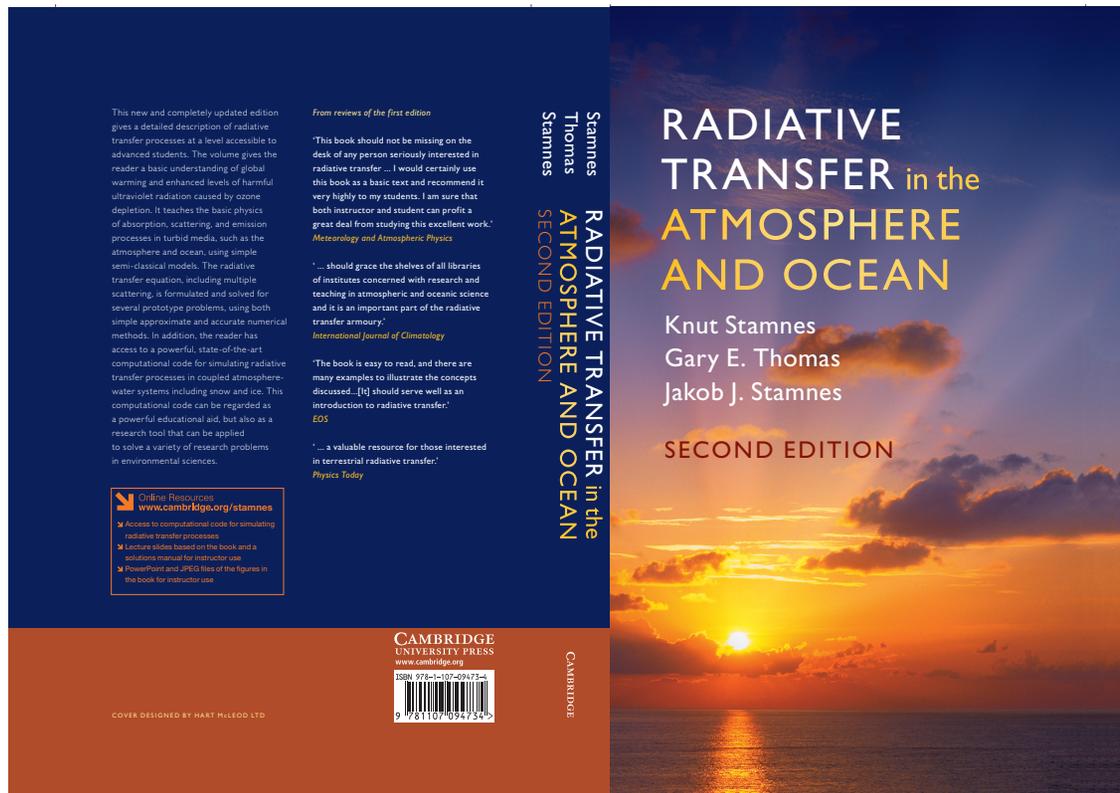


Lecture Notes: Basic Absorption Processes – I



Based on Chapter 4 in K. Stamnes, G. E. Thomas, and J. J. Stamnes, Radiative Transfer in the Atmosphere and Ocean, Cambridge University Press, 2017.

K. Stamnes, G. E. Thomas, and J. J. Stamnes • STS-RT_ATM_OCN-CUP • April 2017

Absorption by Solid, Aqueous, and Gaseous Media (1)

Absorption by particles causes the incident radiation to be further weakened (in addition to scattering) by losses within the particles themselves:

- the net effect of scattering and absorption is called attenuation or extinction.

Absorption is inherently a quantum process resulting from the fact that matter contains energy levels that can be excited by the absorption of radiation:

- A transition from an initial quantum state to a higher-energy state is highly dependent on the frequency or energy of the incident light.

If photon energy is close to the energy difference between initial and final state:

- the atoms and light are said to be in **resonance**, and absorption is high.

Conversely, if the photon energy is NOT close to the transition energy:

- absorption is often much weaker than scattering, and is not easily measurable.
- **This energy selectivity is the outstanding characteristic of absorption.**

Absorption by Solid, Aqueous, and Gaseous Media (2)

Selective absorption leads to very complex molecular absorption spectra:

- The resonances are usually very sharp, and because of the many modes of excitation of molecules, there may exist tens to hundreds of thousands of discrete absorption lines in polyatomic molecular spectra.

The dominant characteristic of such spectra is:

- the presence of **broad spectral features called molecular absorption bands**, in which lines are clustered closely in frequency groups. Under low resolution these bands appear to be continuous functions of frequency.

Figure 1 shows the computed transmittance* spectrum of air, including the separate contributions from molecules (Rayleigh scattering and near-IR absorption by water vapor and molecular oxygen) and aerosol scattering.

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*The transmittance is the ratio between the computed irradiance and the extraterrestrial solar irradiance.

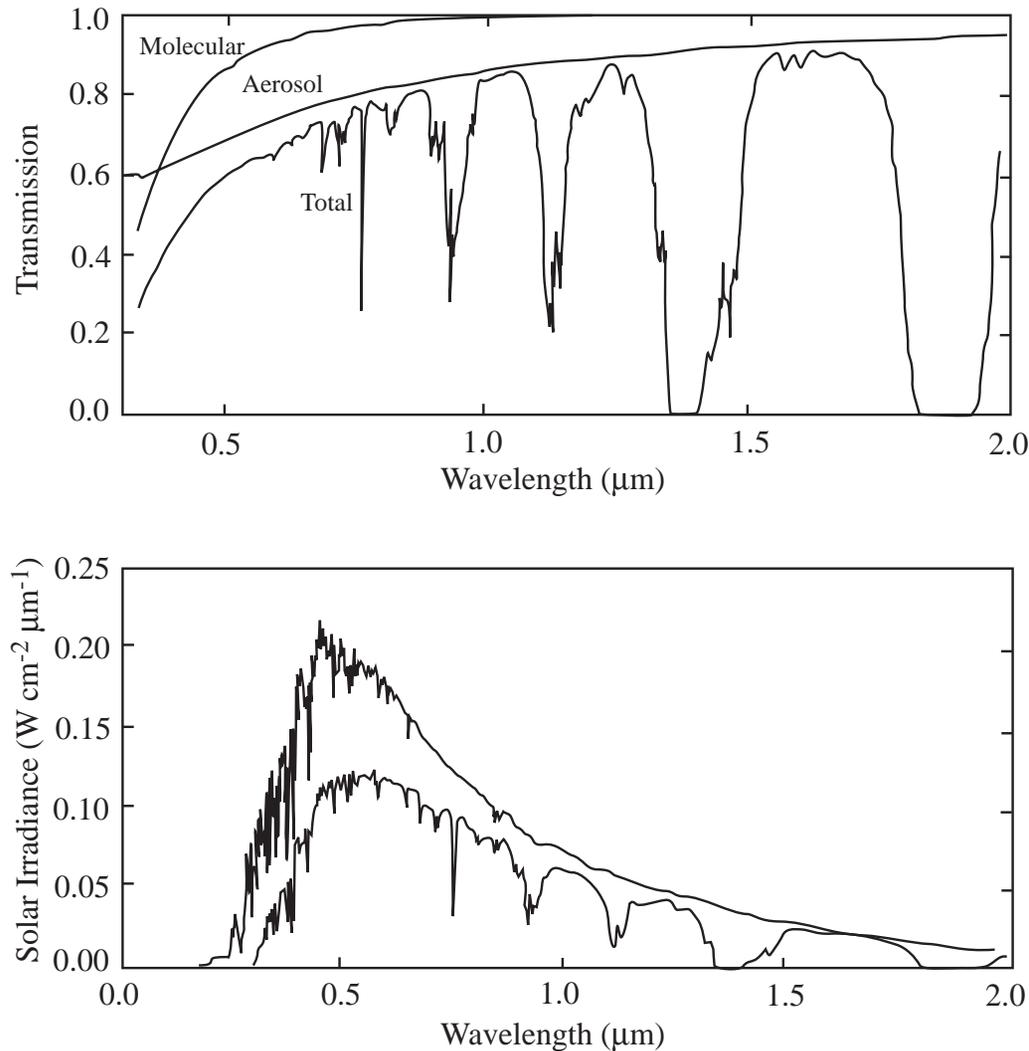


Figure 1: **Upper panel:** Computed low-resolution transmittance spectrum from three atmospheric components: molecular scattering, aerosol scattering, and molecular absorption. The atmospheric absorption bands are mainly due to IR absorption by H₂O. **Lower panel:** The upper curve is the extraterrestrial solar irradiance outside the atmosphere. The lower curve is the solar irradiance observed vertically through the (clear) atmosphere.

Absorption by Solid, Aqueous, and Gaseous Media (3)

We mainly consider radiative processes which occur in:

- the solar near infrared or **near-IR** ($1 \leq \lambda \leq 3 \mu\text{m}$) and
- the thermal infrared or **IR** ($\lambda \geq 3 \mu\text{m}$).

In these IR spectral ranges, in contrast to the visible:

- extinction is dominated by absorption due to the multitude of quantum states that become accessible to low-energy photons.

IR radiative transfer occurs as a series of emissions and absorptions:

- the temperature of the medium plays a vital role in the IR, because:
- in the high density media of interest to us, it controls the rate of emission through Kirchhoff's Law (Chapter 5).
- **We briefly consider:** absorption in the UV and visible, which involves not only rotation and vibration, but also electronic excitation.

Absorption on Surfaces, Aerosols, and within Aqueous Media (4)

The general physical consequence of light absorption is the deposition of energy in the medium. If light absorption leads to excitation of a **bound** excited state:

- the energy of the excited state is usually promptly converted into thermal energy, by means of a collision with a neighboring gas molecule, or
- for a solid or liquid, by a dissipation of the energy through vibrations of the surrounding lattice, or fluid cluster.

Alternatively:

- the chemical energy of the medium may be altered. Because of its increased reactivity:
- an individual excited molecule may participate in a so-called photo-induced or **photochemical reaction** with its neighbors.

Absorption on Surfaces, Aerosols, and within Aqueous Media (5)

At higher photon energies (in the UV and at shorter wavelengths) the excited molecular state may be **unbound**:

- the kinetic energy of the resultant atomic (or molecular) fragment, is not quantized, but is a continuous function of the incident photon energy.
- This process of **photodissociation** is important for the photochemistry (*e.g.* ozone formation) and heating of the Earth's middle atmosphere.

At still higher photon energies:

- the absorption into an unbound electronic state may cause an electron to be removed from its parent molecule, leaving behind a positively charged **ion**.
- This absorption into an unbound electronic state – called **photoionization** – is the basic mechanism giving rise to the ionosphere, and
- it accounts for the existence of free electrons whenever high-energy radiation is present.

Absorption on Surfaces, Aerosols, and within Aqueous Media: **SOLIDS** (6)

Absorption, reflection and transmission properties of solids vary with frequency in a complex fashion. They may:

- vary smoothly with frequency, or
- **sharply change** in the neighborhood of **resonances**,

where the absorbed energy coincides with energy differences between various types of quantized states of the solid.

Consider first the high energy process whereby:

- an electron is transferred from a lower energy state into an unoccupied higher energy state.
- Many such states cluster together in “bands”, so that we speak of a transition involving two bands.

Absorption on Surfaces, Aerosols, and within Aqueous Media: **SOLIDS** (7)

We distinguish between **conductors** and insulators:

- **Conductors** (metals) have incompletely-filled bands, or bands which overlap in energy with adjacent unoccupied bands: The availability of nearby unoccupied energy levels makes it possible for low energy photons to be absorbed;
- **Insulators** (such as water and most soil minerals) have well-separated bands, such that the low-energy bands are filled, and the upper energy bands are unfilled: Only photons with energy greater than the “band-gap” may be absorbed.

Generally speaking:

- **conductors** are highly absorbing and reflecting in the visible and IR, whereas
- **insulators** are more or less transparent over this spectral range, becoming absorbing in the UV.

Example 4.1: Color and Brightness of an Object (8)

The overlapping of numerous absorption lines in solids does not mean that broad spectral absorption features, absorption “edges”, etc. are absent. In fact:

- it is this selectivity that is responsible for nearly all **color** of objects in our natural environment.
- Objects are red because of their selective absorption of blue light.

An exception to this general rule is:

- Rayleigh scattering, which is responsible for the blue color of clear skies, oceans, blue-jay feathers, and the eyes of new-born infants. Scattering contributes to the perception of the texture, sheen etc. of objects, but it is:
- the selective removal of various wavelengths that gives objects their characteristic appearance. Most other **BLUE** colors are due to selective absorption of red and yellow light by various absorbing pigments.

Absorption on Surfaces, Aerosols, and within Aqueous Media: **SOLIDS** (9)

In the thermal IR:

- absorption causes excitation of lattice vibrations (**phonons**), molecular vibrational states, and so-called
- intermolecular vibrations, associated with collective interactions between molecules, that depend sensitively on the density and phase of the material.

For so-called **polar substances**, materials consisting of molecules which have a permanent electric dipole moment (such as water):

- the oscillating electric field tends to align the dipoles. In the microwave:

collisional (**Debye**) **relaxation** of the water molecules tends to convert the absorbed energy of alignment into heat, and is responsible for

- intense absorption of microwave energy by liquid water.

Absorption on Surfaces, Aerosols, and within Aqueous Media: **SOLIDS** (10)

Because the damping effects are much less significant in water ice:

- radar backscatter cross sections depend sensitively upon whether the particles are raindrops or hailstones.

Most laboratory results for the reflectance, transmittance and absorbance of solids

- apply only to “smooth” (polished) surfaces, BUT

Most natural surfaces are irregular over many size scales:

- laboratory results are not immediately applicable.

Determination of the boundary properties of a rough surface, or of small suspended particles, requires:

- a more fundamental knowledge of the bulk properties of a substance, embodied in the **optical constants**, the real (m_r) and imaginary (m_i) refractive indices.

Absorption on Surfaces, Aerosols, and within Aqueous Media: **SOLIDS** (11)

For a plane wave propagating in an infinite dielectric medium:

- m_i determines the absorption coefficient α through the dispersion relation

$$\alpha = 2\pi m_i / \lambda.$$

How are the optical constants (they are not actually constants, since they vary with frequency) determined? Typically this determination might involve:

- working backwards from measurements of transmittance and reflectance of a thin sample, via **Fresnel's equations (Appendix D)**.

Given the optical constants, it is possible to determine through theory:

- the scattering and absorptive properties of polished pure solids.

Since most natural substances are irregular and of mixed composition:

- it is usually necessary to perform experiments on the bulk samples.

Absorption on Surfaces, Aerosols, and within Aqueous Media: **AEROSOLS** (12)

What happens to the optical properties when the material is finely divided into small particles?

- If the particles are large compared to the wavelength of light, then geometrical optics will apply: may use raytracing techniques to derive the optical properties.
- If the particle dimensions are smaller than several hundred wavelengths, the concepts of transmittance, reflectance, and absorptance are not useful: Must deal with the properties of dispersed matter: **absorption and scattering coefficients**.

Radiation that penetrates the particles undergoes interference effects which depend sensitively upon the size and shape of the particles:

- Interference can affect both the absorption and scattering in very different ways than in the bulk state.
- But are the bulk optical constants still relevant to small particles?

Absorption on Surfaces, Aerosols, and within Aqueous Media: **AEROSOLS** (13)

Experience shows that:

- the same bulk optical constants (m_r and m_i) apply down to the smallest (0.1 μm radius) particles of practical interest to us.

Provided aerosol particles are homogeneous, spherical, and of known composition:

- their absorption and scattering coefficients can be determined by solving a classical boundary-value problem.

With the advent of fast computers:

- numerical solutions for other idealized shapes, such as spheroids have become possible. Also, approximate techniques, such as the **discrete-dipole method**, have been developed to handle arbitrarily-shaped particles.
- Thus, given an ensemble of independently scattering and absorbing particles, of known shapes, sizes and optical constants (refractive indices), it is possible, at least *in principle*, to compute the scattering and absorption coefficients.

Absorption on Surfaces, Aerosols, and within Aqueous Media: LIQUIDS (14)

Absorption in pure liquids result from the mutual interactions between the inter-molecular forces. The results of this added complexity are:

1. it is very difficult to calculate from first principles the quantitative details of the transitions (such as absorption line strengths and band frequency positions): Laboratory and/or *in situ* measurements of absorption spectra are essential;
2. the number of transitions is so large that overlapping of adjacent spectral absorption lines (or bands) yields an *almost continuous absorption spectrum*: Paradoxically, their complexity causes condensed media to have a much *simpler* absorption spectrum than that of its constituent molecules;
3. radiative transfer in aquatic media has a practical advantage over that in the atmosphere: the spectral sampling interval for the aquatic radiation field can be much larger than that required in atmospheric radiation problems.

Absorption on Surfaces, Aerosols, and within Aqueous Media: **LIQUIDS** (15)

Unfortunately the above advantages are offset by the fact that:

- except for the purest waters, the optical properties of the ocean are largely governed by dissolved and suspended impurities, of both inorganic and organic origin.

The compositional variability from location to location:

- makes it difficult to create “standard” optical models, such as those used widely in atmospheric studies.

An attempt to optically classify various water types is shown in Fig. 2:

- Generally speaking, sea water is most transparent in the 400 – 600 nm region.

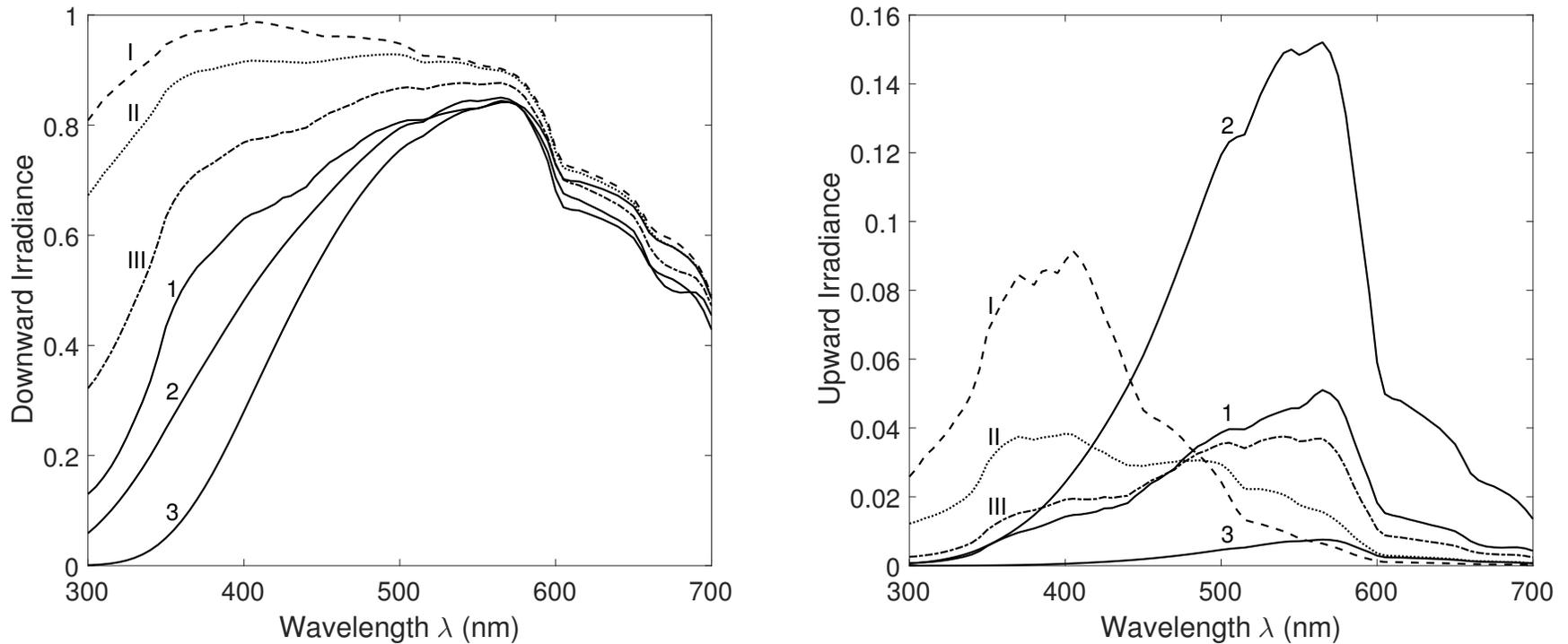


Figure 2: **Left panel:** Spectral variation of the total **downward irradiance** (normalized by the TOA irradiance) at 1 m depth in deep ocean water. **The curves labeled I, II, and III** refer to **open ocean water** with CHL-a concentrations of $0.1 \text{ mg} \cdot \text{m}^{-3}$ ($\alpha_{\text{CDOM}}(443 \text{ nm}) = 0.001 \text{ m}^{-1}$), $1.0 \text{ mg} \cdot \text{m}^{-3}$ ($\alpha_{\text{CDOM}}(443 \text{ nm}) = 0.01 \text{ m}^{-1}$), $5.0 \text{ mg} \cdot \text{m}^{-3}$ ($\alpha_{\text{CDOM}}(443 \text{ nm}) = 0.05 \text{ m}^{-1}$), and $\text{MIN} = 0.01 \text{ g} \cdot \text{m}^{-3}$. **The curves labeled 1, 2, and 3** refer to **turbid (coastal) chlorophyll-dominated** (CHL-a = $10 \text{ mg} \cdot \text{m}^{-3}$, $\text{MIN} = 0.1 \text{ g} \cdot \text{m}^{-3}$, $\alpha_{\text{CDOM}}(443 \text{ nm}) = 0.1 \text{ m}^{-1}$), **mineral-dominated** (CHL-a = $0.5 \text{ mg} \cdot \text{m}^{-3}$, $\text{MIN} = 5.0 \text{ g} \cdot \text{m}^{-3}$, $\alpha_{\text{CDOM}}(443 \text{ nm}) = 0.1 \text{ m}^{-1}$), and **dissolved matter-dominated** (CHL-a = $0.5 \text{ mg} \cdot \text{m}^{-3}$, $\text{MIN} = 0.1 \text{ g} \cdot \text{m}^{-3}$, $\alpha_{\text{CDOM}}(443 \text{ nm}) = 0.5 \text{ m}^{-1}$) **water**, respectively. **Right panel:** Same as left panel, but for the **upward irradiance**. The computations were done using the AccuRT radiative transfer model with a spectral resolution of 5 nm (see §10.5).

