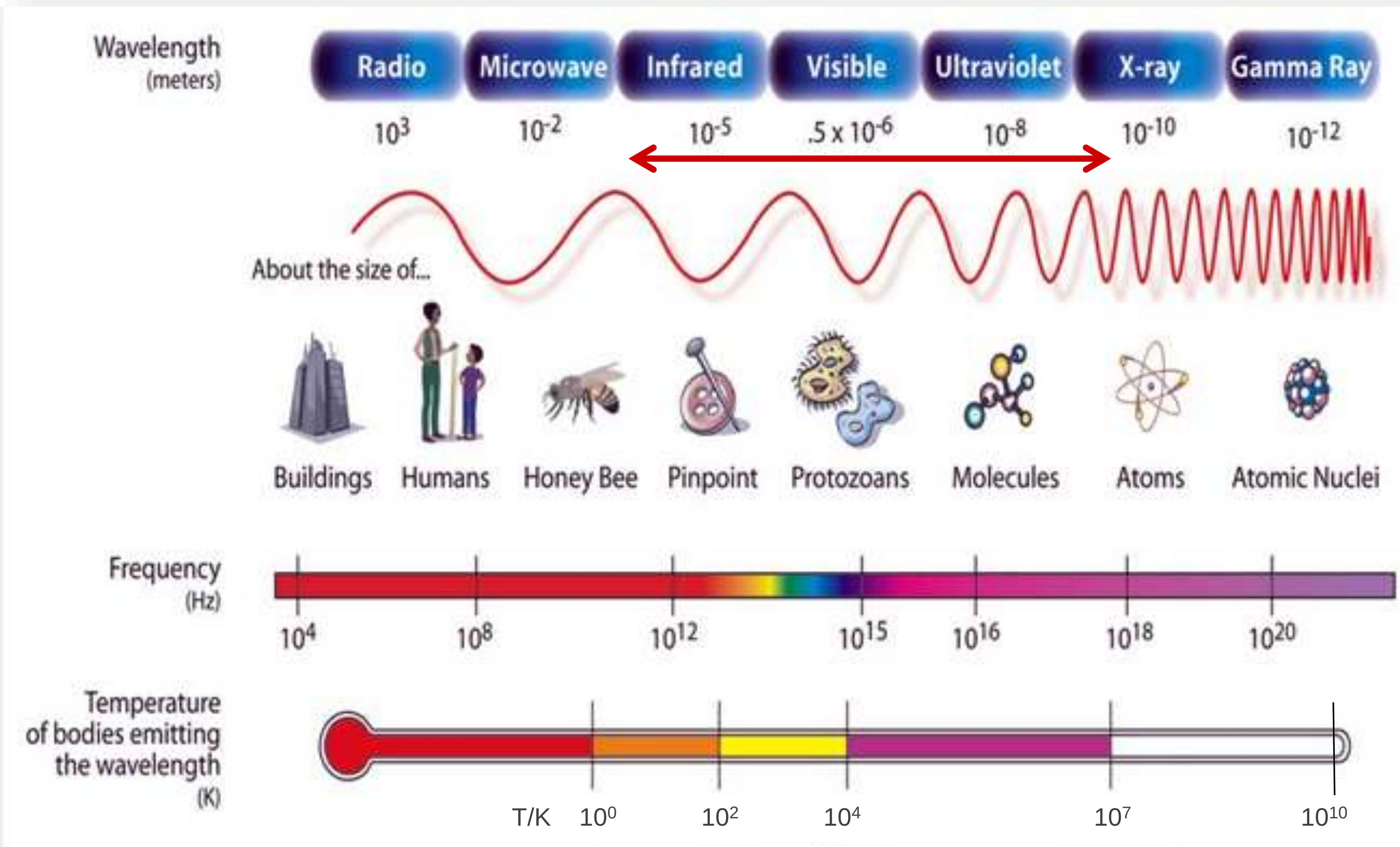
Absorption of atmospheric gas composition as function $f(\nu, \lambda)$

- *Atmospheric absorption of solar radiation → high temps (energies)*
- *Atmospheric absorption of terrestrial radiation → infrared*

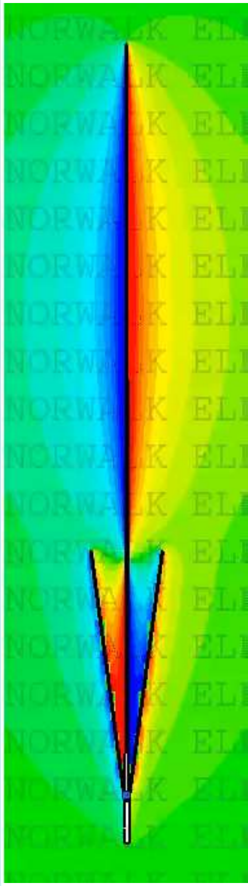
Strategy: Macroscopic absorption → atomic cross section → quantum degrees of freedom → energy spectrum → specific molecular absorption cross section for elm. radiation