Molecular Absorption in Gases (1)

Atmospheric molecules are highly selective in their ability to absorb radiation:

- This selectivity is particularly true in the thermal infrared (IR) part of the spectrum, where a large number of spectral absorption features occur.

Figure 3 shows synthetic IR atmospheric radiance along a vertical path looking down at the surface from several altitudes.

- The surface emits thermal radiation (dashed curve) approximately like a black-body with a maximum near $10 \mu\text{m}$.
- The solid lines show upward spectral radiances at moderate spectral resolution ($0.1 \mu\text{m}$, or $\approx 2 \text{ cm}^{-1}$) computed under different assumptions:
- LEFT PANELS: To delineate the effect of absorption on the transmitted radiation field, the atmospheric emission was not included. Note that:
- highly opaque regions exist side-by-side with transparent regions: These **molecular bands** exist where the excitation energies coincide with those of various normal modes of molecular vibration.

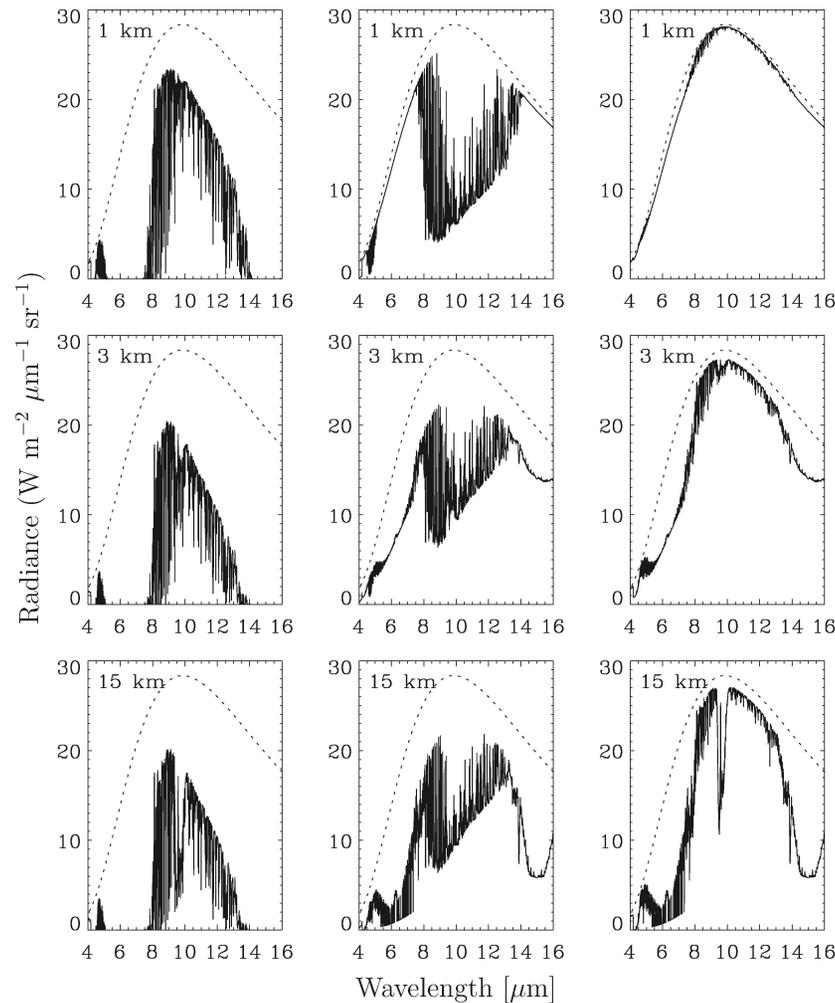


Figure 3: **Clear-sky upward spectral radiance for a vertical path from sea level to 1, 3, and 15 km computed with MODTRAN. Dashed line: Blackbody curve for surface temperature of 294 K. Left panels: Atmospheric emission ignored. Middle panels: Same as left panels, but for atmospheric emission only (no surface emission). Right panels: Same as left panels, but for emission from both surface and atmosphere.**

Molecular Absorption in Gases (2)

- **MIDDLE PANELS:** Here we show the synthetic spectrum computed in the same way, except that we ignored the surface emission, but included the atmospheric emission. Note that:
 - the absorption features in the left panels appear as emission features, as a consequence of **Kirchhoff's Law**;
 - in the opaque region between 5 and 7 μm , and between 14 and 16 μm , the radiance in the lower atmosphere (1 km level) is close to the Planck curve.
- **RIGHT PANELS:** Here we show the total contribution to the upward radiance from both surface and atmospheric emission. Note that:
 - at high altitude (15 km level), the spectrum resembles what a downward looking sensor above the atmosphere would observe.
 - Regions of high transparency, called **spectral windows**, are very important for atmospheric remote sensing of the planetary surface: The 10–12 μm window evident in Fig. 3 is particularly significant for cooling the Earth's surface.

Molecular Absorption in Gases (3)

At higher spectral resolution, molecular bands reveal their underlying structure – that of closely-spaced lines. Figure 4 shows:

- a small portion of the transmittance in the strong $15\ \mu\text{m}$ band of CO_2 measured by a Michelson interferometer on board the Space Shuttle Challenger in 1985.
- The transmittance is the ratio of the irradiance, measured along a line of sight through the atmosphere, to the extraterrestrial solar irradiance.
- Each absorption line corresponds to a transition between two quantum states of a specific molecule.
- The frequency of each transition is a unique “fingerprint” of the particular species. Under still higher resolution (see Fig. 5), an individual line has a finite spectral width.
- At altitudes below about 50 km in the Earth’s atmosphere, both the strength of the line and its spectral width depend upon atmospheric pressure and temperature.

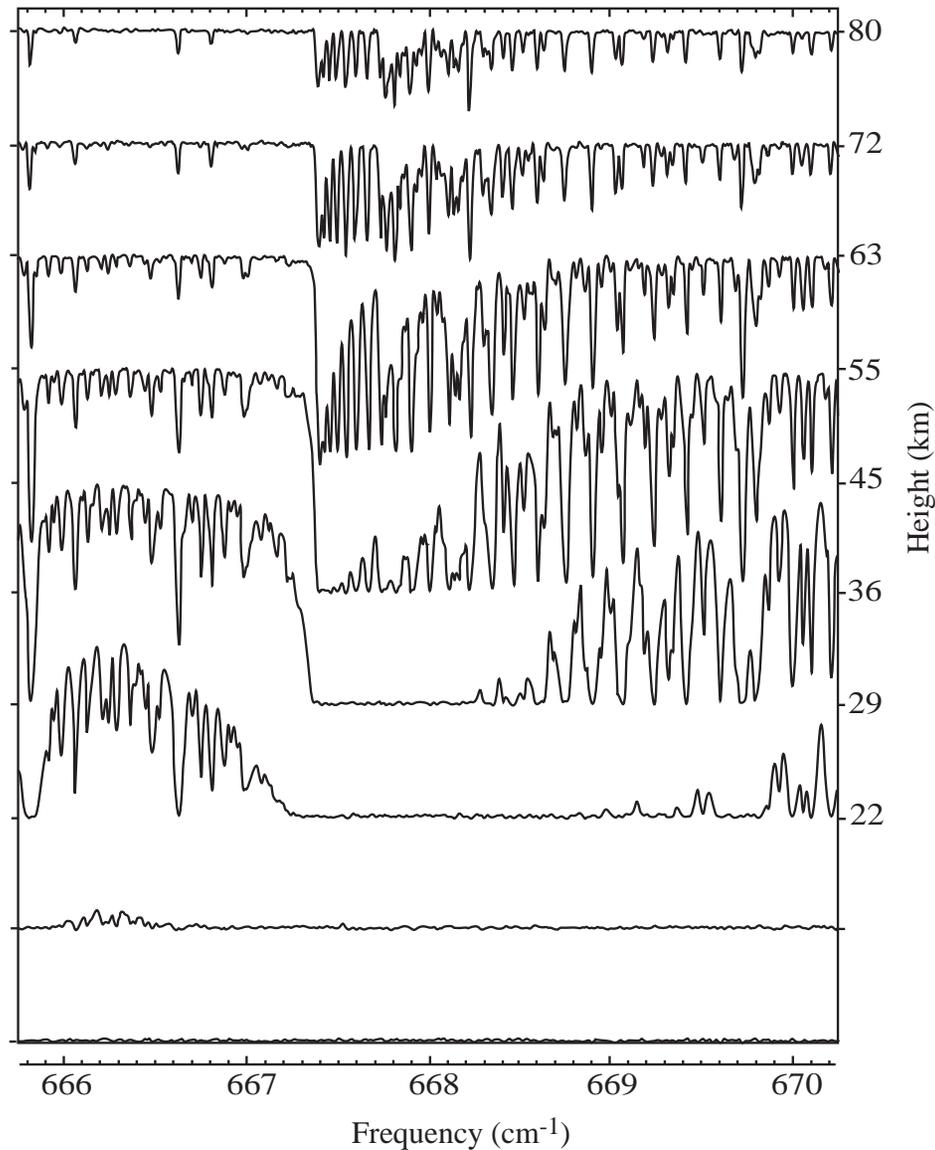


Figure 4: **High-resolution (0.01 cm^{-1}) transmittance spectrum of Earth's stratosphere and mesosphere measured by the ATMOS Michelson interferometer experiment from the NASA Space Shuttle.** Note that 666 cm^{-1} corresponds to $10,000/666 = 15 \mu\text{m}$.

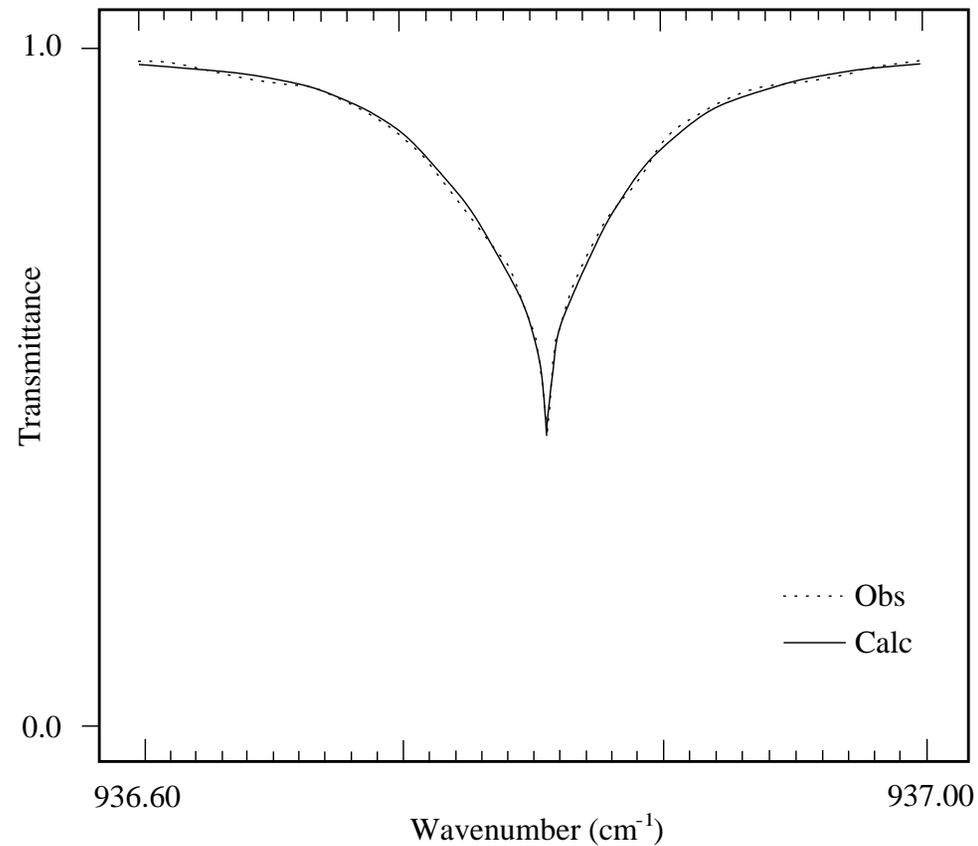


Figure 5: **Dots: Ultra-high-resolution measurement of an individual molecular absorption line of CO₂ in the 936 cm⁻¹ region from solar spectra obtained with an interferometer. Solid curve: theoretical line profile.** Note that 936 cm⁻¹ corresponds to $10,000/936 = 10.7 \mu\text{m}$.

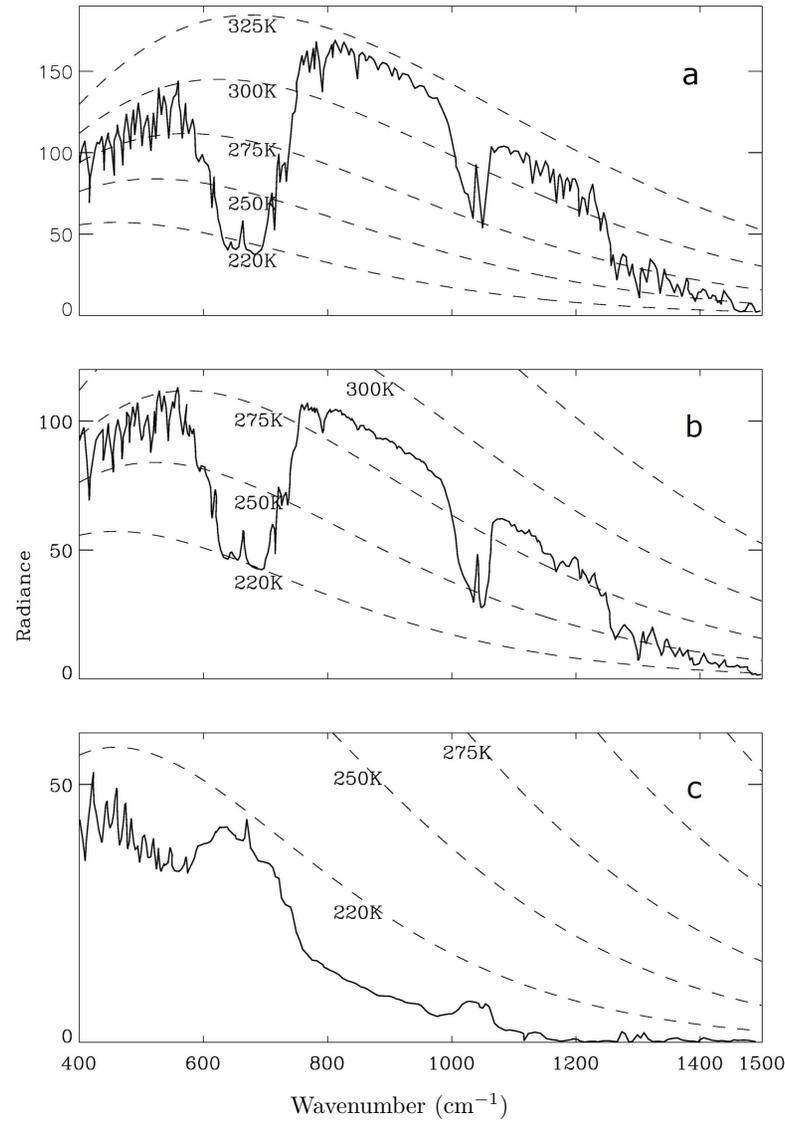


Figure 6: **Thermal emission spectra of the Earth measured by the IRIS Michelson interferometer in the *Nimbus 4* spacecraft. Also shown are radiances of blackbodies at several temperatures. (a) Sahara region; (b) Mediterranean; (c) Antarctic.**

Molecular Absorption in Gases (4)

The effect of windows is evident in Fig. 6, which shows the emission spectrum of the Earth measured by a high-resolution interferometer from an orbiting spacecraft.

- In the high transparency regions, the Earth's surface emission is evident. The contribution of the upwelling atmospheric radiation occurs within the opaque bands, at an effective temperature lower than that of the surface.
- The emitted radiance is reduced in the regions of high opacity, because the radiation received by the satellite instrument is emitted from the upper colder atmospheric regions, where the lines are optically thin.

Notice that in the case of the Antarctic, where the surface is colder than the atmosphere:

- more radiation is emitted from the warmer atmosphere in the vicinity of the bands, than from the surface (in the windows).

Thermal Emission and Radiation Laws (1)

Thermal emission is the inverse of absorption:

- Every particle of matter at a temperature greater than absolute zero contains excited quantum states. The spontaneous decay of these states is accompanied by the creation of radiative energy.

If only thermal emission were acting:

- all the molecules would eventually revert to their ground-state levels, and all the energy would reside in the radiation field.

Of course, in reality:

- the medium and its radiation field are continually exchanging energy by absorption and emission. For example:
- solar radiation is absorbed by a planet, with some of the energy going into thermal energy, some into mechanical energy (fluid motion) and some into chemical energy (change of state). The remainder of the absorbed energy goes into emission of thermal radiation, which is re-absorbed or lost to space.

Thermal Emission and Radiation Laws (2)

When the incoming and outgoing radiative powers are in balance:

- the planet is said to be in **planetary radiative equilibrium**. A more restricted equilibrium occurs when the amount of energy absorbed locally is equal to that emitted locally. We call this situation **radiative equilibrium**.

Other kinds of equilibria refer to the temperature and motion fields, and to the chemical composition:

- **Thermal equilibrium** occurs in a constant temperature medium. No heat flows in the absence of a temperature gradient.
- **Mechanical equilibrium** occurs when there are no net forces or stresses anywhere in the medium. Consequently there is no bulk motion of the fluid.
- **Chemical equilibrium** occurs when the rates of all chemical reactions are balanced by their inverse reactions, so that the chemical composition is fixed throughout the medium.

Thermal Emission and Radiation Laws (3)

When all these equilibria occur, we have the most general state of:

- **thermodynamic equilibrium.**

To attain this situation requires a closed system, called:

- **a blackbody cavity, or a hohlraum,**

with insulating walls completely isolating it from external influences. Planetary media, being “open” systems in the thermodynamic sense:

- would at first glance appear to be far from such an artificial condition.

However, as we shall see:

- atmospheres and oceans do share certain properties with a medium in thermodynamic equilibrium. Therefore:
- we are particularly interested in **the properties of the equilibrium radiation field**, and its interaction with matter within a **hohlraum**.

Planck's Spectral Distribution Law (4)

These properties of the equilibrium radiation field, expressed in the famous **Radiation Laws**, first established by Kirchhoff in 1860, depend only upon:

- the **temperature** of the medium and are **totally independent of the nature of the matter** occupying the **hohlraum**.

Suppose that a tiny opening is made in a containing wall of a **hohlraum**, and consider first the effect it has on incident radiation. Clearly:

- opening will completely absorb the incident radiation, because its likelihood of being reflected inside the hohlraum, and making it back out is negligibly small:
- **opening is perfectly absorbing, or “black”**.
- Radiation **escaping** enclosure through the opening will have reached thermal equilibrium with the matter inside enclosure, BUT loss of energy due to this leakage is assumed to be very small compared with the total energy.
- Radiation emanating from this “black” surface is called **blackbody radiation**.

Planck's Spectral Distribution Law (5)

Planck derived the hemispherical blackbody spectral irradiance F_ν^{BB} :

$$F_\nu^{\text{BB}} = \frac{m_r^2}{c^2} \frac{2\pi h\nu^3}{(e^{h\nu/k_B T} - 1)} \quad (1)$$

where h is Planck's constant, m_r is the real part of the refractive index, and k_B is Boltzmann's constant. Throughout the *hohlraum*:

- Radiation field is isotropic and unpolarized, and net irradiance is everywhere zero.

Approximations for F_ν^{BB} are **Wien's limit**, for high photon energies, $E_\nu = h\nu$:

$$F_\nu^{\text{BB}} \approx \frac{m_r^2}{c^2} 2\pi h\nu^3 e^{-h\nu/k_B T} \quad (h\nu/k_B T \gg 1) \quad (2)$$

and the **Rayleigh-Jeans limit**, for very low energies (useful for $\lambda > 1$ mm $\implies h\nu/k_B T \ll 1$, and thus: $e^{h\nu/k_B T} \approx 1 + h\nu/k_B T$)

$$F_\nu^{\text{BB}} \approx \frac{2\pi\nu^2 m_r^2 k_B T}{c^2} \quad (h\nu/k_B T \ll 1). \quad (3)$$

Planck's Spectral Distribution Law (6)

As a result of the isotropy, the blackbody radiance is related to the hemispherical irradiance through $F_\nu^{\text{BB}} = \pi I_\nu^{\text{BB}}$ where:

$$I_\nu^{\text{BB}} = B_\nu(T) \equiv \frac{m_r^2}{c^2} \frac{2h\nu^3}{(e^{h\nu/k_B T} - 1)}. \quad (4)$$

- $B_\nu(T)$ is called the **Planck function** (same units as radiance). The closely related function $B_\lambda(T)$ is illustrated in Fig. 7 for a range of temperatures.

Note:

- preceding equations apply separately to each polarization component of the electric field.
- We usually deal with unpolarized light, which is the **sum** of these (equal) components.
- Also: when we deal with gases we will set $m_r = 1$.

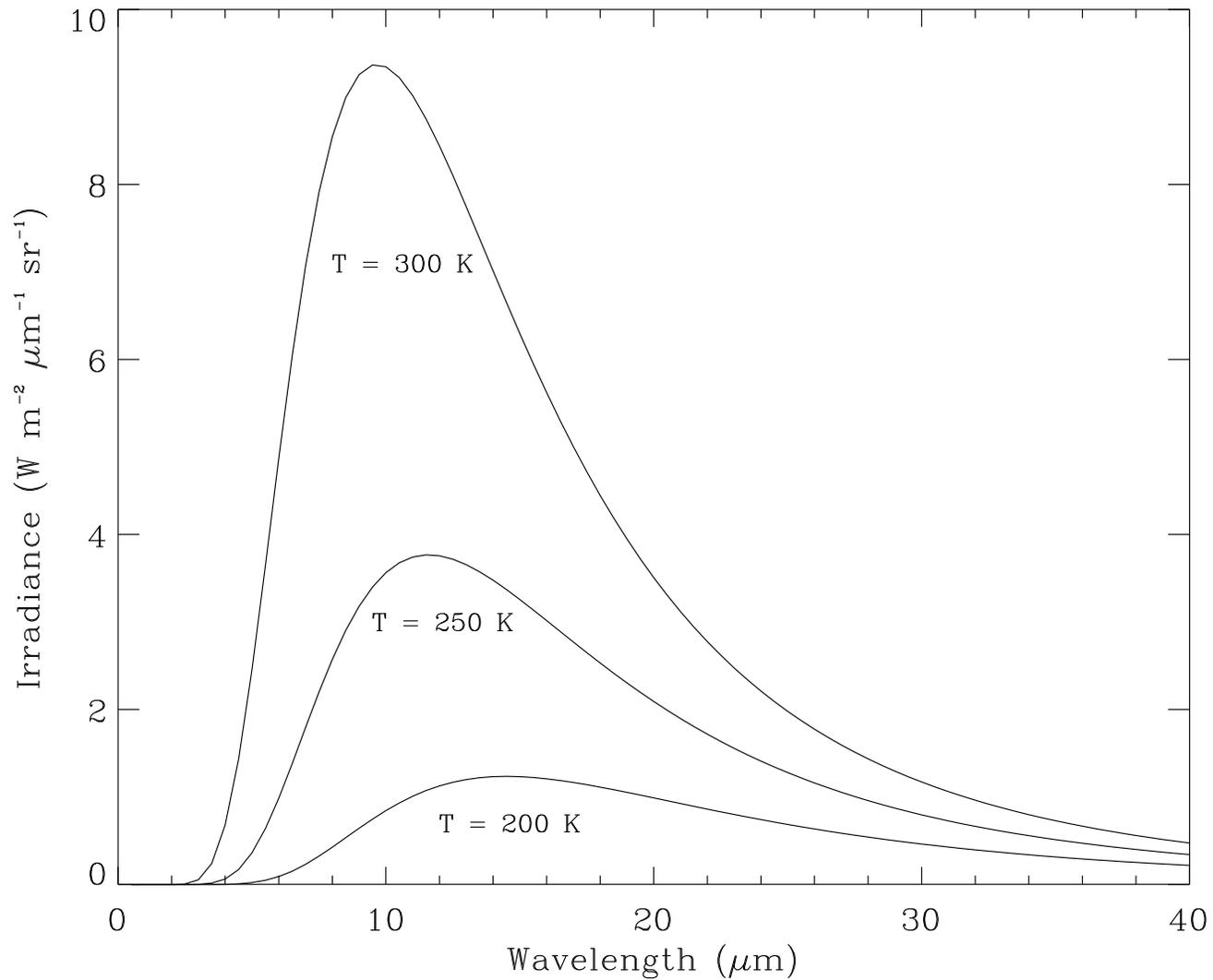


Figure 7: **The blackbody radiance B_λ versus wavelength λ . The relationship between B_ν and B_λ is $B_\lambda d|\lambda| = B_\nu d|\nu|$. Since $\lambda = c/\nu$ then $|d\nu| = (c/\lambda^2)d|\lambda|$.**

Planck's Spectral Distribution Law (7)

By differentiating the Planck function (Eq. 4), one finds that the spectral distribution of blackbody radiation has its maximum value at frequency ν_m , or wavelength λ_m , where (Wien's Displacement Law):

$$\nu_m T = 5.88 \times 10^{10} \quad [\text{Hz} \cdot \text{K}] \quad \text{or} \quad \lambda_m T = 2897.8 \quad [\mu\text{m} \cdot \text{K}]. \quad (5)$$

- **Wien's Displacement Law** states that **the wavelength of peak blackbody emission is inversely proportional to temperature.**

The frequency-integrated hemispherical irradiance leaving the hohlraum is:

$$F^{\text{BB}} = \int_0^\infty d\nu \int_{2\pi} d\omega \cos \theta I_\nu^{\text{BB}} = \pi \int_0^\infty d\nu B_\nu(T). \quad (6)$$

Substituting Eq. 4 in Eq. 6, setting $x = h\nu/k_B T$ and $m_r = 1$, we obtain the expression for the frequency-integrated emergent blackbody irradiance:

$$F^{\text{BB}} = \frac{2\pi(k_B T)^4}{h^3 c^2} \overbrace{\int_0^\infty \frac{dx x^3}{(e^x - 1)}}^{\pi^4/15} = \left(\frac{2\pi^5 k_B^4}{15 h^3 c^2} \right) T^4.$$

Planck's Spectral Distribution Law (8)

We have derived the important

Stefan-Boltzmann Law

$$F^{\text{BB}} = \sigma_{\text{B}} T^4 \quad (7)$$

where:

$$\sigma_{\text{B}} = 2\pi^5 k_{\text{B}}^4 / 15h^3 c^2 = 5.6703 \times 10^{-8} \text{ [W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}\text{]}$$

is the **Stefan-Boltzmann constant**.

Radiative Excitation Processes in Molecules: General (1)

A rigorous treatment of the interaction of matter and radiation requires both the matter and the radiation to be a fully-coupled, quantized assembly.

We use the **semi-classical theory**, in which:

- the radiation is described by the classical electromagnetic theory, whereas
- the structure of matter is specified by the quantum theory.

In the modern theory:

- the coefficients of interaction are calculated by quantum mechanical **Perturbation Theory**.

In the semi-classical theory we will continue to describe:

- the radiation field in terms of its radiance, irradiance, and energy density, and
- the “matter field” in terms of the populations of the excited states, either discrete or continuous.

Radiative Excitation Processes in Molecules: General (2)

Absorption of a photon of energy $E = h\nu$ results in excitation of a state, thus:

- reducing the population of the initial state population n_0 (normally the ground state) by one
- increasing the excited state population n_i by one.

Here n_i ($i = 1, 2, \dots$) is the number of molecules (atoms) per unit volume in the state having energy E_i . BUT:

- an excited state can **decay**, either by spontaneous or induced emission (to be described in detail later), and the reverse will happen.
- The continual exchange of energy between the matter and radiation is described in terms of rate equations for the various processes.

Radiative Excitation Processes in Molecules: General (3)

Photon-matter processes are classified in terms of three basic kinds of interactions:

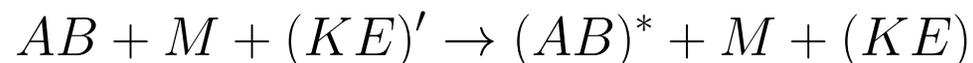
- (a) **bound-bound processes** – the exchange of energy when the initial and excited states are both **discrete states**, schematically ($E_i \rightarrow E_j$);
- (b) **bound-free processes** – transitions between **discrete** and **continuous** states, schematically ($E_i \rightarrow E_j, E_j + dE_j$); and
- (c) **free-free processes** – transitions between **two continuous** states, schematically ($E_i, E_i + dE_i \rightarrow E_j, E_j + dE_j$).

Only the bound-bound processes are important in infrared radiative transfer in planetary atmospheres.

Process (b) is important in some ultraviolet absorption processes, such as the absorption by ozone in the **Hartley bands** (200 – 300 nm), in which an oxygen atom is removed from the ozone (O_3) molecule in the process of photoabsorption.

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (4)

Let AB be a molecule with atoms A and B bound together, and M be a second molecule ('third body'). Consider the following **collisional "reaction"**:



where

- $(KE)'$ and (KE) are the sum of the kinetic energies of the reactants and products, respectively, and
- $(AB)^*$ indicates internal excitation of the AB molecule (electronic, vibration, rotation, or some combination)

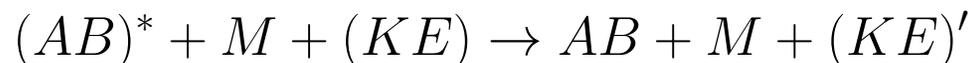
The above reaction describes:

- a **collisional excitation** of the molecule AB .

In this case, $(KE) < (KE)'$ of course, and energy is extracted from the thermal "pool", and placed into energy of excitation.

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (5)

The inverse reaction is:



which is called **collisional de-excitation**, or **collisional quenching**. The above are examples of **inelastic** collisions, in which:

- energy is transferred from kinetic to internal excitation energy, or **vice versa**.

By contrast, in an **elastic** collision:

- there is no net transfer of energy from kinetic to excitation energy;
- exchanges of momentum and kinetic energy occur, but the totals of each remain the same.

To quantify the collisional and radiative processes, we describe the **rates** at which the various reactions occur in terms of:

- **cross sections**.

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (6)

- The **collision cross section** σ is defined analogously to the radiative cross section, in terms of the differential flux of incoming **particles**.
- The change of this flux over a distance (say ds) is proportional to the product of **the flux**, and **the number of target molecules** within a cylinder of unit cross section having a length ds . The constant of proportionality is σ .
- The cross section σ depends upon the properties of incident and target molecules, as well as their relative speeds.
- If we specify that the incident molecules change their directions, but not their speeds, we get the **elastic cross section**.
- If we also specify that the molecules be deflected in a particular direction Θ (per unit solid angle), we get the **differential** elastic collision cross section:

$$\frac{d\sigma_{\text{el}}(\Theta)}{d\omega}.$$

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (7)

The total elastic cross section is given by:

$$\sigma_{\text{el}} = \int_{4\pi} d\omega \frac{d\sigma_{\text{el}}(\Theta)}{d\omega}.$$

Alternatively:

- the **inelastic cross section** σ_{in} involves a change in the molecules' internal excitation. It is important to indicate the **particular** excited state of interest, in which case we have a smaller **partial** cross section.
- The total inelastic cross section is the sum of all the partial cross sections.

Typical orders-of-magnitude of collisional cross sections are:

- Elastic cross sections are of order 10^{-19} m^2 .
- Inelastic cross sections are much smaller of order $10^{-23} - 10^{-25} \text{ m}^2$.
- This large difference will be important later on when we consider the maintenance of various thermal equilibrium distributions.

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (7b): Digression (1)

Collision Time and Scattering Cross Section

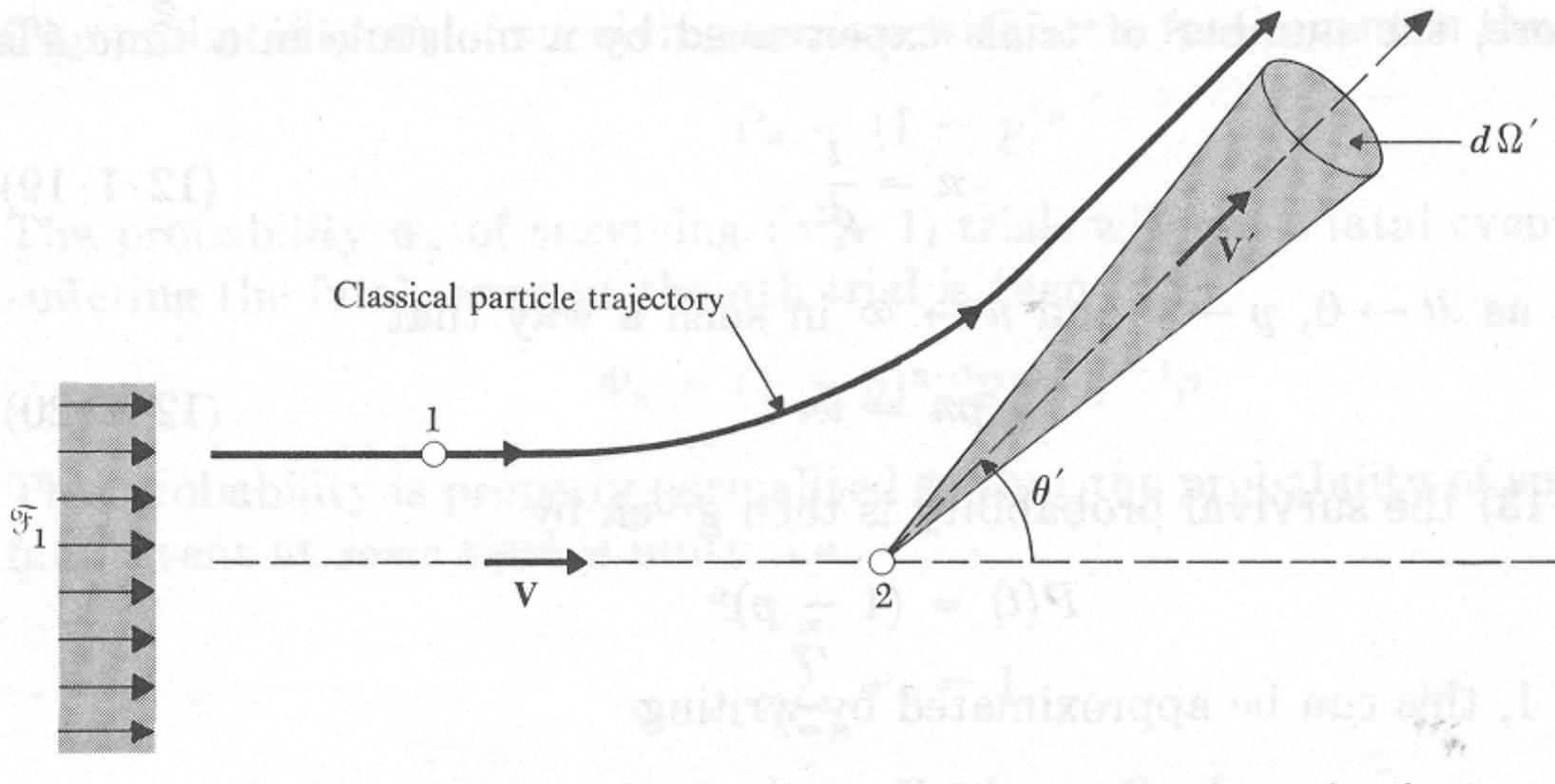


Figure 8: Scattering process viewed from the frame of reference where the target particle 2 is at rest.

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Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (7b): Digression (2)

Consider two particles of masses m_1 and m_2 , with position vectors \vec{r}_1 and \vec{r}_2 , and velocities \vec{v}_1 and \vec{v}_2 .

From a frame of reference fixed with respect to particle 2, the motion of particle 1 relative to 2 is described by:

$$\begin{aligned} \vec{R} &= \vec{r}_1 - \vec{r}_2 && \longleftarrow && \text{relative position vector} \\ \vec{V} &= \vec{v}_1 - \vec{v}_2 && \longleftarrow && \text{relative velocity vector} \\ V &= |\vec{V}| && \longleftarrow && \text{relative speed.} \end{aligned}$$

Consider a uniform flux \mathcal{F}_1 of type 1 particles per unit area per unit time incident with relative velocity \vec{V} on target particle 2. Then:

- $d\mathcal{N}$ = number of type 1 particles emerging per unit time at a large distance from the target with final velocity between \vec{V}' and $\vec{V}' + d\vec{V}'$ within solid angle $d\Omega'$ about direction $\hat{V}' \equiv \vec{V}'/|\vec{V}'|$ of the scattered beam.

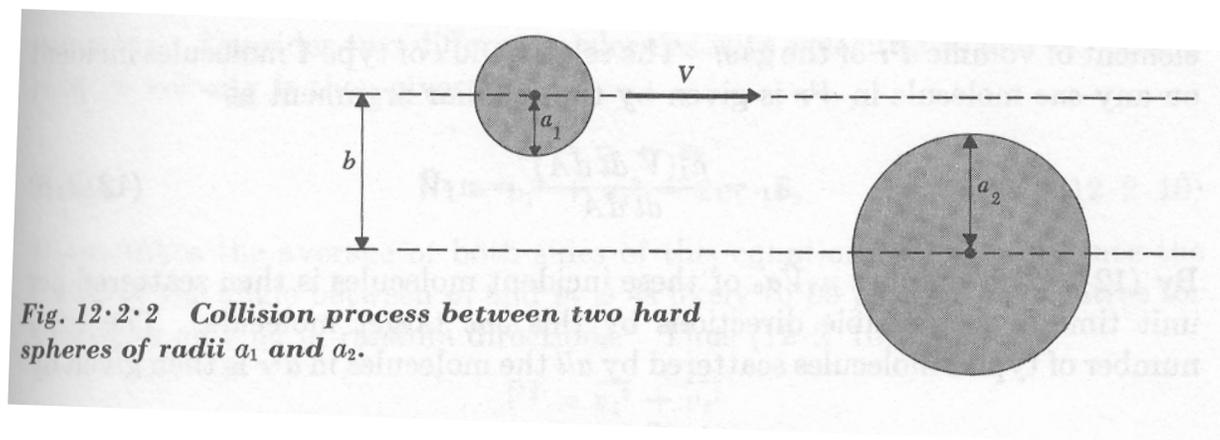
$d\mathcal{N}$ is proportional to the incident flux and the solid angle:

$$d\mathcal{N} = \mathcal{F}_1 \sigma d\Omega'$$

σ = factor of proportionality = “**differential scattering cross section**”

$\sigma = \sigma(V; \hat{V}')$ \longleftarrow depends on the magnitude of the relative speed V of the incident particle and on the direction \hat{V}' of the scattered beam relative to the incident beam.

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (7b): Digression (3)



Note: σ (dimension of area) can be computed by classical or quantum mechanics if interaction potential is known. Integration over all directions yields:

$$\mathcal{N} = \int_{\Omega'} \mathcal{F}_1 \sigma(V; \hat{V}') d\Omega' \equiv \mathcal{F}_1 \sigma_0(V) \quad (8)$$

$$= \text{total number of particles scattered, where} \quad (9)$$

$$\sigma_0(V) = \int_{\Omega'} \sigma(V; \hat{V}') d\Omega' \quad \longleftarrow \quad \text{total scattering cross section,}$$

which in general depends on relative speed V of the incident particles. For a “**hard sphere**” collision, the interaction potential is:

$$\begin{aligned} V(R) &= 0 & R &> (a_1 + a_2) \\ V(R) &\rightarrow \infty & R &< (a_1 + a_2). \end{aligned}$$

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (7b): Digression (4)

Hard sphere scattering occurs only if **impact parameter** $b < (a_1 + a_2)$. Hence, of an incident flux of \mathcal{F}_1 particles per unit area per unit time, **only** that fraction of particles incident on the circular area $\pi(a_1 + a_2)^2$ is scattered. Thus:

$$\sigma_0 = \frac{\mathcal{N}}{\mathcal{F}_1} = \pi(a_1 + a_2)^2 \quad \text{“hard sphere” cross section.}$$

For two identical spheres, $\sigma_0 = \pi d^2$ where $d = 2a$, diameter of the spherical particle.

Relation between collision time and scattering cross section

Consider a gas consisting of only a single kind of molecules. Let

n = mean number of molecules per unit volume

\bar{v} = mean speed, and \bar{V} = mean relative speed of these molecules

σ_0 = mean total scattering cross section (at relative speed V).