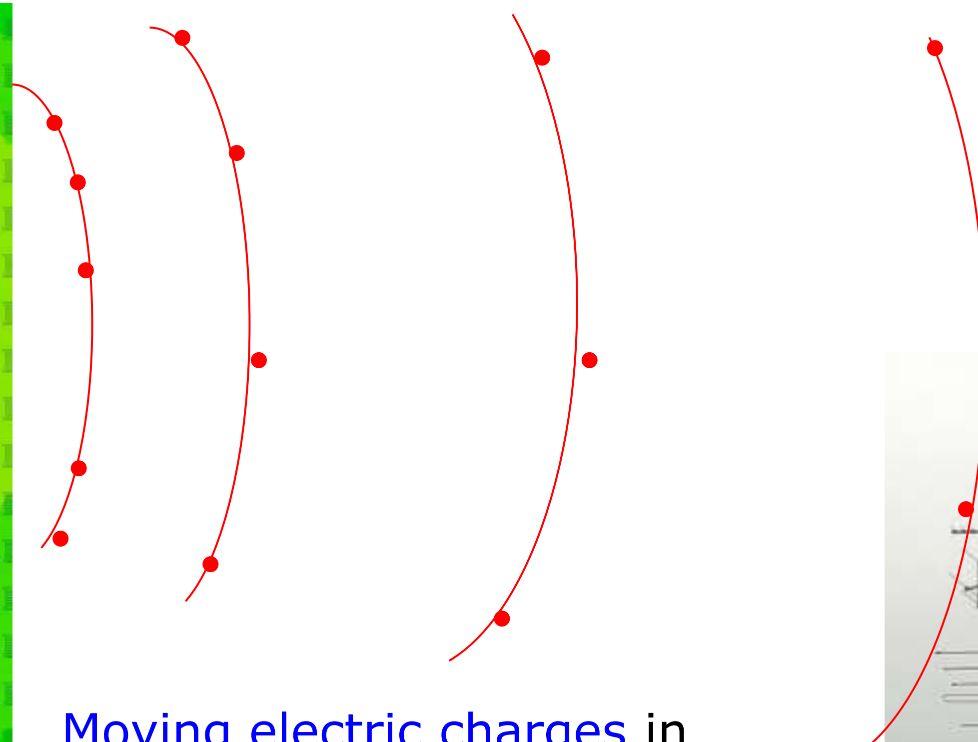
W. Udo Schröder, 2021

The Electromagnetic Spectrum Size Comparisons

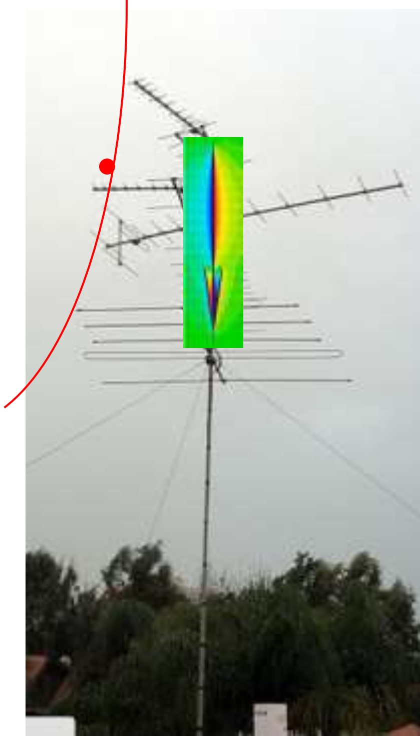


Energy Transfer by Photons





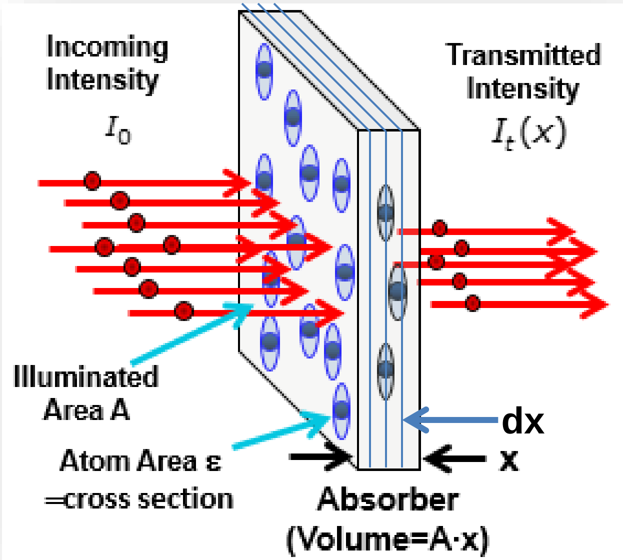
Moving electric charges in broadcast antenna emit electromagnetic radiation fields characteristic (frequency, wave length) of the electric currents



Electromagnetic waves transfer quanta (photons) which can be absorbed by electrons in a receiver antenna, causing them to move in synch with the emitter.

Absorption of elm Radiation: Beer-Lambert Law

Absorption of individual photons by individual atoms/molecules



Incoming intensity $I_0 = I(x=0)$ *blocked by* ε *per atom*

Intensity absorbed along path length $\Delta x : I \to I - \Delta I$

$$-dI = df \cdot I \quad \to df = \varepsilon \cdot \frac{N_{part}}{A} = \varepsilon \cdot \rho(x) \cdot dx$$

Probability $(=$ *fraction* $f)$ *for absorption of* dI, *change* $= - dI$

$$df = dP_{abs}(x) = \frac{-dI}{I(x)} = \mu \cdot dx \quad (\text{fraction of } I \text{ abs.})$$

$$\frac{dI(x)}{dx} = -\mu \cdot I(x) \quad \to \text{DEq for exponential}$$

Absorption of elm Radiation: Beer-Lambert Law

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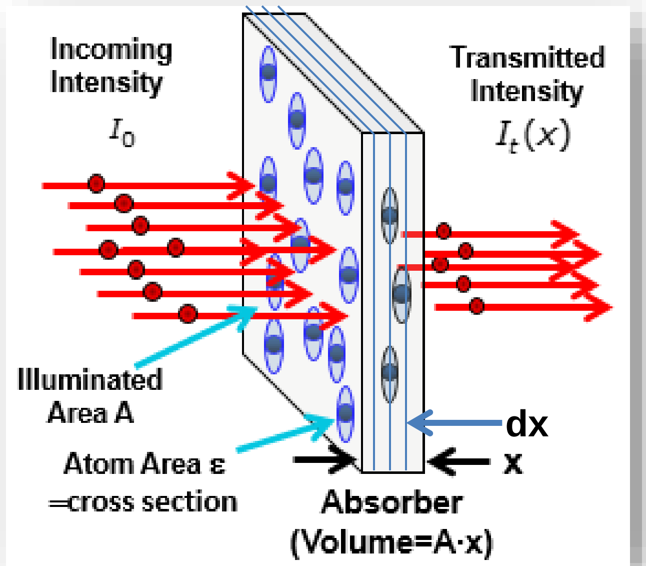

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$$\text{Transmitted}: \boxed{I_t = I(x) = I_0 \cdot e^{-\mu \cdot x}} \qquad \mu := \rho_{particle} \cdot \varepsilon$$

cm

$\# part/cm^3$

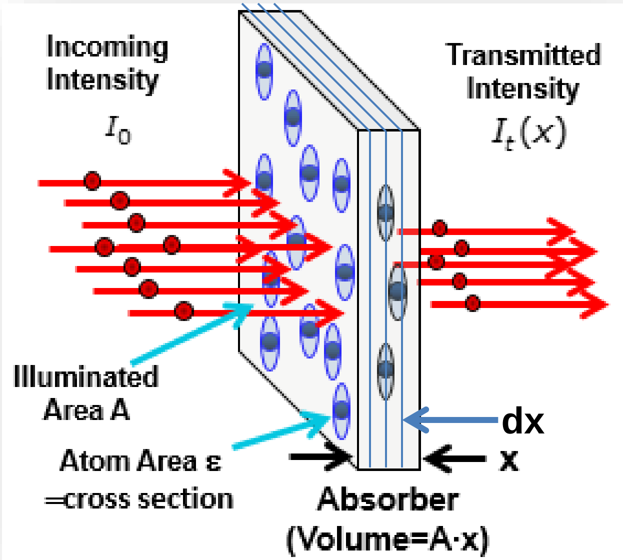
cm^2

Atomic Cross Section

$$\text{Absorbed}: \boxed{I_a = I_0 - I(x) = I_0\left(1 - e^{-\mu \cdot x}\right)}$$

Absorption of elm Radiation: Beer-Lambert Law

Absorption of individual photons by individual atoms/molecules



Incoming intensity $I_0 = I(x=0)$ blocked by ε per atom

Intensity absorbed along path length Δx : $I \rightarrow I - \Delta I$

$$-dI = df \cdot I \quad \rightarrow df = \varepsilon \cdot \frac{N_{part}}{A} = \varepsilon \cdot \rho(x) \cdot dx$$

Probability (= fraction f) for absorption of dI, change $= -dI$

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cm   # part/cm³   cm²

Atomic Cross Section

Absorbed : $\boxed{I_a = I_0 - I(x) = I_0\left(1 - e^{-\mu \cdot x}\right)}$

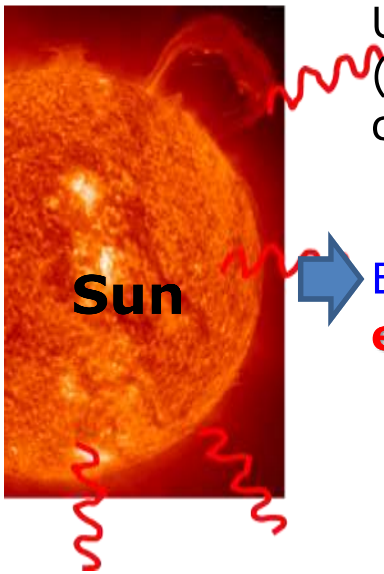
Can use base ***10*** instead of base ***e=2.718….*** Customary: use $\log_{10}$ instead of ***ℓn***.