Focus attention on a particular type of molecule (type 1), and consider how this type is scattered by all the molecules in an element of volume $d^3\vec{r}$ of the gas. Then:

$$\mathcal{F}_1 = \frac{n_1(\bar{V} dt dA)}{dt dA} = n_1 \bar{V} =$$

relative flux of type 1 molecules incident on **any one** molecule in $d^3\vec{r}$.

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (7b): Digression (5)

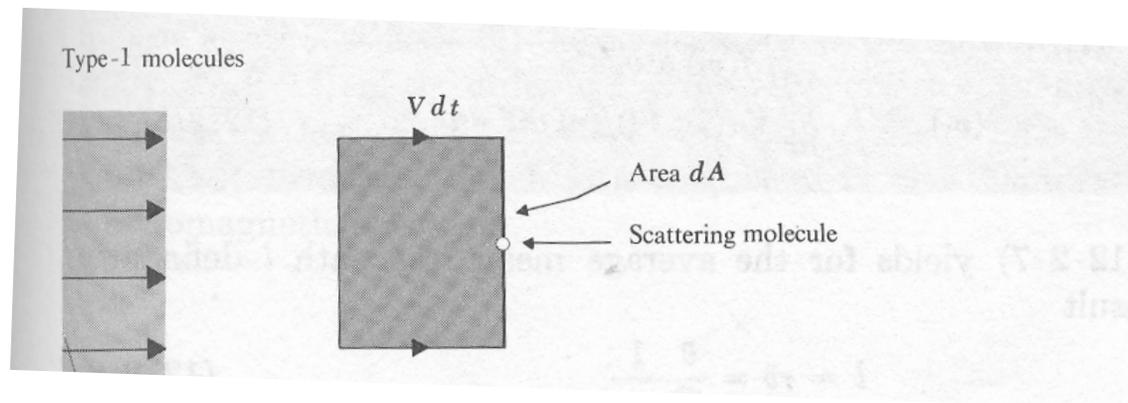


Figure 9: If there are n_1 molecules per unit volume with relative velocity near V , all of these contained in the volume $(Vdt dA)$ collide with the area dA in time dt and thus constitute a flux $n_1 V$ incident upon the scattering molecule.

But a number $\mathcal{F}_1 \sigma_0 = n_1 \bar{V} \sigma_0$ of these type 1 molecules is scattered per unit time in all possible directions **by this one target molecule**. Thus:

$$(n_1 \bar{V} \sigma_0)(n d^3 \vec{r}) =$$

total number of type 1 molecules **scattered by all** $n d^3 \vec{r}$ molecules in $d^3 \vec{r}$.

Dividing by $n_1 d^3 \vec{r}$ of type 1 molecules in the element of volume under consideration, we obtain:

$$w = \tau^{-1} \equiv \bar{V} \sigma_0 n = \text{collision probability per unit time for one molecule of type 1.}$$

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (7b): Digression (6)

The average mean free path becomes ($w = \tau^{-1} \equiv \bar{V} \sigma_0 n$):

$$l = \tau \bar{v} = \frac{\bar{v}}{\bar{V}} \frac{1}{n \sigma_0}.$$

To estimate \bar{v}/\bar{V} :

$\vec{V} = \vec{v}_1 - \vec{v}_2 \implies V^2 = v_1^2 + v_2^2 - 2\vec{v}_1 \cdot \vec{v}_2$, which upon averaging gives

$$\overline{V^2} = \overline{v_1^2} + \overline{v_2^2}$$

since $\overline{\vec{v}_1 \cdot \vec{v}_2} = 0$.

Neglecting distinction between rms and mean values (*i.e.* setting $\overline{v^2} \approx \bar{v}^2$), we have [$\bar{V} = \sqrt{\overline{v_1^2} + \overline{v_2^2}} \approx \sqrt{2}\bar{v}$ if $\bar{v}_1 = \bar{v}_2 = \bar{v}$ (identical molecules)]:

$$\bar{V} \approx \sqrt{2}\bar{v}.$$

Thus:

Mean free path:

$$l = \frac{1}{\sqrt{2} n \sigma_0}.$$

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (7b): Digression (7)

For a typical gas at room temperature (300 K) and atmospheric pressure (10^6 dynes cm^{-2}):

$$n = \frac{\bar{p}}{kT} = \frac{10^6}{(1.4 \times 10^{-16})(300)} = 2.4 \times 10^{19} \text{ molecules/cm}^3$$

$$d \approx 2 \times 10^{-8} \text{ cm (twice Bohr radius) molecular diameter.}$$

Hence:

$$\sigma_0 = \pi(2 \times 10^{-8})^2 \approx 12 \times 10^{-16} \text{ cm}^2 \text{ imply}$$
$$l = \frac{1}{\sqrt{2} n \sigma_0} = 3 \times 10^{-6} \text{ cm} \rightarrow l \gg d \implies$$

approximations based on relatively infrequent encounters between molecules are justified.

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (8)

The rate of increase of the population of excited states, $d[AB]^*/dt$, due to a particular inelastic process is defined in terms of:

- the product of the reactants, and because of the dependence on relative speeds, the sum (integral) over all possible relative speeds $v_{rel} = |\vec{v}_{AB} - \vec{v}_M|$:

$$\frac{d[AB]^*}{dt} = [AB][M] \underbrace{\int d^3 v_{rel} f_{AB}(\vec{v}_{AB}) f_M(\vec{v}_M)}_{k_{in}} \frac{d\sigma_{in}}{d\omega}. \quad (10)$$

- $[AB]$ denotes the concentration of species AB . f_{AB} and \vec{v}_{AB} are the velocity distribution and velocity of species AB , etc..

The integral is over all possible relative speeds $v_{rel} = |\vec{v}_{AB} - \vec{v}_M|$ of AB and M , *i.e.* over all relative velocities of the colliding particles, given by the *Maxwell-Boltzmann distribution* of velocities of a species of mass m in thermal equilibrium:

$$f_{MB}(\vec{v}) = \left[\frac{m}{2\pi k_B T} \right]^{3/2} \exp \left[-\frac{E_{kin}}{k_B T} \right], \quad E_{kin} = \frac{1}{2} m v^2. \quad (11)$$

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (9)

- The Maxwell-Boltzmann distribution of velocities, given by Eq. 11, is maintained by **elastic** collisions between molecules of the gas.
- Equation 10 can be written more compactly as:

$$\frac{d[AB]^*}{dt} = k_{\text{in}}[AB][M] \quad [\text{cm}^{-3} \cdot \text{s}^{-1}]. \quad (12)$$

- k_{in} is the **collisional excitation coefficient**, which can be approximated as:

$$k_{\text{in}} \approx a \left(\frac{T}{300} \right)^b e^{-c/T} \quad [\text{cm}^3 \cdot \text{s}^{-1}]. \quad (13)$$

- a is a combination of molecular constants, b is a dimensionless constant of order unity. $c \equiv \Delta E/k_B$ is called the **activation temperature** in Kelvins, ΔE is the energy of excitation, and $e^{-c/T}$ is called the **Boltzmann factor**.

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (10)

- A similar expression is obtained for the **decrease** of the excited-state populations due to collisions (collisional **quenching**):

$$\frac{d[AB]^*}{dt} = -k'_{in}[AB^*][M]. \quad (14)$$

- k'_{in} is the **quenching coefficient**, which is related to the excitation coefficient k_{in} through the *Principle of Detailed Balance*.
- The coefficients for either elastic or inelastic collisions are written in terms of the **mean molecular speed**:

$$\langle v \rangle = \int dv v F_{MB}(v) = (8k_B T / \pi m)^{1/2} \quad (15)$$

where $F_{MB}(v) = 4\pi v^2 f_{MB}(v)$, and $f_{MB}(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/k_B T}$ (see Eq. 11) is the MB distribution of speeds given by:

$$F_{MB}(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/k_B T}. \quad (16)$$

Radiative Excitation Processes in Molecules: Inelastic Collisional Processes (11)

From the units [$\text{cm}^3 \cdot \text{s}^{-1}$] of the collisional coefficient (k_{in} or k_{el}), it is clear that:

- k is just the effective volume swept out by a moving molecule per unit time.

If we imagine the other molecules to be stationary, this volume is:

- the product of the cross section and the relative speed, $\langle v \rangle$. Then:
- $k_{\text{el}} \approx \sigma_{\text{el}} \langle v \rangle$, and $k_{\text{in}} \approx \sigma_{\text{in}} \langle v \rangle$.

For $T = 300$ K, and assuming N_2 molecules as third bodies, then:

$\langle v \rangle \approx 480$ [$\text{m} \cdot \text{s}^{-1}$], $\sigma_{\text{el}} \approx 1 \times 10^{-15}$ [cm^2], and the values for the reaction rate coefficients become:

$$k_{\text{el}} \approx 5 \times 10^{-11} (T/300)^{1/2}; \quad k_{\text{in}} \approx 5 \times 10^{-15} - 10^{-17} [\text{cm}^3 \cdot \text{s}^{-1}]. \quad (17)$$

- Thus: **inelastic collisions proceed at about 10^{-4} to 10^{-6} the rate of elastic collisions.**

Maintenance of Thermal Equilibrium Distributions (1)

A second important statistical distribution valid in thermodynamic equilibrium is the **Boltzmann distribution** of excited states:

$$\frac{n_j}{n_i} = \frac{g_j}{g_i} e^{-(E_j - E_i)/k_B T} \quad (18)$$

where n_j , E_j , and g_j denote the volume density, energy, and the statistical weight of the j^{th} excited state, respectively.

Since the excited-state populations are established by **inelastic collisions**:

- **inelastic collisions** maintain the Boltzmann distribution of excited states.

Since **inelastic** collisions occur much less frequently than **elastic** collisions (which maintain the Maxwell-Boltzmann distribution of velocities), we expect that:

- for low gas density, the Boltzmann distribution will become invalid.

The third distribution of interest is the Planck distribution of photon energies:

$$B_\nu(T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/k_B T} - 1}. \quad (19)$$

Maintenance of Thermal Equilibrium Distributions (2)

The Planck distribution is maintained by emission and absorption of photons:

- processes determined by the populations of the various excited states in the medium, and thus: **also maintained by inelastic collision processes.**

In strict thermodynamic equilibrium (TE):

- $B_\nu(T)$ not only describes the blackbody radiation field: $I_\nu^{\text{BB}} = B_\nu(T)$, but also describes the **source function**: $S_\nu = B_\nu(T)$.

From Kirchhoff's law the emission coefficient (rate of thermal emission per unit volume) is given by:

$$j_\nu = \alpha(\nu)B_\nu(T).$$

Here $\alpha(\nu)$ is the absorption coefficient. (We ignore scattering here.) Since:

$$S_\nu \equiv j_\nu/\alpha(\nu)$$

in TE, $S_\nu = B_\nu(T)$.

Maintenance of Thermal Equilibrium Distributions (3)

This result also follows from the radiative transfer equation:

$$dI_\nu/d\tau_\nu = -I_\nu + B_\nu.$$

In TE the radiance is uniform and isotropic, and $dI_\nu/d\tau_\nu = 0$. Thus:

$$S_\nu = I_\nu^{\text{BB}} = B_\nu,$$

which applies to a closed system in equilibrium.

What about an “open system”, such as an atmosphere or ocean, that receives energy from the Sun and radiates energy to space?

- Under rather general conditions, such systems also share certain properties of a system in TE.
- As will be shown in greater detail for a two-level atom, the source function is Planckian, $S_\nu = B_\nu(T)$, (but $I_\nu \neq B_\nu$) in **local thermodynamic equilibrium**, or LTE.

Maintenance of Thermal Equilibrium Distributions (4)

- LTE applies if the photon energy is sufficiently low ($h\nu < k_B T$) and the molecular density is sufficiently high for the rate of collisional excitation/de-excitation processes to greatly exceed the corresponding radiative processes.
- This condition for is the same as the one for which the Boltzmann distribution of excited states (Eq. 18) is valid. In fact, Eq. 18 being valid is a necessary and sufficient condition for LTE.

Thus, LTE applies if the **gas density is sufficiently high** to ensure that:

- the collisional lifetime of an excited state t_{coll} is much smaller than the radiative lifetime t_{rad} . This condition is fulfilled in the thermal IR ($\lambda > 3 \mu\text{m}$).

For vibrational states, t_{rad} is typically 0.1-1 s. For the 15- μm band of the CO_2 under STP conditions, $t_{\text{coll}} \sim [AB]^* / d[AB^*]/dt = 1/k'_{\text{in}}[M] \sim 10^{-5}$ s. Therefore:

- LTE would exist in this band down to pressures of 0.001-0.1 mb, which occurs near 75 km: the **level of vibrational relaxation**. Above this height:
- the upper state “relaxes” to a population different from that given by the Boltzmann distribution of excited states (Eq. 18): **nonlocal thermodynamic equilibrium** (NLTE).

The Two-Level Atom: Microscopic Radiative Transfer Equation (1)

Assume now that **all** the radiative and collisional processes act together, and that the values of the rate processes are given. Our goal is to derive:

- **equations describing the transfer of radiation through the system.**

Many of the properties of a complex system are embodied in the **two-level atom** concept:

- we must consider **five separate processes** (see Fig. 10) connecting the two energy levels of the atom.

We begin by considering the radiative processes:

- The radiation field is assumed to be a result of transitions from the single excited level (state 2) to the ground level (state 1) of a radiatively-active species.
- The gas will be a two-component mixture consisting of the radiatively-active species, and a **radiatively inert ‘buffer’ gas**.

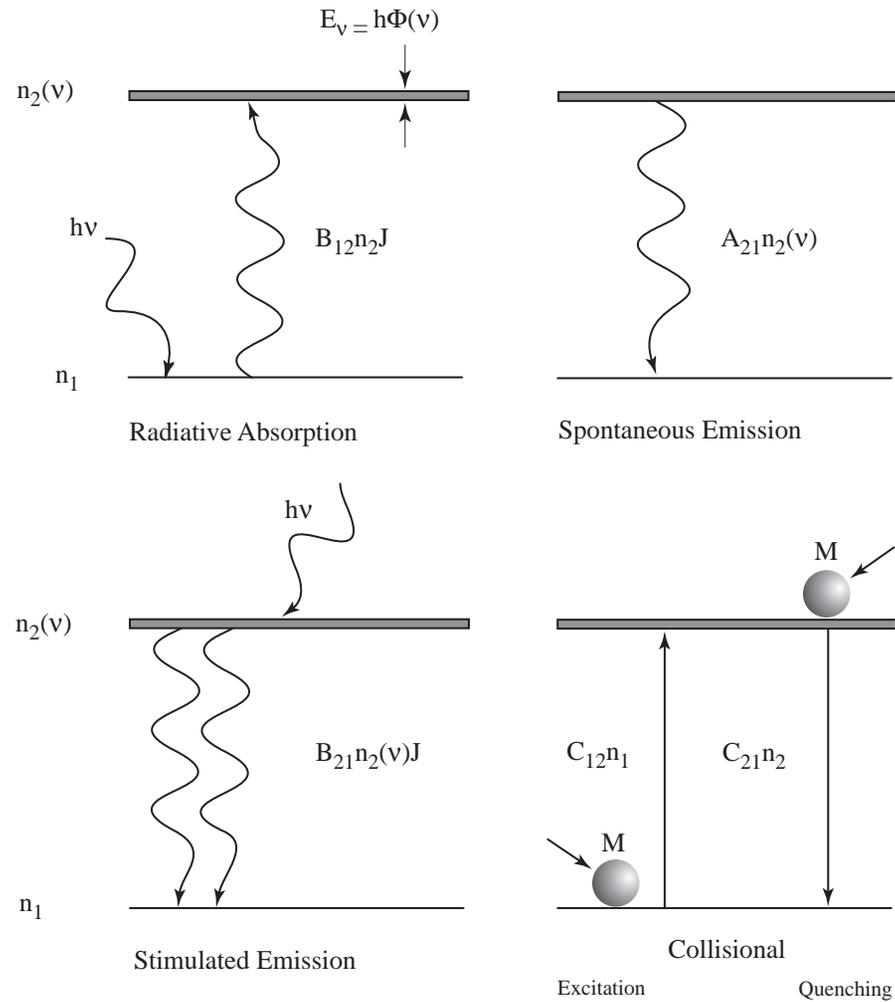


Figure 10: **Illustration of the five radiative and collisional processes involved in the rate of population of energy levels in a two-level atom.**

The Two-Level Atom: Microscopic Radiative Transfer Equation (2)

The **buffer gas** plays the role of:

- collisionally transforming the excited level to the ground state and vice versa.
- The populations in the two levels are denoted n_1 and n_2 . The sum $n = n_1 + n_2 =$ constant, $n =$ density of the radiatively-active species.

The average energy difference between the states is $E_{21} = E_2 - E_1 = h\nu_0$, but:

- there is a small spread in frequencies, due to spectral broadening.

The radiative processes (see Fig. 10) are:

- (1) **Absorption:** $h\nu + n_1 \rightarrow n_2$
- (2) **Spontaneous emission:** $n_2 \rightarrow n_1 + h\nu$
- (3) **Stimulated emission:** $n_2 + h\nu \rightarrow n_1 + h\nu + h\nu$.

In Process (3) the **emitted radiation is exactly coherent with the incident radiation**, both direction and phase. (1) and (3) may be understood from classical physics, but (2) requires quantum theory for a fundamental description.

The Two-Level Atom: Microscopic Radiative Transfer Equation (3)

In the semi-classical theory, we assign a rate to:

- the stimulated emission which is independent of the surroundings of the atom.

The rates at which the three radiative processes occur are described by:

- the **Einstein coefficients** B_{12} (absorption), A_{21} (spontaneous emission), and B_{21} (stimulated emission).

We now consider the rate equations for each individual process:

- Process (1) describes the rate at which absorption depletes the lower state, and is proportional to:
 - (i) the number of atoms in the ground state n_1 , (ii) the absorption cross section $\alpha_n(\nu)$, and (iii) the number of photons in solid angle $d\omega$, $(I_\nu/h\nu)d\omega$. Integrating over all frequencies and photon directions, we find:[†]

$$(dn_2/dt)_{\text{abs}} = n_1 \int_0^\infty d\nu \int_{4\pi} d\omega \alpha_n(\nu) (I_\nu/h\nu) = 4\pi n_1 \int_0^\infty d\nu \alpha_n(\nu) (\bar{I}_\nu/h\nu). \quad (20)$$

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[†]Recall: $\bar{I} \equiv \frac{1}{4\pi} \int_{4\pi} d\omega I(\omega)$

The Two-Level Atom: Microscopic Radiative Transfer Equation (4)

- Process (2) is the rate at which photons depopulate the upper state. According to Einstein:

$$(dn_2/dt)_{\text{spon}} = -A_{21}n_2. \quad (21)$$

The above equation shows that the:

- excited states decay via this process **independently of its surroundings**.
- Process (3) is given by an expression similar to Eq. 20, since its rate is also proportional to the number of photons available:

$$\begin{aligned} (dn_2/dt)_{\text{stim}} &= -n_2 \int_0^\infty d\nu \int_{4\pi} d\omega \alpha_n(\text{stim}; \nu) (I_\nu/h\nu) \\ &= -4\pi n_2 \int_0^\infty d\nu \alpha_n(\text{stim}; \nu) (\bar{I}_\nu/h\nu) \end{aligned} \quad (22)$$

where $\alpha_n(\text{stim}; \nu)$ is the absorption cross section for stimulated emission.

The Two-Level Atom: Microscopic Radiative Transfer Equation (5)

We now write the absorption cross sections in terms of the Einstein coefficients:

- $\alpha_n(\nu) \equiv h\nu B_{12}\Phi(\nu)/4\pi$, and
- $\alpha_n(\text{stim}; \nu) \equiv h\nu B_{21}\Phi(\nu)/4\pi$.

$\Phi(\nu)$ is the normalized **line-profile function**:

$$\int_0^\infty d\nu \Phi(\nu) = 1. \quad (23)$$

We made two assumptions:

- The line profiles for stimulated emission and absorption are the same.
- The **line shape**, $\Phi(\nu)$, determined by the properties of the atom (molecule) and its surroundings, **is known**.

The Two-Level Atom: Microscopic Radiative Transfer Equation (6)

The rates of the above three processes are related. We will show that it is:

- sufficient to know the value of one Einstein coefficient to determine the other two.

For this purpose we assume a special case of thermodynamic equilibrium (TE), and then argue that the result so obtained has more general validity. In TE:

- $I_\nu = B_\nu$, and the populations n_1 and n_2 are related through the Boltzmann distribution of excited states, Eq. 18: $\frac{n_j}{n_i} = \frac{g_j}{g_i} e^{-(E_j - E_i)/k_B T}$.
- We denote the ratio of the two populations in TE as n_2^*/n_1^* to distinguish it from the more general ratio n_2/n_1 .