$\rightarrow$ Transmittance : $-Log_{10}\left(\frac{I_t}{I_0}\right) = \mu \cdot x = \varepsilon \cdot c \cdot x$ Units of μ and ε depend on unit of *c*.

1-f

Specific for absorber material, depends on internal structure, electric dipole moment. Otherwise, μ ≠ 0 only for ionized ideal gas.

Emission and Absorption Mechanism for Photons



Unbound electric charges such as electrons in a hot body ("blackbody") of ionized gas (e.g., Sun) **emit and absorb** continuous electromagnetic spectra.

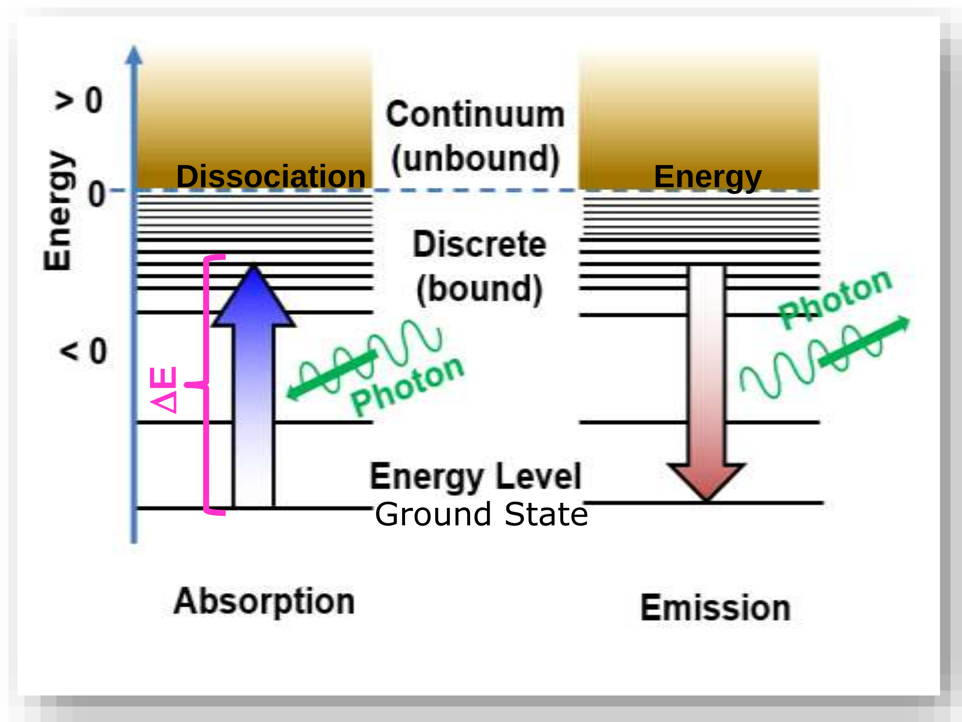
Black bodies → thermal spectrum

Bound electric charges (e.g., electrons in atoms, molecules) **emit and absorb** discrete ("line") energy (wavelength) spectra.

Energy transfer by photons in bound systems:

Absorption or emission of light occurs in transitions between discrete energy levels.

Characteristic spacing → spectr. ID



$$|\Delta E| = h\nu = hc/\lambda$$

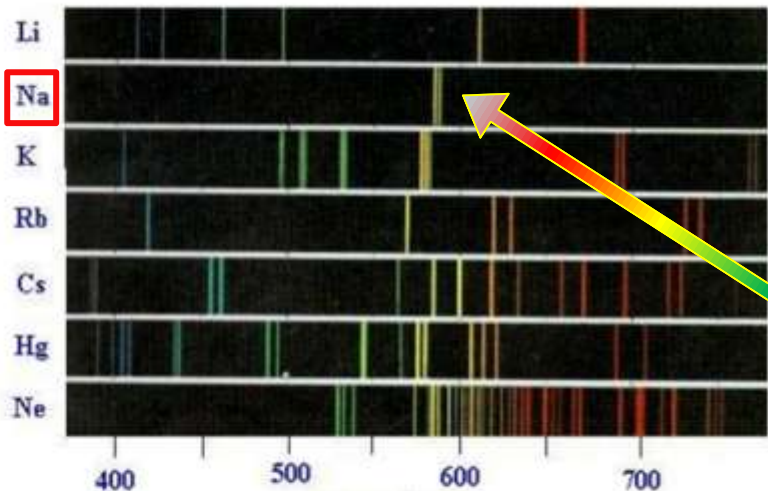
$h = 6.62606957 \times 10^{-34}\ m^2\ kg\ /\ s$

Planck's constant

Energy Spectra and Transfer Through Radiation

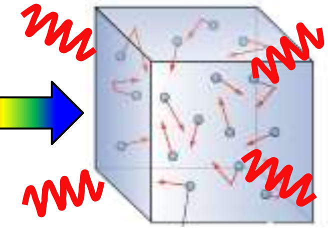
Wave length spectrum for thermal equilibrium

Wave length spectrum for atomic transitions



Wave Length λ (nm) →

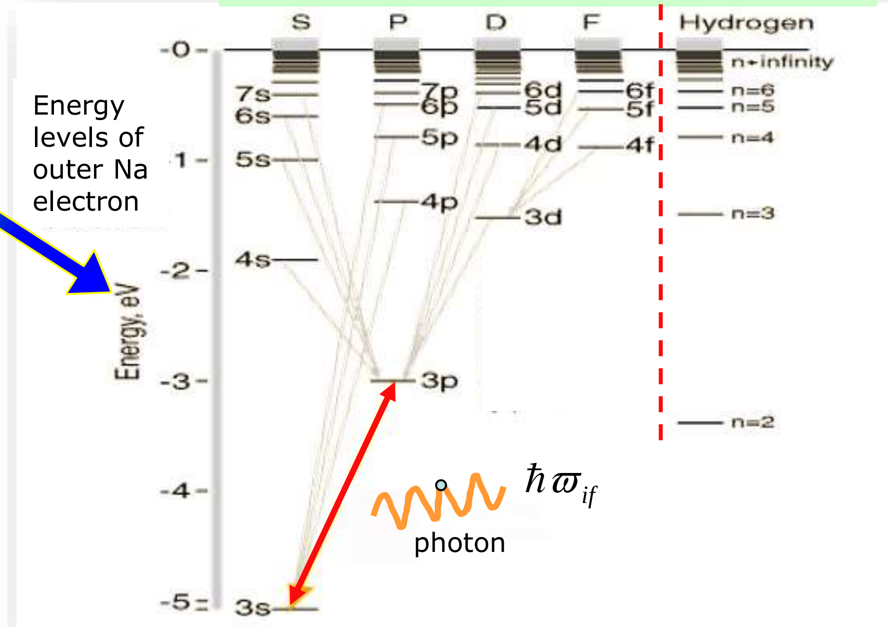
Continuous thermal spectrum. Emitted and/or absorbed by charged particles in random motion



Charged/Polarized Particles

Energy Levels of Na and H (1-electron atoms)

Energy levels of outer Na electron



$$Internal\ atomic\ /\ molecular\ energies\ are\ quantized$$

$$Transition\ between\ levels: i \rightarrow f$$

$$\Delta E_{if} = E_f - E_i = h\nu_{if} = \hbar\varpi_{if} = hc/\lambda_{if}$$

$$Planck's\ constant\ h = 6.626 \cdot 10^{-34}\ J \cdot s$$

$$\hbar = h/2\pi,\ c = 0.2998\,m/ns\ speed\ of\ light$$

1 eV = 1.602 176 53(14) × 10^{-19} J (Joule)

Energy related spectroscopic observables

ν: 2.417 989 40(21) × 10^{14} Hz

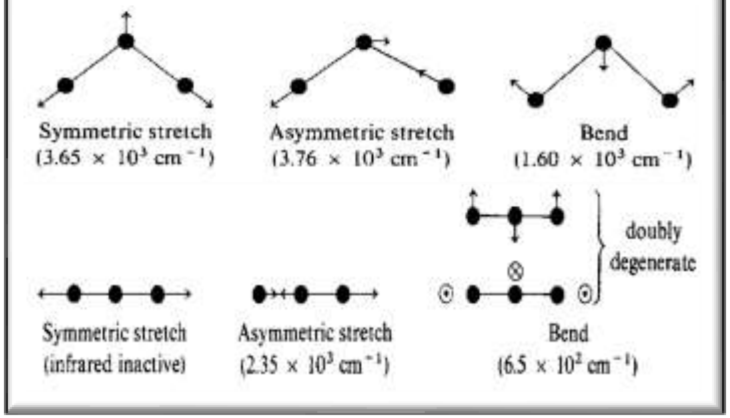
$\bar{\nu}$: 8 065.544 45(69) cm^{-1}

λ: 1 239.841 91(11) nm

T: 11 604.505(20) K (Kelvin)

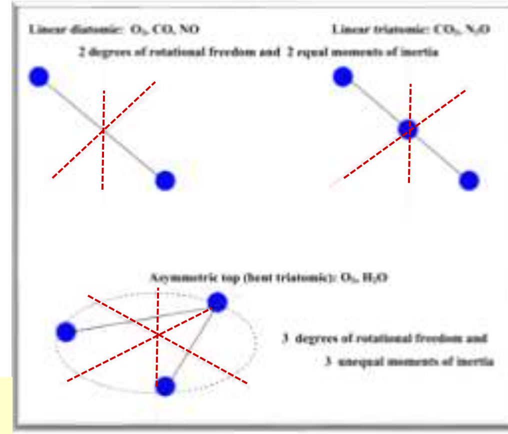
Molecular Emission/Absorption Spectroscopy