From Eq. 18, we have:

$$n_2^*/n_1^* = (g_2/g_1) \exp(-h\nu_0/k_B T) \quad (24)$$

where the g_i are the statistical weights. (Note that we have used the average energy difference between the two states $E_{21} = E_2 - E_1 = h\nu_0$.)

The Two-Level Atom: Microscopic Radiative Transfer Equation (7)

Assuming steady-state: $dn_1^*/dt = -dn_2^*/dt = 0$ we have:

$$dn_1^*/dt = 0 = n_2^*A_{21} + n_2^*B_{21} \int_0^\infty d\nu B_\nu \Phi(\nu) - n_1^*B_{12} \int_0^\infty d\nu B_\nu \Phi(\nu). \quad (25)$$

- We may simplify this expression because the Planck function B_ν is slowly-varying over the line profile, and can be set to $B_\nu = B_{\nu_0} = \text{constant}$.

Then, using the normalization property of $\Phi(\nu)$, Eq. (23): $\int_0^\infty d\nu \Phi(\nu) = 1$, we find:

$$n_2^*A_{21} + n_2^*B_{21}B_{\nu_0} = n_1^*B_{12}B_{\nu_0}.$$

Solving for B_{ν_0} , we find:

$$B_{\nu_0} = \frac{(A_{21}/B_{21})}{(g_1B_{12}/g_2B_{21}) e^{h\nu_0/k_B T} - 1}.$$

The Two-Level Atom: Microscopic Radiative Transfer Equation (8)

But we already know the functional form of the Planck function:

$$B_{\nu_0} = \frac{2h\nu_0^3/c^2}{e^{h\nu_0/k_B T} - 1}. \quad (26)$$

Making the correspondence of the above two equations, we obtain:

The Einstein Relations

$$A_{21} = (2h\nu_0^3/c^2)B_{21} \quad (\text{a}); \quad g_1 B_{12} = g_2 B_{21} \quad (\text{b}). \quad (27)$$

These relationships are independent of the state of the gas (temperature or density). They depend only on the basic properties of the atom itself:

- **the Einstein relations are quite general**, independent of the situation assumed in their derivation, and should apply to the more general NLTE situation.

The Two-Level Atom: Microscopic Radiative Transfer Equation (9)

We now use the above relationships to write down the continuity equation for photons, which is just the radiative transfer equation. We first note that:

- dI_ν/ds is the rate at which radiative energy is lost, or gained, along a beam.

Then we can write this quantity as being equal to the gains less the losses due to the three radiative processes. The result is:

The Microscopic Radiative Transfer Equation

$$\frac{dI_\nu}{ds} = -\frac{h\nu_0}{4\pi}n_1B_{12}I_\nu\Phi(\nu) + \frac{h\nu_0}{4\pi}n_2B_{21}I_\nu\Phi(\nu) + \frac{h\nu_0}{4\pi}n_2A_{21}\Phi(\nu). \quad (28)$$

Note: we have introduced the additional assumption that **the line profile for spontaneous emission is also given by $\Phi(\nu)$** .

The Two-Level Atom: Microscopic Radiative Transfer Equation (10)

Equation 28 may now be related to our conventional radiative transfer equation (Eq. 2.28), which we can now call the **macroscopic** radiative transfer equation:

$$\frac{dI_\nu}{ds} = -k(\nu) (I_\nu - S_\nu). \quad (29)$$

Equating the factors multiplying I_ν in Eqs. 28 and 29, we find:

$$k(\nu) = \frac{h\nu_0}{4\pi} \Phi(\nu) (n_1 B_{12} - n_2 B_{21}) = \frac{h\nu_0}{4\pi} \Phi(\nu) n_1 B_{12} \left(1 - \frac{n_2 B_{21}}{n_1 B_{12}} \right) \quad (30)$$

which allows us to relate **microscopic** quantities to **macroscopic** quantities.

In the case of LTE, we replace the quantities n_1 and n_2 by n_1^* and n_2^* :

$$k^*(\nu) = \frac{h\nu_0}{4\pi} \Phi(\nu) n_1^* B_{12} \left(1 - \frac{n_2^* B_{21}}{n_1^* B_{12}} \right) \quad (31)$$

where $k^*(\nu)$ denotes the LTE value of the effective extinction coefficient.

The Two-Level Atom: Microscopic Radiative Transfer Equation (11)

From the Boltzmann relation for the ratio n_2^*/n_1^* [Eq. (24): $n_2^*/n_1^* = (g_2/g_1) \exp(-h\nu_0/k_B T)$], and the Einstein relation $g_2 B_{21} = g_1 B_{12}$, we find:

$$k^*(\nu) = \frac{h\nu_0}{4\pi} \Phi(\nu) n_1^* B_{12} (1 - e^{-h\nu_0/k_B T}). \quad (32)$$

Here $k^*(\nu)$ is the extinction coefficient in LTE, **corrected for stimulated emission**:

- stimulated emission is simply **negative absorption**, since the emitted photon is coherent with, and in the same direction as the incident photon.

Thus, our macroscopic equation needs a slight adjustment for the LTE situation:

$$\frac{dI_\nu}{ds} = -k^*(\nu) (I_\nu - S_\nu) \quad (33)$$

where $k^*(\nu)$ is given by Eq. 32.

The Two-Level Atom: Microscopic Radiative Transfer Equation (12)

Note that in many atmospheric problems:

- the factor $e^{-h\nu_0/k_B T} \ll 1$ and the effect of stimulated emission is negligible.

In the more general NLTE situation, we should equate the source terms in Eqs. 28 $[\frac{h\nu_0}{4\pi}n_2A_{21}\Phi(\nu)]$ and (29) $[k(\nu)S_\nu]$, and use Eq. 30 for $k(\nu)$ $[k(\nu) = \frac{h\nu_0}{4\pi}\Phi(\nu)(n_1B_{12} - n_2B_{21})]$. Using the Einstein relationships, Eq. 27a,b, we get:

$$S_\nu = S_{\nu_0} = \frac{n_2A_{21}}{n_1B_{12} - n_2B_{21}} = \frac{2h\nu_0^3/c^2}{(n_1g_2/n_2g_1) - 1}. \quad (34)$$

Note 1: this NLTE source function contains **no** frequency-dependence, because we assumed that the line profiles for stimulated emission, spontaneous emission, and absorption are identical (**complete frequency redistribution**).

Note 2: if we assume LTE, $n_2/n_1 = n_2^*/n_1^*$, then this NLTE source function becomes the Planck function Eq. 26, as can be seen from Eq. 24: $n_2^*/n_1^* = (g_2/g_1) \exp(-h\nu_0/k_B T)$.

Note 3: Eq. 34 contains another unknown, **the ratio of the two populations**, which must be **determined by considering inelastic collisions**.

The Two-Level Atom: Effects of Collisions on State Populations (1)

In addition to the effects of radiation on the excited states, we must consider:

- the effects of **collisional excitation and quenching**.

To simplify the notation, we define (see Eqs. 12 and 14):

- the collisional excitation rate per atom as[‡] $k_{\text{in}}[M] \equiv C_{12}$, and the collisional quenching rate per atom as[§] $k'_{\text{in}}[M] \equiv C_{21}$.

In a **steady state** we set to zero:

- the rate at which both collisions and radiation populate the excited state:

$$\begin{aligned} \frac{dn_1}{dt} = & -n_1 C_{12} - n_1 B_{12} \int_0^\infty d\nu \Phi(\nu) \bar{I}_\nu \\ & + n_2 C_{21} + n_2 B_{21} \int_0^\infty d\nu \Phi(\nu) \bar{I}_\nu + n_2 A_{21} = 0. \end{aligned} \quad (35)$$

- This equation is called the **statistical equilibrium equation**.

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[‡]Recall $\frac{d[AB]^*}{dt} = k_{\text{in}}[AB][M]$, where k_{in} is the collisional excitation coefficient.

[§]Recall: $\frac{d[AB]^*}{dt} = -k'_{\text{in}}[AB^*][M]$, where k'_{in} is the quenching coefficient.

The Two-Level Atom: Effects of Collisions on State Populations (2)

Equation 35 provides an equation in addition to Eq. 34, which

- allows us to solve for **both** unknowns, n_2/n_1 , and the source function, S_ν .

Recall: We derived the Einstein relationships by assuming TE, ignoring collisions and balancing the radiative processes. We now use the same idea with collisions: **assume TE, ignore radiative processes, and set the two rates equal:**

$$n_2^* C_{21} = n_1^* C_{12}. \quad (36)$$

Using the definitions of the coefficients, and invoking the Boltzmann distribution of excited states, Eq. 18: $\frac{n_j}{n_i} = \frac{g_j}{g_i} e^{-(E_j - E_i)/k_B T}$, we find:

$$C_{21} = C_{12} \frac{g_1}{g_2} e^{h\nu_0/k_B T}. \quad (37)$$

As in the case of the Einstein relationships: **the above relationship is more general than the assumption used in deriving it.**

The Two-Level Atom:

Effects of Collisions on State Populations (3)

We cannot argue that Eq. 37 describes an inherent atomic property, because of its dependence on the temperature. However, we observe that:

- the collisional excitation rate Eq. 10: $\frac{d[AB]^*}{dt} = k_{\text{in}}[AB][M]$, where $k_{\text{in}} = \int d^3 v_{\text{rel}} f_{AB}(\vec{v}_{AB}) f_M(\vec{v}_M) \frac{d\sigma_{\text{in}}}{d\omega}$ is determined by integrating the product of the Maxwell-Boltzmann (MB) velocity distributions of the reactants.

Recall: the MB velocity distributions are maintained by **elastic collisions**, which are millions of times more efficient than **inelastic collisions**. Thus, we expect that:

- Equation 37 would be valid in non-equilibrium situations, **as long as the velocity distribution is Maxwellian**.

To emphasize that there may be several different temperatures in a NLTE situation, the quantity entering the (MB) velocity distribution is often referred to as:

- the **kinetic** or **translational** temperature.

The Two-Level Atom: Effects of Collisions on State Populations (4)

Solving the statistical equilibrium equation (Eq. 35) for n_1/n_2 , we obtain:

$$\frac{n_1}{n_2} = \frac{C_{21} + B_{21}J + A_{21}}{C_{12} + B_{12}J} \quad \text{where} \quad J \equiv \int_0^\infty d\nu \Phi(\nu) \bar{I}_\nu \quad (38)$$

the ratio of **the net excitation rate** to **the net quenching rate**, or the **‘source’** divided by the **“sink”** of excited states.

Eqs. 34 and 38 are two equations in the two unknowns, S_ν and n_1/n_2 .

Using Eq. 37: $C_{21} = C_{12} \frac{g_1}{g_2} e^{h\nu_0/k_B T}$ to eliminate C_{12} and Eq. 27b: $g_1 B_{12} = g_2 B_{21}$, to eliminate the Einstein coefficient B_{12} in Eq. 38, we find:

$$\frac{n_1}{n_2} = \frac{A_{21} + B_{21}J + C_{21}}{(g_2/g_1)C_{21}e^{-h\nu_0/k_B T} + (g_2/g_1)B_{21}J} \quad (39)$$

where T is the kinetic temperature of the gas.

The Two-Level Atom: Effects of Collisions on State Populations (5)

Thus:

- **the velocity distribution** of the atoms in the gas is in **LTE**, while **the populations of the energy states** may be **far from an LTE distribution**.

We rewrite the above equation as:

$$\frac{n_1 g_2}{n_2 g_1} = \frac{A_{21} + B_{21} J + C_{21}}{B_{21} J + C_{21} e^{-h\nu_0/k_B T}} \quad (40)$$

which is the combination that appears in the denominator of Eq. 34:

$$S_\nu = S_{\nu_0} = \frac{n_2 A_{21}}{n_1 B_{12} - n_2 B_{21}} = \frac{2h\nu_0^3/c^2}{(n_1 g_2/n_2 g_1) - 1}.$$

Substitution of Eq. 40 into 34 yields:

$$S_{\nu_0} = \frac{2h\nu_0^3}{c^2} \left[\frac{A_{21} + B_{21} J + C_{21}}{B_{21} J + C_{21} e^{-h\nu_0/k_B T}} - 1 \right]^{-1}.$$

The Two-Level Atom: Effects of Collisions on State Populations (6)

The equation above may be rewritten as:

$$S_{\nu_0} = \frac{(2h\nu_0^3/c^2)(B_{21}J + C_{21}e^{-h\nu_0/k_B T})}{A_{21} + C_{21} - C_{21}e^{-h\nu_0/k_B T}}$$

and using the first of the Einstein relations, Eq. 27a: $A_{21} = (2h\nu_0^3/c^2)B_{21}$, we obtain:

$$S_{\nu_0} = \frac{J + (2h\nu_0^3/c^2)(C_{21}/A_{21})e^{-h\nu_0/k_B T}}{1 + (C_{21}/A_{21})(1 - e^{-h\nu_0/k_B T})}.$$

To simplify the above expression for S_ν , we define a new parameter, ϵ_ν :

$$\epsilon_\nu \equiv \frac{C_{21}}{C_{21} + A_{21}(1 - e^{-h\nu_0/k_B T})^{-1}}. \quad (41)$$

The Two-Level Atom: Effects of Collisions on State Populations (7)

With some additional manipulation using ϵ_ν and Eq. 26, $B_{\nu_0} = \frac{2h\nu_0^3/c^2}{e^{h\nu_0/k_B T} - 1}$, we find:

The NLTE source function

$$S_{\nu_0} = \epsilon_\nu B_{\nu_0} + (1 - \epsilon_\nu)J \quad \text{where} \quad J \equiv \int_0^\infty d\nu \Phi(\nu) \bar{I}_\nu. \quad (42)$$

We have shown that the NLTE source function is the sum of two terms:

- a thermal emission term, plus
- a term which represents the scattering contribution to the source function.
- $\epsilon_\nu B_{\nu_0}$ is interpreted as the emittance per unit volume: its efficiency as a black-body emitter as a function of frequency within the spectral line.

In terms of the macroscopic absorption $[\alpha(\nu)]$ and extinction $[k(\nu)]$ coefficients:

- $\epsilon_\nu = \alpha(\nu)/k(\nu)$ (note that the frequency dependence cancels in the ratio).

The Two-Level Atom: Effects of Collisions on State Populations (8)

The emission coefficient is obtained from its definition [$j_\nu = S_\nu k(\nu)$], yielding:

$$j_\nu = \alpha(\nu)B_\nu(T) + \sigma(\nu) \int_0^\infty d\nu \Phi(\nu) \bar{I}_\nu \quad (43)$$

where we used the relationship $\sigma(\nu) = k(\nu) - \alpha(\nu)$. The first term in Eq. 43 is:

- **Kirchhoff's Law** for a volume element, which states that the thermal emission is the product of the absorption coefficient and the Planck function.
- The second term is the contribution to the volume emission from scattering within the volume (see §5.3.2).

ϵ_ν is a measure of the coupling between the gas and the radiation field:

- When $\epsilon_\nu \rightarrow 1$, the coupling is strong, and there is a rapid exchange between kinetic and internal energy: $S_{\nu_0} \rightarrow B_{\nu_0}$, which is just the LTE limit.

The Two-Level Atom: Effects of Collisions on State Populations (9)

In the opposite case of weak coupling: ($\epsilon_\nu \rightarrow 0$), the source function approaches the pure-scattering limit:

$$S_{\nu_0} \rightarrow J = \int_0^\infty d\nu \Phi(\nu) \bar{I}_\nu \quad (44)$$

which might be called:

- **an extreme condition of NLTE**, in which the excited states are populated exclusively by radiation and collisions no longer play a role.

Moving up into lower densities and pressures in a planetary/stellar atmosphere:

- there will be a transition from LTE to NLTE as the coupling between the gas and the radiation field disappears.

Absorption in Molecular Lines and Bands (1)

The infrared (IR) spectral range consists of the:

Solar near-infrared (NIR): 1–3 μm

Thermal infrared radiation (IR): 3–100 μm .

The molecular excited states of interest are those of:[¶]

Vibration: 500 – 10,000 cm^{-1} , and **Rotation:** 1 – 500 cm^{-1} .

Note: the higher-lying **electronic states:** 10,000 – 100,000 cm^{-1} interact primarily with visible and ultraviolet radiation.

The internal excitation energy is the sum of these three types of energy: **electronic** (E_e), **vibrational** (E_v), and **rotational** (E_r).

(Note: the kinetic energy of the molecules plays an important indirect role in determining the populations of the various absorbing states.)

Mastery of IR spectroscopy requires a thorough familiarity with quantum mechanics, which is beyond the scope of this course. Our approach is to:

- consider only a few of the simpler ideas underlying the physics of vibrational and rotational spectra.

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[¶]Conversion: 1 $\mu\text{m} = 10,000 \text{ cm}^{-1}$. Hence: 500 cm^{-1} corresponds to $(10,000/500) \frac{\mu\text{m}}{\text{cm}^{-1}} \text{ cm}^{-1} = 20 \mu\text{m}$.

Absorption in Molecular Lines and Bands (2)

Fortunately, an understanding of the radiative transfer process itself does not require detailed spectroscopic knowledge due to:

- the availability of accurate compilations of line strengths and frequencies for all the major terrestrial molecular species. We will follow this empirical approach.

First, note that the major molecular species of the Earth's atmosphere:

- O_2 and N_2 have essentially no impact on IR absorption due to:
- the symmetrical structure of homonuclear, diatomic molecules.

Four of the most important IR-absorbing molecular species are the minor constituent **polyatomic** molecules:

- water vapor (H_2O), carbon dioxide (CO_2), ozone (O_3) and methane (CH_4).

Dozens of other minor species have a small effect on the heat budget, when considered **together**, and are important in remote sensing.

- The absorption of light gives rise to excited states, which may be a combination of electronic, vibrational and rotational motion.

Absorption in Molecular Lines and Bands (3)

Let's first consider **molecular vibration** (ignoring electronic or rotational energy). To help visualize the physics of the absorption process, we assume that:

- the constituent atoms are held together in a semi-rigid structure by attractive forces provided by the electron 'cloud' shared by all the atoms, and
- the bonding forces can be either electrostatic (ionic bonding) or quantum-mechanical (exchange or covalent bonding).
- The nature of these forces does not concern us here. We need only consider their behaviour as 'springs' binding the various positively-charged nuclei together.

The simplest example is a diatomic molecule acting like a classical oscillator:

- When it collides with another molecule or absorbs a photon of the proper frequency:
- the constituent atoms are set into internal motion, alternately stretching and compressing the molecule. In addition:
- the bonds may 'bend' so that the angles between the various axes may also oscillate.

Absorption in Molecular Lines and Bands (4)

Classically, the energy of oscillation of a molecule can vary continuously, but due to the quantum nature of energy states, the number of such states is a discrete set. According to classical mechanics:

- the internal motion of a semi-rigid system, no matter how complicated, can be decomposed into a sum of elementary motions, the so-called **normal modes**.

A diatomic molecule, modelled as a simple harmonic oscillator, has **only one normal mode** of oscillation, along the internuclear axis. However:

- with increasing complexity of the molecule, more normal modes are possible.

The general rule is that if a molecule has N atoms:

- the number of independent modes (or degrees of freedom) is $3N - 6$ **for a non-linear molecule** ($N > 2$), and $3N - 5$ **for a linear molecule**.
- Figure 11 illustrates some of the normal modes of N_2 , O_2 , CO_2 , and H_2O .

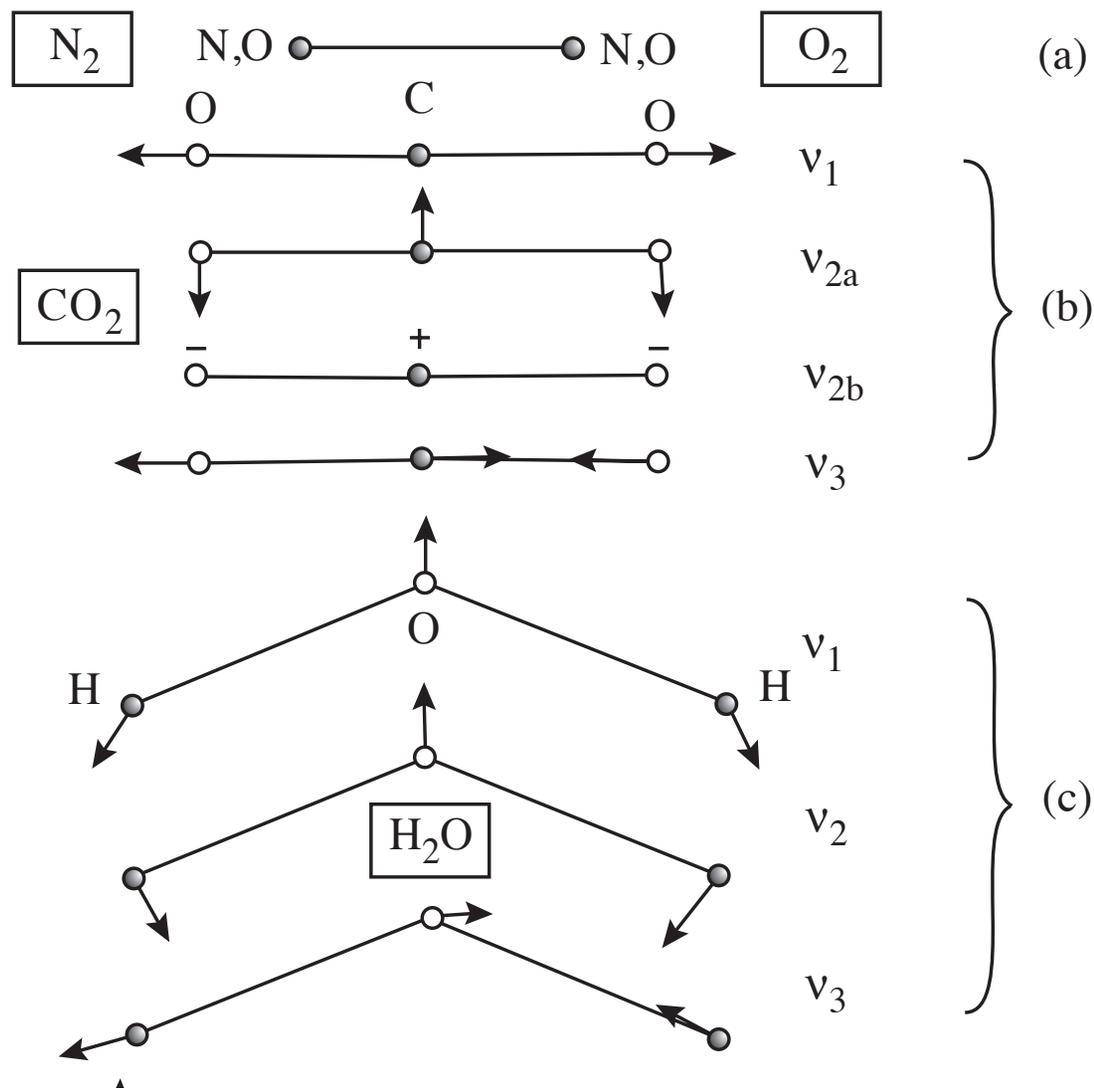


Figure 11: **Normal modes of vibration of N_2 , O_2 , CO_2 , and H_2O .** (a) N_2 and O_2 are diatomic, homonuclear molecules with only one mode of vibration. (b) CO_2 is a linear, triatomic molecule. (c) Both H_2O and O_3 (not shown) have three normal modes.

Absorption in Molecular Lines and Bands (5)

If the motions are small-amplitude, the quantum mechanical result for the total vibrational energy is (the subscript v stands for vibration):

$$E_v = \sum_k h\nu_k(v_k + 1/2) \quad (v_k = 0, 1, 2 \dots) \quad (45)$$

where the sum is over all modes denoted by the index k , and

- $h\nu_k$ is the **vibrational constant** for that mode, ν_k is the mode frequency and v_k is an integer, the **vibrational quantum number**.
- The value of $h\nu_k$ will depend upon the molecule, and the particular electronic energy state. It is usually in the range $300 - 3000 \text{ cm}^{-1}$ ($0.37 - 3.7 \text{ eV}$).
- The constant $1/2$ is a quantum-mechanical feature associated with the “zero-point energy.” The lowest vibrational energy levels are somewhat higher than thermal energy^{||} $\sim k_B T \sim 210 \text{ cm}^{-1}$ for $T = 300 \text{ K}$.
- For a classical simple harmonic oscillator, $h\nu_k$ depends upon the square-root of the “spring constant” k_e divided by the reduced mass. It is usually written in terms of a **vibrational constant** (ω_e in cm^{-1}) as $h\nu_k = hc\omega_e$.

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^{||}Since $1 \text{ eV} = 1.16049 \times 10^4 \text{ K}$, $300 \text{ K} = (300/1.16049) \times 10^{-4} \text{ eV} = 0.0259 \text{ eV}$. Also $1 \text{ eV} = 8067 \text{ cm}^{-1}$, so $0.0259 \text{ eV} = 8067 \times 0.0259 \text{ cm}^{-1} = 209 \text{ cm}^{-1}$.

Absorption in Molecular Lines and Bands (6)

The intermolecular force for a diatomic molecule is given by the spatial derivative of the potential energy function $V(r)$: $-k_e(r - r_e)$ ($r_e =$ equil. nuclear separation). Figure 12 shows $V(r)$ for the H_2 molecule, and its vibrational energy states.

In addition to being excited by molecular collisions:

- molecular vibrations may also be induced by absorption of radiation provided the radiative energy is in resonance with a normal mode.

Classically we can think of this interaction as the temporary creation of an **induced electric dipole moment** by the incident electromagnetic field, occurring **if**:

- the new configuration results in an electron distribution whose first moment (“center of gravity”) **is displaced from its original position**.

In their ground, or lowest energy states, the ***dipole moment of symmetrical molecules***, such as N_2 , O_2 , CO_2 , and CH_4 **is zero**. However:

- there are asymmetrical stretching or bending modes of vibration (for example the ν_2 state of CO_2) which result in an electric dipole.

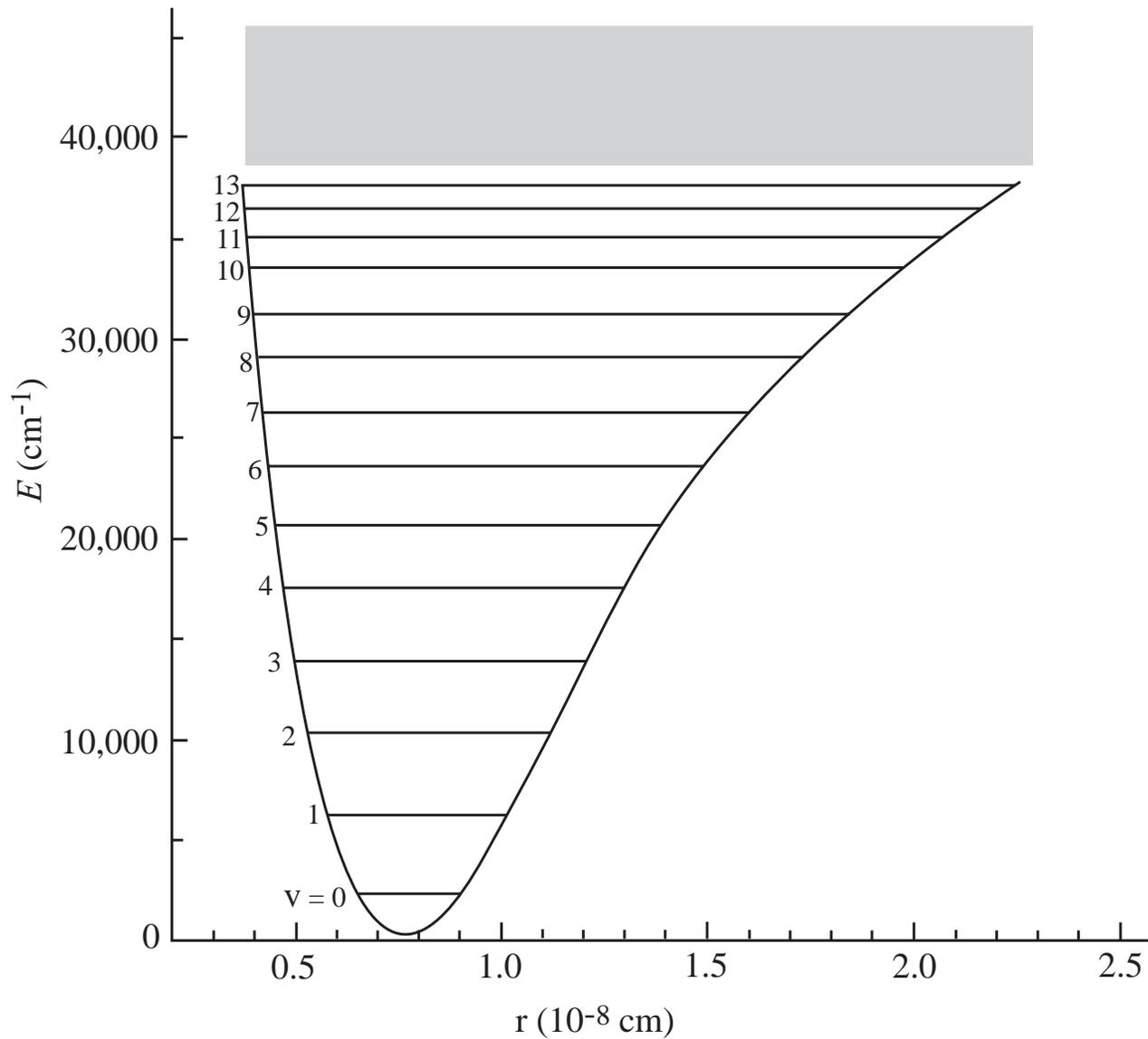


Figure 12: **Potential curve for H_2 ground state with vibrational levels and continuous term spectrum.** The continuous term spectrum, above $v = 14$, is indicated by hatching (since $1 \text{ eV} = 8067 \text{ cm}^{-1}$, $10,000 \text{ cm}^{-1} = 1.24 \text{ eV}$).

Absorption in Molecular Lines and Bands (7)

- Radiative transitions between these states and the ground state are allowed if there is a **change** in the dipole moment. Note that the homonuclear molecules:
- N_2 and O_2 are symmetrical in both their ground and (single) excited state, and therefore have no vibrational spectra: they are **radiatively inactive**.

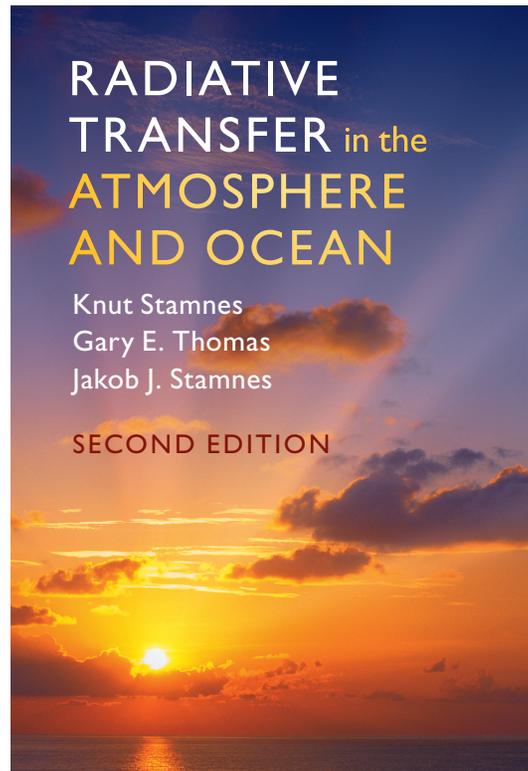
In quantum theory, absorption takes place provided there is:

- a finite dipole **matrix element** between the initial and excited states.
- Sometimes this matrix element is zero, and the transition is **forbidden**, at least for dipole transitions. Higher-order moments, such as:
- **electric quadrupole** and **magnetic dipole** moments may exist, but their associated absorptions are much weaker than electric dipole transitions.

Selection rules state if a transition is “dipole-allowed” or “dipole-forbidden”:

- The wavenumber of a vibrational transition is given by $hc\tilde{\nu} = E_v(v') - E_v(v'')$ with the selection rule $\Delta v = v' - v'' = \pm 1$, the so-called **fundamental**.

Lecture *Notes*: Basic Absorption Processes – II



Based on Chapter 4 in K. Stamnes, G. E. Thomas, and J. J. Stamnes, *Radiative Transfer in the Atmosphere and Ocean*, Cambridge University Press, 2017.

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Molecular Rotation: the Rigid Rotator (1)

Molecular rotation is easy to understand in principle. For simplicity:

- we assume that the molecule is a **rigid rotator**: the internuclear separation is fixed, regardless of the rotation.

A diatomic molecule will be characterized classically by its moment of inertia:

- $I = M_1 r_1^2 + M_2 r_2^2$, where M_1, M_2 are the nuclear masses, and r_1, r_2 the radial distances along the principal axis from the center of gravity of the nuclei:

$$r_1 = \frac{M_2}{M_1 + M_2} r \quad \text{and} \quad r_2 = \frac{M_1}{M_1 + M_2} r.$$

Thus, $r = r_1 + r_2$ is the internuclear separation.

The classical expression for the energy of rotation is:

- $E_r = I\omega^2/2 = \mathcal{L}^2/2I$, where ω is the angular velocity of rotation about the principal axis, I is the corresponding moment of inertia ($I = M_1 r_1^2 + M_2 r_2^2$), and \mathcal{L} is the angular momentum.

Molecular Rotation: the Rigid Rotator (2)

The usual QM ‘prescription’ is to replace the classical angular momentum with $(h/2\pi)$ times an integer (h is Planck’s constant). Since we are dealing with the square of the angular momentum:

- the QM equivalent is $\mathcal{L}^2 \rightarrow (h/2\pi)^2 J(J + 1)$ where J is a positive integer, the **rotational quantum number**.

Thus, the rotational energy of a rigid-rotator is given by:

$$E_r(J) = \frac{1}{2I} \left(\frac{h}{2\pi} \right)^2 J(J + 1) = hcB_v J(J + 1) \quad (J = 0, 1, \dots) \quad (46)$$

where $B_v \equiv h/(8\pi^2 cI)$ is the **rotational constant** corresponding to a particular electronic and vibrational state (subscript v on B_v).

Since B_v is inversely proportional to the moment of inertia ($I = M_1 r_1^2 + M_2 r_2^2$), and therefore to the molecular mass, it follows that:

- light molecules, such as H_2 , will have more widely separated rotational energy levels than heavier molecules, implying that there are relatively few rotational states populated by collisions (see Fig. 15).

Molecular Rotation: the Rigid Rotator (3)

How does rotation affect absorption and emission? Again, a **changing electric dipole** must be involved. In this case for radiative interaction:

- it is necessary to have a **permanent** electric dipole moment.

Since the dipole moment is a vector quantity, a change of the **direction** of this dipole moment would constitute a change in the dipole moment, leading to:

- pure rotational transitions, whose energies occur in the far-infrared and microwave portion of the spectrum.

The wavenumber of the emitted or absorbed photon is $\Delta E_r/hc$, so that Eq. 46 gives:

$$\tilde{\nu} = B_v J'(J' + 1) - B_v J''(J'' + 1), \quad (47)$$

where the selection rule is $\Delta J = \pm 1$, that is, J may change or “jump” by only one unit:

- **The pure rotational spectrum of a rigid rotator consists of a sequence of equidistant lines.**

Molecular Rotation: the Rigid Rotator (4)

- Linear molecules (N_2 , O_2 , or CO_2), are symmetrical in their ground states:
- They have **no permanent dipole moment** and thus **no pure rotational spectrum**.

Finally, it should also be mentioned that:

- pure rotational transitions prevail in the microwave spectrum.

For example (1 GigaHertz = 1×10^9 Hz):

- H_2O exhibits intense microwave absorption at 22 and 183 GHz.

The ground state of O_2 possesses no electric dipole moment, BUT:

- it does have an unusually large magnetic dipole. Thus:
- weak (“forbidden”) magnetic dipole transitions occur in the microwave range, important for atmospheric absorption because of the very high abundance of O_2 .

Molecular Vibration and Rotation: the Vibrating Rotator (1)

Since vibration and rotation can occur simultaneously, we consider the **vibrating rotator**. If there were no interaction between rotation and vibration:

- the energy levels can be written as so-called **term values**:

$$\frac{E(v, J)}{hc} = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + B_v J(J + 1) - D_v J^2(J + 1)^2, \quad (48)$$

where ω_e and $\omega_e x_e$ are vibrational constants, expressed in wavenumber units.

- The quadratic terms are the “interaction” terms for an **anharmonic oscillator**.
- Note the presence of two rotational constants, B_v and D_v , whose subscripts v indicate dependence on the vibrational mode.
- The term involving $\omega_e x_e$ is an **anharmonic correction**, accounting for departures from simple harmonic oscillator motion.

Molecular Vibration and Rotation: the Vibrating Rotator (2)

The total molecular energy includes the electronic energy E_e . Thus, the:

- rotational constants may also depend upon the **electronic** energy state.

The wavenumber of a spectral line in a **vibration-rotation band** within a given electronic state is given by the difference:

- of the **term values** of the two states defined by (v', J') and (v'', J'')

$$\tilde{\nu} = \tilde{\nu}_k + B_{v'}J'(J' + 1) - B_{v''}J''(J'' + 1) \quad [\text{cm}^{-1}] \quad (49)$$

where $\tilde{\nu}_k$ is the basic wavenumber of the pure vibrational transition without taking into account any rotation (that is when J' and J'' are set equal to zero).

With $\Delta J = J' - J'' = +1$ and $\Delta J = J' - J'' = -1$, we obtain the wavenumbers of the **R-branch** and **P-branch**, respectively:

$$\tilde{\nu}_R = \tilde{\nu}_k + 2B_{v'} + (3B_{v'} - B_{v''})J'' + (B_{v'} - B_{v''})J''^2 \quad (J'' = 0, 1, \dots) \quad (50)$$

$$\tilde{\nu}_P = \tilde{\nu}_k - (B_{v'} + B_{v''})J'' + (B_{v'} - B_{v''})J''^2 \quad (J'' = 1, 2, \dots). \quad (51)$$

Molecular Vibration and Rotation: the Vibrating Rotator (3)

Figure 13 shows the various transitions in a vibration-rotation band, illustrating the separation into two branches. The above description of a diatomic molecule is still **approximate**:

- **The electrons** (having small masses compared to the nuclei) **have a small moment of inertia about the internuclear axis**. Nevertheless:
- their total angular momentum $\vec{\Lambda}$ is comparable to the nuclear value (which we now denote by \vec{N}), because they move much faster in their orbits.
- Only the **component** of this angular momentum along the axis, is non-zero (the others average to zero) with associated quantum number $\Lambda > 0$, because
- the electric field points along the axis of symmetry.

The total angular momentum \vec{J} of the molecule is thus the vector sum of:

- the nuclear angular momentum \vec{N} (pointing \perp to the axis) and the electronic angular momentum $\vec{\Lambda}$ (pointing \parallel the axis).

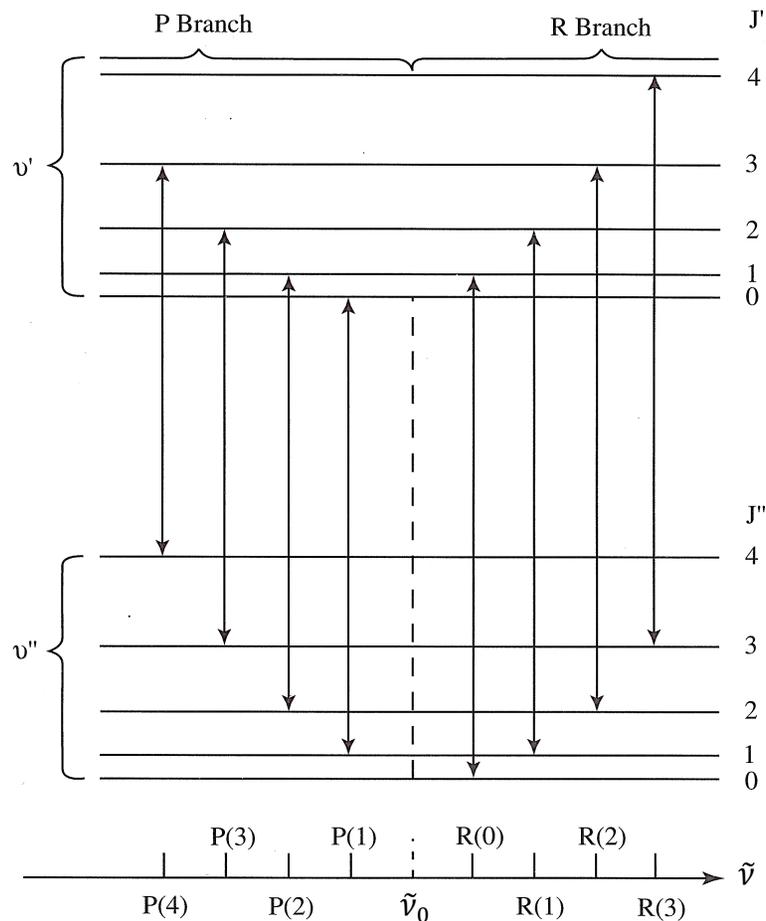


Figure 13: **Energy levels of the vibrating rotator.** v'' and J'' are the vibrational and rotational quantum numbers of the lower state. v' and J' refer to the upper (excited) state. The vertical lines indicate allowed transitions ($\Delta J = \pm 1$). $R(j)$ ($j = 1, 2, 3, 4$) denotes the R -branch ($\Delta J = +1$) ending in the $J' = j$ state. In the lower part of the diagram, idealized absorption is shown versus wavenumber. $P(j)$ ($j = 0, 1, 2, 3$) denotes the P -branch ($\Delta J = -1$) ending in the $J'' = j$ state. The vertical dashed line indicates the band head at $\tilde{\nu} = \tilde{\nu}_0$, which is missing in homonuclear diatomic molecules, because the transition from $v' = 0$ to $v'' = 0$ is forbidden.