Intrinsic Harmonic Excitation Modes

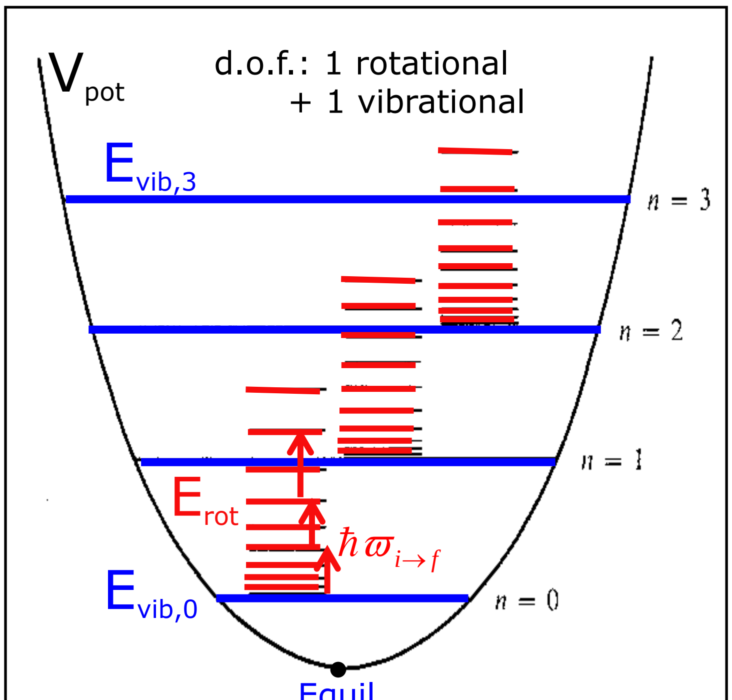


Normal degrees of freedom of motion of a 3-atomic molecule:

1) translational as a whole,
2) rotational (diff. axes),
3) vibrational (diff. modes),
4) electronic.



IR absorption if molecule has electric dipole moment



$$\boxed{E = E_{trans}(\upsilon) + E_{rot}(J_i) + E_{vib}(n) + E_{el}(\ldots)}$$

Translation energy E_{trans} has continuous "thermal" spectrum, generated by multiple collisions.
Mean energy about kT≈ 400 cm^{-1} (T =300 K), infrared (IR)
Can absorb or emit any energy amount (E conserved).
Quantized degrees of freedom absorb/emit discrete energy packages

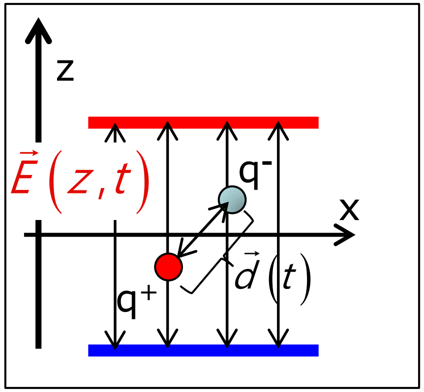
$$\boxed{\hbar\varpi_{i\to f} = \pm\left(E_f - E_i\right) \to rot - vib\ spectrum}$$

Rotational energy E_{rot} is quantized (line spectrum), typical Energies= (1-500) cm^{-1} (far-IR to microwave)

Vibrational energy E_{vib} is quantized (line spectrum): energy of vibrating nuclei about their equilibrium positions; E ~ (500 to 10^4) cm^{-1} (near-IR to far-IR)

Electronic energy E_{el} is quantized (line spectrum), typical energies (10^4-10^5) cm^{-1} (UV and visible).

Spectroscopy of CO_2



$$\textit{Molecule is electrically polarized}: \textit{dipole moment } q \cdot d$$

$$\textit{Elm radiation}: \mathcal{E}(z,t) = \mathcal{E}_0(z) \cdot e^{i\cdot\varpi\cdot t};$$

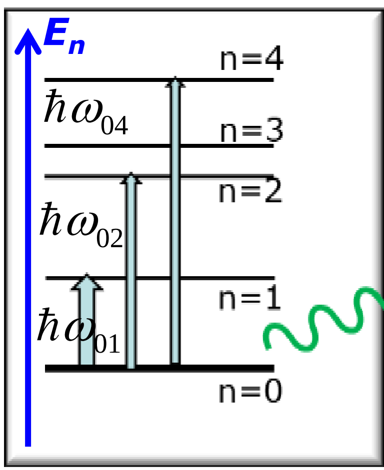
$$\textit{frequency } \varpi = 2\pi c/\lambda, \textit{ wave length } \lambda$$

$$\textit{Oscillating force on charge } q:$$

$$F(z,t) = q \cdot \mathcal{E}(z,t) = q \cdot \mathcal{E}_0(z) \cdot e^{i\cdot\varpi\cdot t}$$