Molecular Vibration and Rotation: the Vibrating Rotator (4)

The magnitude of \vec{J} is constant and quantized according to:

- $|\vec{J}| = \sqrt{J(J+1)}h/2\pi$ where h is Planck's constant. The quantum number J ($\geq \Lambda$) is given by $J = \Lambda, \Lambda + 1, \dots$.
- For $\Lambda \neq 0$, there is a precession of \vec{N} and $\vec{\Lambda}$ about the (constant) vector \vec{J} .

Thus, a more accurate picture of the diatomic molecule is a:

- **symmetric top** nutating about the direction of the tot. ang. momentum.

The energy levels that result are thus the sum of the nuclear rotational energy and the nutational energy:

$$E_r/hc = B_v J(J+1) + (A_v - B_v)\Lambda^2 \quad \text{where} \quad B_v = \frac{h}{8\pi^2 c I_B} \quad \text{and} \quad A_v = \frac{h}{8\pi^2 c I_A}.$$

I_B = primary moment of inertia, and

I_A = much smaller moment about the internuclear axis: $\Rightarrow A_v \gg B_v$.

Λ is usually a small (integral) value.

Molecular Vibration and Rotation: the Vibrating Rotator (5)

Thus for a given electronic state, the levels of the symmetric top are the same as the simple rotator, except that there is:

- a shift of magnitude $(A_v - B_v)\Lambda^2$, and levels with $J < \Lambda$ are absent.

Ignoring electronic transitions, the selection rules are rather simple, since Λ does not change during the transition. Then for:

- $\Lambda = 0$, $\Delta J = \pm 1$, and for $\Lambda \neq 0$, $\Delta J = 0, \pm 1$.
- When $\Lambda = 0$, $(A - B)\Lambda^2 = 0$, and we obtain exactly the same branches as discussed for the simple rotator.
- When $\Lambda \neq 0$, there is a constant shift, but otherwise the term values are the same. However, more importantly, a new branch arises, the so-called:
- **Q-branch** with $\Delta J = 0$. The wave numbers of the lines in this branch are:

$$\tilde{\nu}_Q = \tilde{\nu}_k + (B_{v''} - B'_v)\Lambda^2 + (B_{v'} - B_{v''})J + (B_{v'} - B_{v''})J^2. \quad (52)$$

Molecular Vibration and Rotation: the Vibrating Rotator (6)

The only **diatomic** molecule with a Q-branch of atmospheric interest is nitric oxide (NO), because $\Lambda \neq 0$ in its ground state. Its:

- IR band at $5.3 \mu\text{m}$ contributes to the energy of Earth's lower thermosphere.

Q-branches are more common in **polyatomic** molecular spectra. For example in:

- the pure bending mode of the ν_2 mode of CO_2 , where the $\Delta v = 1$ transitions “pile up” at very nearly the same frequency, accounting for the very strong Q-branch in the $15 \mu\text{m}$ band ($667 - 668 \text{ cm}^{-1}$, see Fig. 14).

More complex molecules are categorized in terms of the relationships of the various moments of inertias.

- If all three moments of inertia are **different and also unequal to zero**: the configuration is called an **asymmetric top**, represented by the important molecules, H_2O and O_3 .
- If **all three moments are equal**: the configuration is called a **spherical top**, represented by CH_4 .

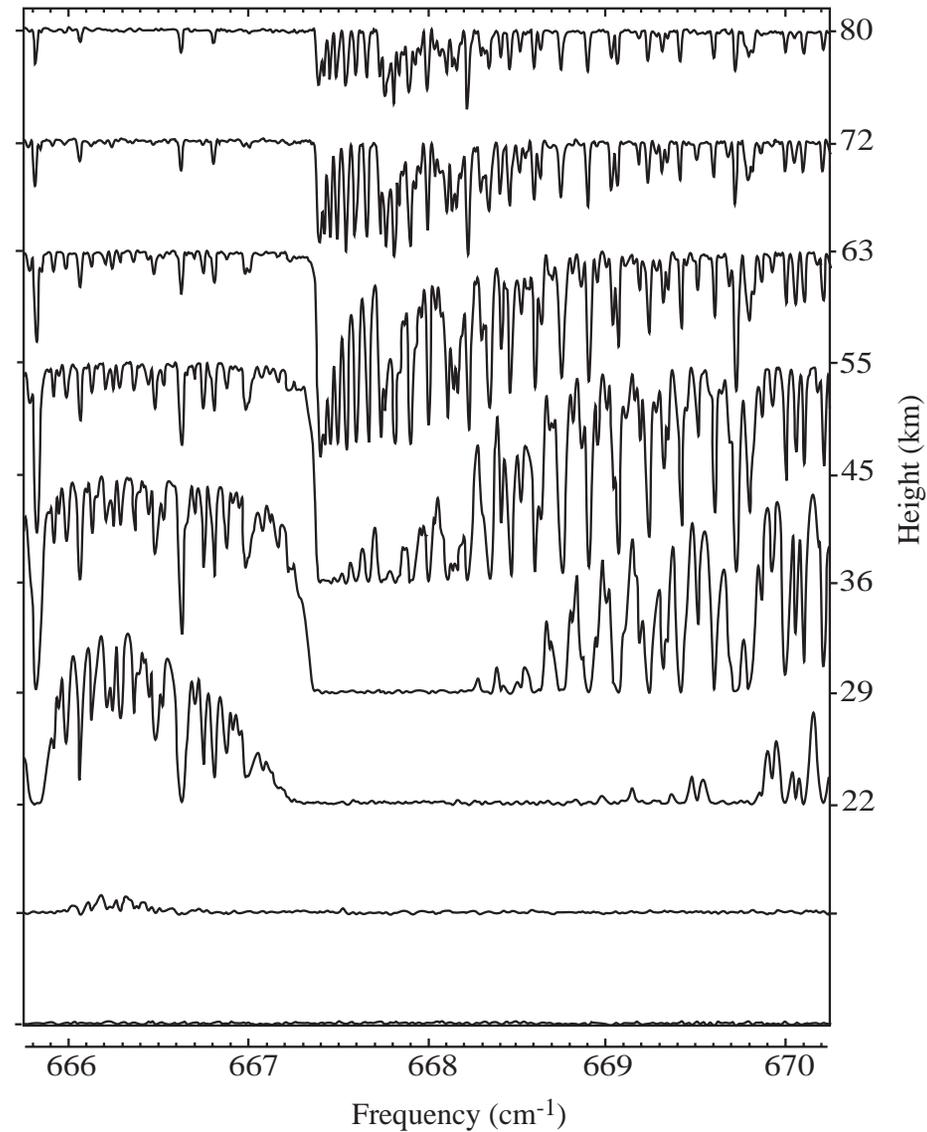


Figure 14: **High-resolution (0.01 cm^{-1}) transmittance spectrum of Earth's stratosphere and mesosphere measured by the ATMOS Michelson interferometer experiment from the NASA Space Shuttle.** Note that 666 cm^{-1} corresponds to $10,000/666 = 15 \text{ }\mu\text{m}$.

Molecular Vibration and Rotation: the Vibrating Rotator (7)

- If **two of the three moments are equal**, we have a **symmetric top** (mentioned in the case of a diatomic molecule), represented by CFCl_3 .

Finally, if one of the moments of inertia is effectively zero, we have a **linear** molecule, examples of which are:

- CO_2 , N_2O , CO and NO . Eqn. 46 [$E_r(J)/hc = B_v J(J + 1)$, $J = 0, 1, \dots$] applies to the rotational energy for both the spherical top ($A_v = B_v$) and the linear molecule ($\Lambda = 0$). However:
- linear molecules and spherical tops do not have the same rotational structure; levels of equal J will “split” in different ways due to all the various couplings between electronic, vibrational and rotational energies.
- Electron and nuclear **spin** leads to additional selection rules, and changes single energy levels into multiple levels.
- **Fine structure** results from interaction of the **magnetic dipole** of the spinning electron with the electric field of the other electrons.
- **Hyperfine structure** results from a similar interaction of the **nuclear spin**.

Line Strengths (1)

The task of spectroscopy is to:

- analyze the line frequencies of an absorption or emission spectrum in terms of the various quantum numbers, rotational and vibrational constants, etc.

We will use a much simpler empirical approach and assume that we are given:

- the **spectroscopic constants** (ω_e , $\omega_e x_e$, B , D , etc.) necessary to determine the frequency of all transitions within a specified frequency range.

In addition to the spectroscopic constants, modern compilations of the **absorption line strengths** are also readily available. The **line strengths** are needed for:

- determining the **opacity** of the atmosphere as a function of frequency.

The strengths depend not only upon the nature of the individual transition:

- but also upon the equilibrium number of ground-state molecules. Thus:
- we need the **Boltzmann distribution of energy states**, Eq. 18:

$$\frac{n_j}{n_i} = \frac{g_j}{g_i} e^{-(E_j - E_i)/k_B T}.$$

Line Strengths (2)

Consider a vibration-rotation band produced by a simple harmonic-oscillator rigid-rotator, and assume LTE conditions so that:

- the distribution of excited states is given by Boltzmann's formula (Eq. 18).

First, consider molecular rotation only: the energy levels are denoted by the quantum number J and the statistical weight by $g_J = 2J + 1$. Then:

$$\frac{n(J)}{n(J')} = \frac{2J + 1}{2J' + 1} \exp \left\{ -\frac{hcB_v}{k_B T} [J(J + 1) - J'(J' + 1)] \right\}. \quad (53)$$

A more convenient ratio is that of an excited state population to the total number of states $n = \sum_{J'} n(J')$ within a given electronic and vibrational state:

$$\frac{n(J)}{n} = \frac{(2J + 1)}{Q_r} \exp \left[-\frac{hcB_v}{k_B T} J(J + 1) \right] \quad (54)$$

where Q_r is the **rotational partition function**:

$$Q_r = \sum_{J'} (2J' + 1) \exp \left[-\frac{hcB_v J'(J' + 1)}{k_B T} \right]. \quad (55)$$

Line Strengths (3)

For sufficiently large T or small B_v , the spacing is very small compared with the total rotational energy. Thus, we may replace the sum with an integral:

$$Q_r \approx \int_0^\infty dJ(2J + 1) \exp[-hcB_v J(J + 1)/k_B T] = \frac{k_B T}{hcB_v}.$$

The distribution of rotational energies with rotational quantum number J (see Fig. 15) is very important for the absorption coefficient, because:

- the number of molecules in the ground (vibrational and electronic) state determines the rate of excitation. Note that (Fig. 15):
- when the average separation between states is relatively high, as in H_2 , there are relatively few rotational states populated by collisions.

The LTE absorption cross section $\alpha_{in}^*(\nu)$ for an individual vibration-rotation line (denoted by i) can be written as:

$$\alpha_{in}^*(\nu) = \mathcal{S}_i \Phi_i(\nu) \quad (56)$$

where $\Phi_i(\nu)$ is a frequency-dependent line profile.

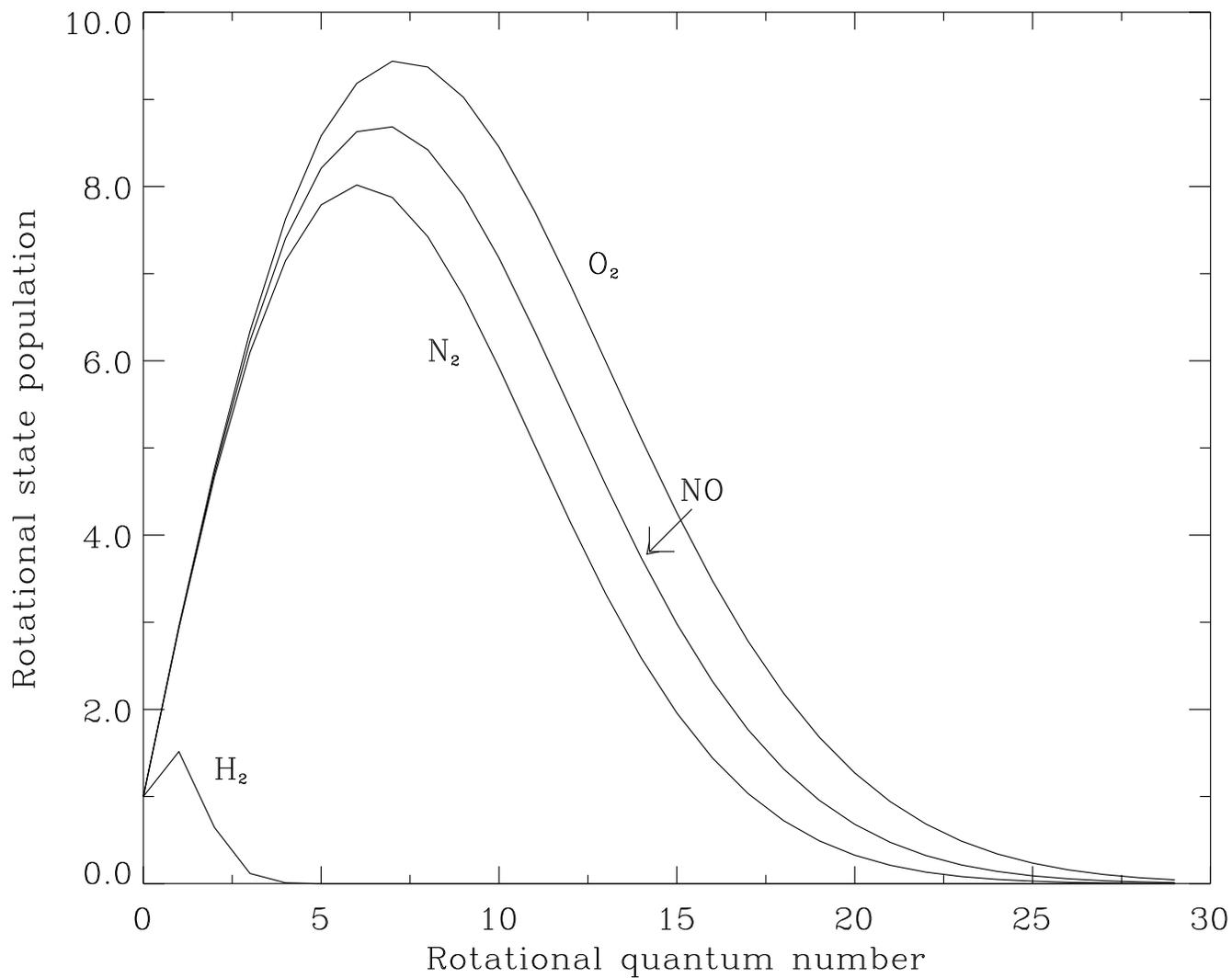


Figure 15: **Distribution of rotational energy with rotational quantum number J for the molecules O_2 , H_2 , N_2 , and NO , assuming $T = 250$ K.**

Line Strengths (4)

\mathcal{S}_i is the **line strength** of the i^{th} line $(v'', J'') \rightarrow (v', J')$ given by (double primes '' denote the lower state, and single primes ' denote the excited state):

$$\mathcal{S}_i = \int d\nu \alpha_{in}^*(\nu) \quad [\text{m}^2 \cdot \text{s}^{-1}] \quad (57)$$

where the frequency integration is over the width of a single line.

In tropospheric radiation problems, it is permissible to assume LTE, so that Eq. 32 applies: $k^*(\nu) = \frac{h\nu_0}{4\pi} \Phi(\nu) n_1^* B_{12} (1 - e^{-h\nu_0/k_B T})$. In this equation:

- the initial (absorbing) state in the generalization to a multi-level molecule is $n_1^* \rightarrow n(v'', J'')$. Also, we let $B_{12} \rightarrow B_i$, and $\nu_0 \rightarrow \nu_i$.

Thus, equating Eqs. 32 and 56, we find the following expression for the LTE absorption coefficient [$k^*(\nu) = \alpha^*(\nu)$ in this context, and $\alpha_i^*(\nu) = \alpha_{in}^*(\nu)n$]:

$$k^*(\nu) \rightarrow \alpha^*(\nu) = \frac{h\nu_i}{4\pi} \Phi_i(\nu) n(v'', J'') B_i (1 - e^{-h\nu_i/k_B T}) \equiv \mathcal{S}_i n \Phi_i(\nu). \quad (58)$$

ν_i denotes the central frequency of the line $h\nu_i = E(v', J') - E(v'', J'')$, the difference in energies of the two states connecting the transition i .

Line Strengths (5)

The notation $\Phi_i(\nu)$ reminds us that the line profile may depend upon the particular transition, i , and differ from line to line, and band to band, BUT:

- This variation is usually small and slowly-varying with frequency over lines within the same band.

Solving for the line strength, we find:

$$\mathcal{S}_i = \frac{h\nu_i}{4\pi} B_i \frac{n(v'', J'')}{n} (1 - e^{-h\nu_i/k_B T}). \quad (59)$$

Substitution from Eq. 54:

$$\frac{n(J)}{n} = \frac{(2J + 1)}{Q_r} \exp \left[-\frac{hcB_v}{k_B T} J(J + 1) \right]$$

for the population ratio of a rotational state yields:

$$\mathcal{S}_i = \frac{h\nu_i(2J'' + 1)}{4\pi Q_i} B_i \exp \left[-hcB_v J''(J'' + 1)/k_B T \right] (1 - e^{-h\nu_i/k_B T}). \quad (60)$$

In Eq. 60 we see the explicit dependence of the line strength on temperature through the Boltzmann distribution of initial-state populations.

Line Strengths (6)

So far we have assumed that transitions connect only a ground state with an excited state. BUT:

- absorption can originate from a higher vibrational state, which occurs for the so-called **hot-bands**.

Including the possibility of initial vibrational excitation, we have:

$$\mathcal{S}_i = \mathcal{S}_{io} \frac{Q_v(T_o)Q_r(T_o)}{Q_v(T)Q_r(T)} \frac{e^{-E_i''/k_B T} (1 - e^{-E_i/k_B T})}{e^{-E_i''/k_B T_o} (1 - e^{-E_i/k_B T_o})}. \quad (61)$$

The vibrational partition function, Q_v , is defined analogously to Q_r . E_i'' denotes the initial state energy, and:

- \mathcal{S}_{io} is simply the line strength obtained from Eq. 60 evaluated at the reference temperature T_o .

The result in Eq. 61 may be applied to any polyatomic molecule for which we know the various partition functions, line strengths and central line frequencies.

Line Strengths (7)

For standard tabulations, the temperature dependence of all the various terms are combined into the following semi-empirical expression:

$$\mathcal{S}_i = \mathcal{S}_{io} \left(\frac{T_o}{T} \right)^m \exp \left[-\frac{E_i''}{k_B} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right]. \quad (62)$$

Here m is a dimensionless quantity of order unity which serves as a fitting parameter. The strength of a line can be determined in two basic ways:

- (1) from quantum theoretical calculations, and
- (2) from laboratory measurements.

The first method requires rather accurate knowledge of the wave functions:

- a very difficult problem for polyatomic molecules.

The second method relies on use of the Extinction Law.

Line Strengths (8)

In practise, laboratory results which rely upon the **Extinction Law** are used:

- The Air Force Geophysics Laboratory provides an up-to-date listing of these parameters for atmospheric molecules, including spectroscopic data for seven major atmospheric absorbers: O₂, H₂O, CO₂, O₃, N₂O, CO, and CH₄.

The HITRAN spectroscopic database contains information of several hundred thousand lines. Included in the listing for each line are:

- ν_i , S_{io} , width of the line at standard sea-level pressure and reference temperature, and energy E_i'' of the lower state, etc.

A database such as HITRAN is extremely useful to atmospheric radiative transfer practitioners, because:

- it provides a well-accepted standard against which theory can be compared with data and with other theories.

Absorption Processes in the UV/Visible (1)

As we proceed upwards on the energy ladder from the infrared into the visible and UV:

- the spectroscopy becomes still more complex than previously discussed.

At these higher energies, electronic excited states become accessible. Absorption of a photon causes:

- an electron in an outer shell of the atom or molecule to be transferred to a higher electronic energy state.
- As in vibrational and rotational transitions, the *transfer is accompanied by a change in the electric dipole moment* of the atom or molecule.

In the simple Bohr atom picture of an atom as a miniature solar system:

- the electron “jumps” from its initial orbit (around the massive nucleus) to one of larger radius. Thus:
- a third type of energy must be added to the vibrational and rotational types previously considered.

Absorption Processes in the UV/Visible (2)

Electronic excited states are short-lived in comparison to vibrational or rotational states. If the transition is electric-dipole forbidden:

- the excited state lifetimes are much longer than electric dipole states, and are quenched by collisions well above the Earth's surface.

For example:

- the $O_2(0,1)$ A -band ($b-X$) with band origin at $12,969\text{ cm}^{-1}$ (seen as the absorption feature at 761 nm in Fig. 16) is quenched at about 40 km altitude.