→ Quantization

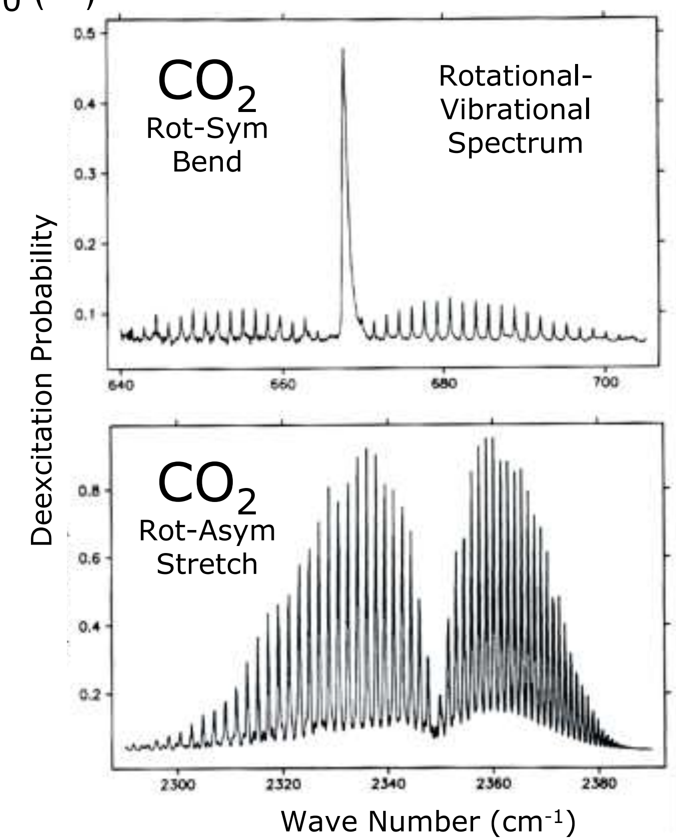
Mol. Energy Levels



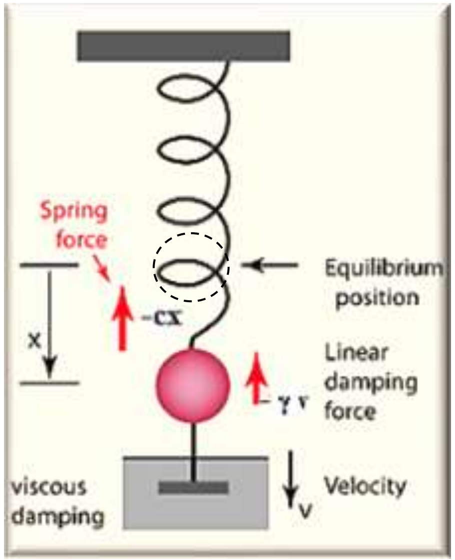
Tune ω to match transition energies $\hbar\omega_{nm}$
→ Excitation *n*→*m*.

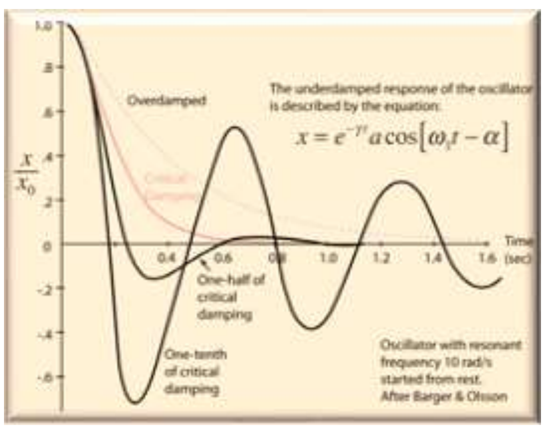
$\mathcal{E}_0 e^{i\cdot\varpi\cdot t}$

Proof of excitation emission spectrum



Energy Transfer via Collisional Relaxation





Internally rot-vib excited di/poly-atomic molecules in atmosphere suffer multiple collisions with other particles in random (thermal) motion, which act as a "viscous heat bath."

$$\langle E_i \rangle_{eq} = \frac{1}{2} k \cdot T \quad (i = 1, 2..., f)$$

$$3D \text{ translational motion } \langle E \rangle_{eq} = \langle E_x \rangle_{eq} + \langle E_y \rangle_{eq} + \langle E_z \rangle_{eq} = 3 \cdot \frac{1}{2} k \cdot T$$

Energy is transferred back and forth between all (***f***) degrees of freedom, until equi-partition

Consequently: for damped oscillation of mass m on a spring

$$Undamped: \; x_{free}(t) = x(t=0) \cdot \cos(\varpi \cdot t) \qquad \varpi = \sqrt{c/m}$$

$$Damping \; coefficient \; \gamma \rightarrow \; x(t) = x(t=0) \cdot e^{-\gamma \cdot t} \cdot \cos(\varpi \cdot t) \rightarrow \langle E(t) \rangle$$

Energy $E(t) \sim (\dot{x}(t))^2$ transfer to bath particles and back until equilibrium is attained (bath heats up).

$$\frac{d}{dt}\langle E \rangle = -\left[\langle E(t) \rangle - E_0\right] / \tau_{relax} \quad , with \; \tau_{relax} \propto \tau_{coll}$$

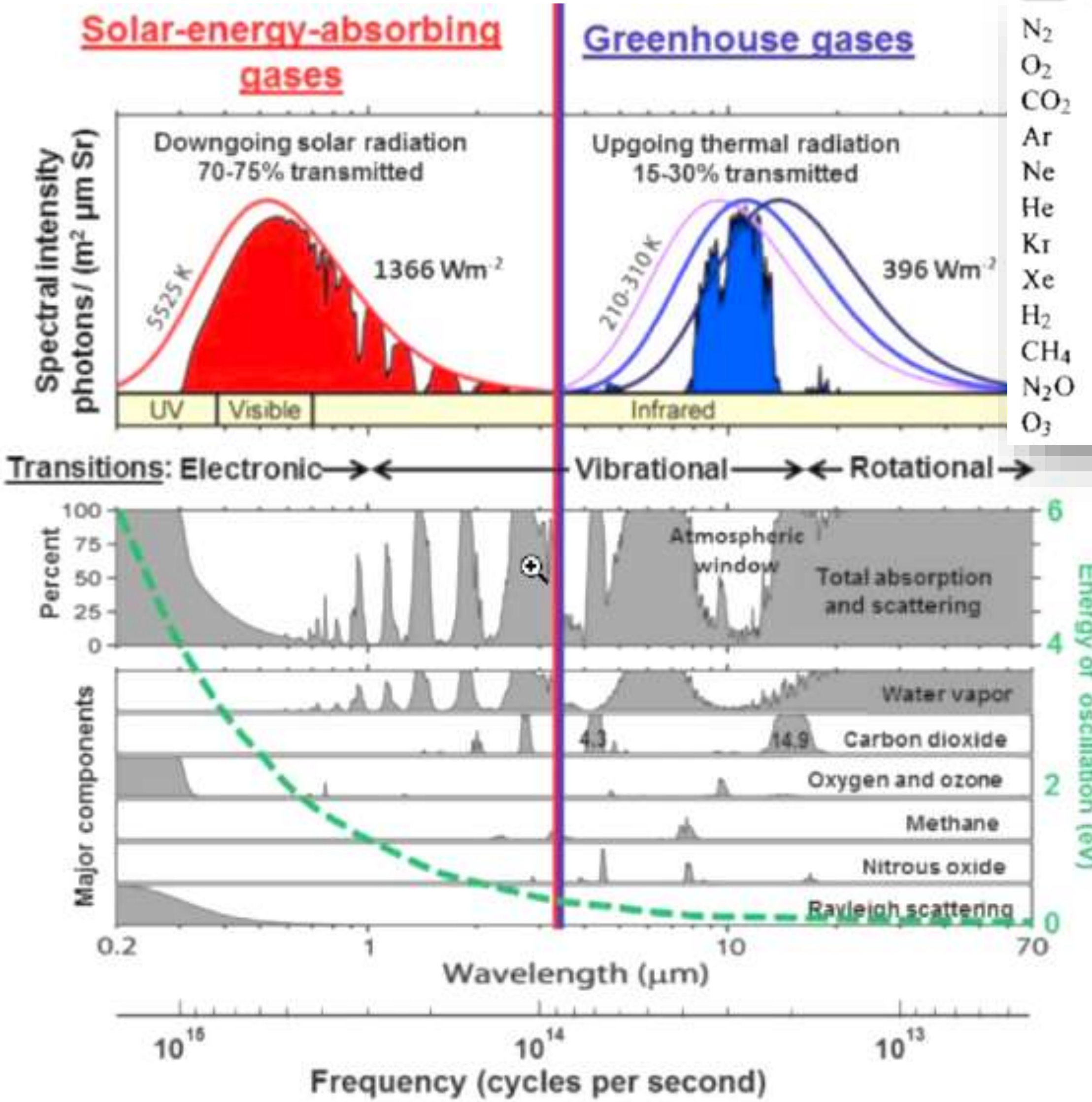
$$collision \; time \; \tau_{coll} = function(density, T)$$

$$\tau_{coll} = \frac{mean \;\; free \;\; path \;\; \lambda}{mean \;\; thermal \;\; speed} \approx \left(\frac{5 \cdot 10^{-3} cm}{p / Torr}\right) \sqrt{\frac{m}{8\pi kT}} \sim 10^{-10} s$$

Fast relaxation/ attainment of equilibrium

Internal molecular energy dissipated quickly and heats surrounding gas @ equilibrium

Selective Filter Effect of Atmosphere



N_2	78.08
O_2	20.95
CO_2	**0.041**
Ar	0.934
Ne	1.82×10^{-3}
He	5.24×10^{-4}
Kr	1.14×10^{-4}
Xe	8.7×10^{-6}
H_2	5.0×10^{-5}
CH_4	$>2.0\times10^{-4}$
N_2O	$>5.0\times10^{-5}$
O_3	$\sim4.0\times10^{-6}$

Mean composition of dry air and absorption spectra for GHG.

$0\% \leq [H_2O] \leq 0.4\%$,

GHG concentrations rising during past century.

Adapted from F.W. Taylor, *ECP*.

Scattered or absorbed radiation energy is not available for warming Earth surface. → $T_E < 255K$

Radiation within the "Atmospheric Window" $\Delta\lambda$ is not absorbed by atmosphere → emitted directly into space. Specific Greenhouse gases may absorb in $\Delta\lambda$ and reflect radiation back to Earth surface→ "warming potential"

https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6174548/

Tutorial

End
Interaction of elm Radiation
With Matter I