Above this height:

- more of the absorbed radiative energy is promptly emitted as airglow emission, rather than ending up as thermal energy.
- High-spectral resolution measurements from space provide a sensitive probe of the temperature, density and wind fields in the mesosphere and lower thermosphere.

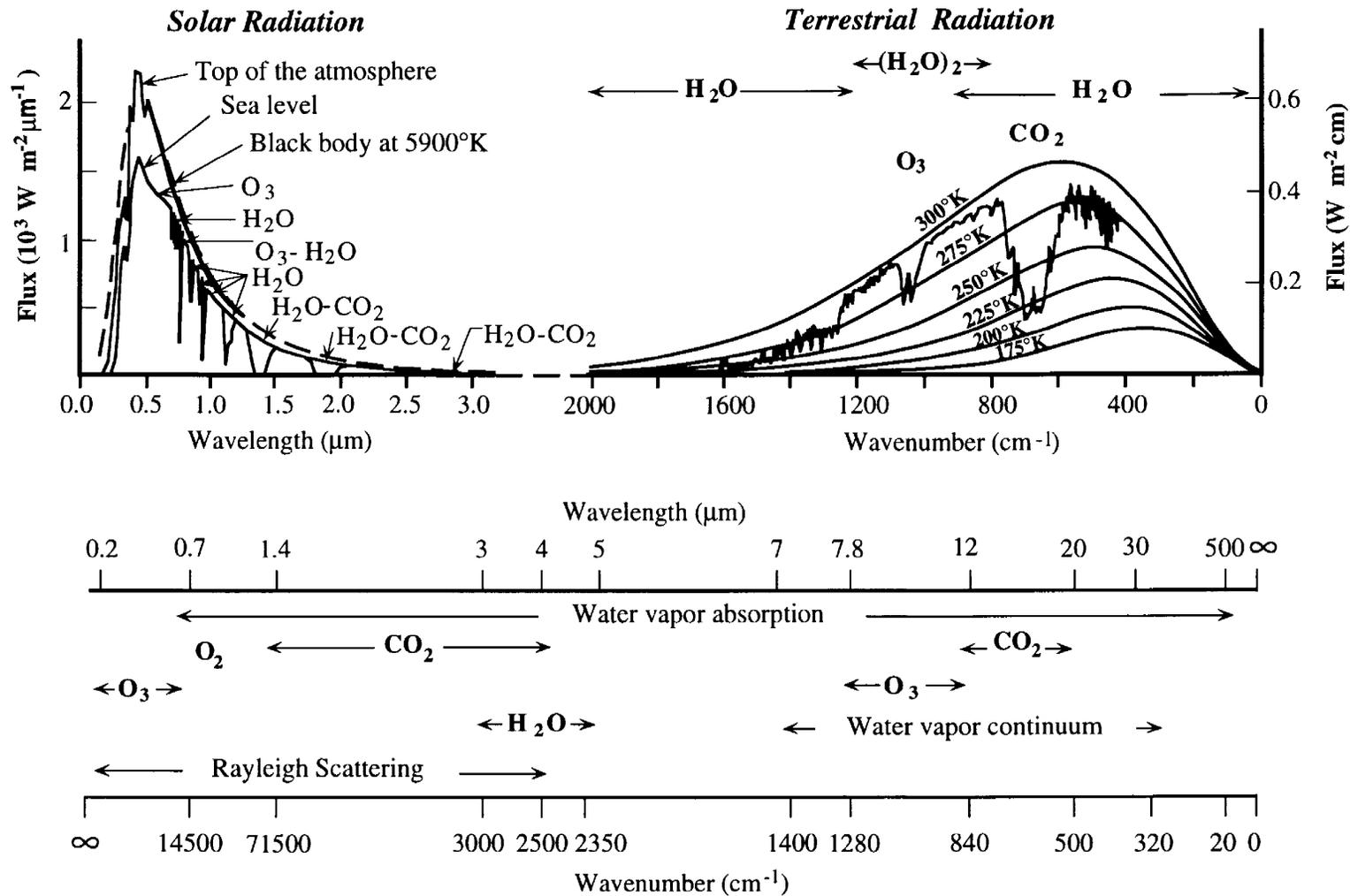


Figure 16: **Spectral distribution of solar and terrestrial radiation fields. Also shown are the approximate shapes and positions of the scattering and absorption features of the Earth's atmosphere.**

Absorption Processes in the UV/Visible (3)

Note that in the visible:

- Neither O₂ nor N₂ absorb appreciably because of the absence of accessible electronic states with energies down to middle-UV wavelengths.

In the UV:

- the **Herzberg continuum**, **Schumann-Runge** bands and **Schumann-Runge** continuum (see Fig. 17) all result in a breakup of the oxygen molecule into free oxygen atoms (O₂ → O + O).

Absorption in:

- the **Herzberg continuum** is a bound-free process which yields two ground-state oxygen atoms.

The **Schumann-Runge bands** are due to a bound-bound transition to discrete upper levels:

- Electrons in this excited state are subject to a “level-crossing” to a repulsive (unstable) electronic state. Thus:

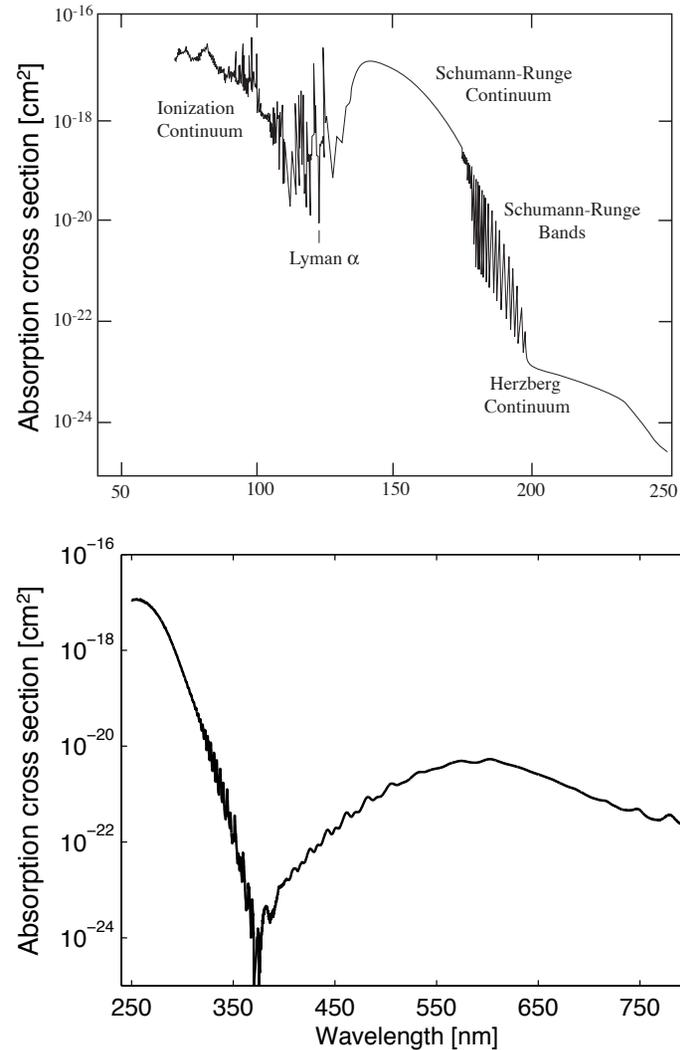


Figure 17: **Top panel: O₂ absorption cross section illustrating the various bands and continua. The deep absorption line at 121.6 nm corresponds almost exactly with the strong solar hydrogen Lyman- α line. Bottom panel: Absorption cross section for O₃. The strong UV feature is called the *Hartley bands*. The weaker visible quasi-continuum is the *Chappuis bands*.**

Absorption Processes in the UV/Visible (4)

- the upper state is very short-lived, and because of the uncertainty principle, the absorption lines are broadened beyond ordinary pressure broadening.
- The unstable O_2 state almost instantaneously converts into two ground state oxygen atoms, a process known as **pre-dissociation**.
- The **Schumann-Runge continuum** is a bound-free process resulting in dissociation of O_2 into two O-atoms: one in the ground-state $O(^3P)$ and the other in an electronically-excited state $O(^1D)$.

Another important example of a bound-free process is:

- the middle-UV **Hartley-band** absorption (see Fig. 17) of O_3 in which the molecule is fragmented into $O(^3P)$ and $O(^1D)$ products.

In contrast to these bound-free continuum processes:

- more structured spectra result from transitions between two discrete electronic levels (bound-bound processes). Because molecules also have vibrational and rotational energy, the result will be a **band system**.

Absorption Processes in the UV/Visible (5)

The total term value is approximately the sum of the **electronic** term value, T_e , the **vibrational** term value, G , and the **rotational** term value, F . Thus, the wavenumber of a transition is written as the difference of two term values**:

$$\tilde{\nu} = T' - T'' = (T'_e - T''_e) + (G' - G'') + (F' - F''). \quad (63)$$

For a given electronic transition, $\tilde{\nu}_e \equiv T'_e - T''_e$ is a constant. The remaining parts of Eq. 63 have forms similar to that for the vibration-rotation spectrum.

The essential difference is that:

- G' and G'' now belong to different vibrational term series with different values of ω_e and $\omega_e x_e$ (see Eq. 48):

$$\frac{E(v,J)}{hc} = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + B_v J(J + 1) - D_v J^2(J + 1)^2].$$

Similarly:

- F' and F'' belong to different rotational term series with different values of B_v and D_v (see Eq. 48).

K. Stamnes, G. E. Thomas, and J. J. Stamnes • STS-RT_ATM_OCN-CUP • April 2017

**As usual, we refer to the upper state with single-primed letters and the ground state with double-primed letters.

Absorption Processes in the UV/Visible (6)

Ignoring rotational “fine structure,” we can obtain a formula for the vibrational structure of an electronic band. Ignoring terms in T higher than v^2 , we obtain:

$$\tilde{\nu} = \tilde{\nu}_e + \omega'_e(v' + 1/2) - \omega'_e x'_e(v' + 1/2)^2 - \omega''_e(v'' + 1/2) - \omega''_e x''_e(v'' + 1/2)^2. \quad (64)$$

For electronic transitions there is no selection rule for the vibrational quantum number v . In principle, **each upper vibrational state:**

- can be combined with **each lower vibrational state.**

Thus:

- a host of vibrational bands (v', v'') will exist within the entire electronic **band system.**

The bands denoted by:

- $(v', 0)$, $(v', 1)$, etc. for a fixed v' are called **v' -progressions.**

The bands denoted by:

- $(0, v'')$, $(1, v'')$, etc. for a fixed v'' are called **v'' -progressions.**

Absorption Processes in the UV/Visible (7)

Another grouping of bands in which $\Delta v = v' - v''$ is a constant is called a **sequence**. Since ω_e and $\omega_e x_e$ are not very different between states:

- sequences are often grouped closely together in a spectrum.

At typical atmospheric temperatures, nearly **all molecules will be in their ground ($v'' = 0$) vibrational state**. Thus:

- absorption bands will exist normally only in a single v' -progression, with $v'' = 0$.

The formula for the wave number of the absorption line progressions is:

$$\tilde{\nu} = \tilde{\nu}_{00} + \omega_o v' - \omega'_o x'_o v'^2 + \dots \quad (65)$$

where $\tilde{\nu}_{00}$ is the term level of the (0,0) band. With increasing v' , the separations between successive vibrational levels approach the value zero, and then:

- a **continuous** term spectrum joins onto the series of discrete vibrational levels.
- This transition occurs at the wavelength corresponding to the dissociation energy of the molecule.

Absorption Processes in the UV/Visible (8)

An example of this transition point is at 175 nm where the structured **Schumann-Runge band** system converts to the smoothly varying **Schumann-Runge continuum** (see Fig. 17):

- This wavelength (175 nm) corresponds to the energy of dissociation plus the energy of the excited O(¹D) oxygen atom.

Most molecules of interest to us (CO₂, H₂O, O₃ and CH₄) are polyatomic molecules. A discussion of their electronic spectra is beyond our scope. BUT:

- many of the concepts discussed above for the diatomic molecule may be carried over directly, and as noted previously:
- **electronic transitions** involving these molecules (CO₂, H₂O, O₃ and CH₄) **are NOT important** for the energy balance of the lower atmosphere.
- However, they play critical roles in airglow, heating and ionization processes in the upper atmosphere.

Absorption Processes in the UV/Visible (9)

The electronic absorption bands (the **Chappuis** and **Hartley bands**) of O_3 are semi-continuous over reasonably large frequency intervals and thus:

- absorption obeys the **Extinction Law**.

For example:

- calculating the irradiance-weighted cross sections over 10 nm bins may yield errors in the ozone photodissociation rate profile of only a few %.

Fortunately, unless one is interested in airglow spectra:

- it is generally not required to master the spectroscopy of polyatomic electronic band spectra.

If necessary:

- one can resort to the empirical method if all the band positions and strengths are available from compilations, such as the HITRAN database.

Transmission in Spectrally-Complex Media (1)

We will now discuss more practical aspects of determining the transmission and radiative transfer within spectrally complex media.

- We first consider how radiation is transmitted through a medium characterized by absorption within a single, spectrally isolated line, and introduce the historically important quantity, the **equivalent width**.
- A generalization of this notion to include progressively more realistic absorption properties brings us to the various parameterizations of complex transmission processes, known as **molecular band models**.
- A large number of **such models** have been introduced over the years, all attempting to **replace a very messy transmission problem** with one or more **analytic functions** having a minimum number of parameters.
- These band parameters are derived from either comparisons with laboratory data or, since the advent of fast computers, with accurate line-by-line (LBL) computations.

Transmission in Spectrally-Complex Media (2)

Since these classical methods are limited in accuracy, and **cannot generally accommodate** the **simultaneous effects of scattering and absorption**:

- we focus on more **modern methods, with emphasis on** performing calculations for **realistic inhomogeneous gaseous media**.

There are two basic reasons why the absorption properties of a molecular gas depend very strongly upon wavenumber:

- The **line strengths can vary drastically** over a given band, and
- within a given line, the **absorption coefficient changes many orders of magnitude** over small wavenumber intervals.

Also, the radiation field itself will generally have strong spectral variations.

- At low spectral resolution **the solar radiation field** approximates a continuous spectrum. However:
- at higher resolution, it **reveals a rich structure** indicative of the physical conditions in the solar atmosphere.

Transmission in Spectrally-Complex Media (3)

The terrestrial IR radiation field has these same general characteristics consisting of:

- (1) a near-blackbody component emitted by the surface or the ocean; and
- (2) a more complicated component arising from the atmospheric emission due to the complex absorption properties of the medium through *Kirchoff's Law*.

Thermal emission is comparatively high at the centers of strong absorption lines, and low in the transparent spectral windows.

- Even though photons are emitted most copiously at line center, their mean free path can be very short. On the other hand:
- very few photons are emitted within the spectral window regions, yet they can be transmitted a long distance in the medium. Consequently:
- it is not obvious which frequencies contribute to a given quantity:
- if we truncate a spectral line wing too close to line center, an important part of the energy in the wings could be missed.

Transmission in Spectrally-Complex Media: Transmission in an Isolated Line (1)

We define the **spectral beam transmittance** $\mathcal{T}_b(\tilde{\nu})$ and **beam absorptance** $\alpha_b(\tilde{\nu})$ as the ratio of the transmitted radiance $I_T(\tau(\tilde{\nu}))$ or absorbed radiance $I_A(\tau(\tilde{\nu}))$ to the incident radiance I_0 :

$$\mathcal{T}_b(\tilde{\nu}) = \frac{I_T[\tau(\tilde{\nu})]}{I_0} = \exp[-\tau(\tilde{\nu})]; \quad \alpha_b(\tilde{\nu}) = \frac{I_A[\tau(\tilde{\nu})]}{I_0} = 1 - \mathcal{T}_b(\tilde{\nu}). \quad (66)$$

For a single line, the optical depth at wavenumber $\tilde{\nu}$ along the path $0 \rightarrow s$ is:

$$\tau(\tilde{\nu}, s) = \int_0^s ds' \mathcal{S}n(s')\Phi(\tilde{\nu}) \quad (67)$$

where \mathcal{S} is the (frequency-integrated) line strength in units of $[\text{m}^2 \cdot \text{s}^{-1}]$. Assuming a homogeneous optical path (e.g. a horizontal path), we have:

$$\tau(\tilde{\nu}, s) = \mathcal{S}\mathcal{N}\Phi(\tilde{\nu}) \quad (68)$$

where $\mathcal{N} = \int_0^s ds' n(s')$ is the column number $[\text{m}^{-2}]$ of absorbing molecules, assumed to be a single absorbing species. If we describe the path in terms of the **column mass**, u , the line strength is defined **per unit mass**, and:

$$\tau(\tilde{\nu}) = \mathcal{S}u\Phi(\tilde{\nu}) \equiv k(\tilde{\nu})u, \quad k(\tilde{\nu}) = \mathcal{S}\Phi(\tilde{\nu}).$$

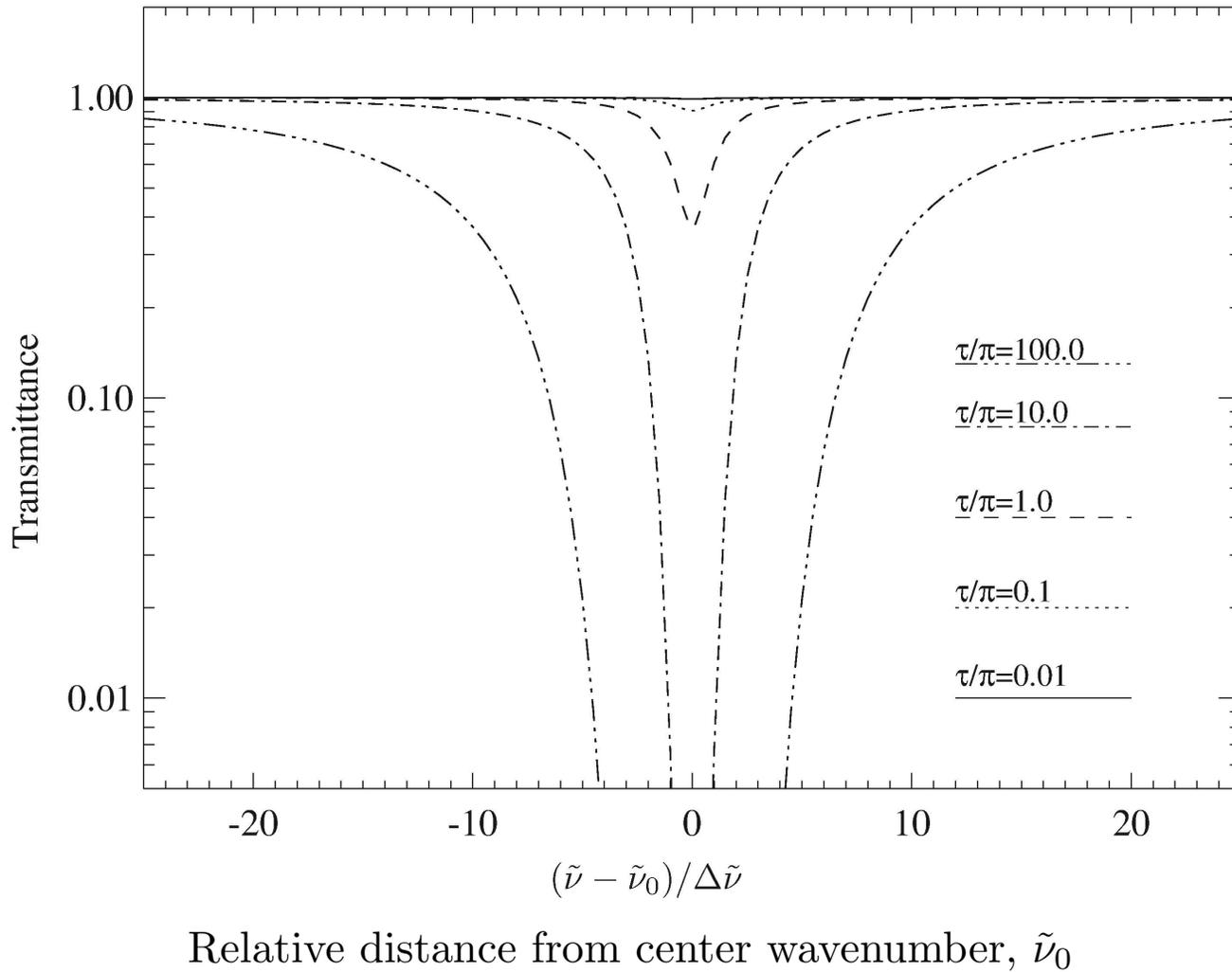


Figure 18: **Transmittance of a homogeneous medium having a Lorentz profile, of varying line-center optical depths, τ/π (0.01, 0.1, 1.0, 10.0, and 100.0). The transmittance is almost unity for $\tau/\pi = 0.01$ and decreases rapidly with increasing τ so that the line center is opaque for $\tau/\pi > 10$. When multiplied by the line half-width α_L , the area under the curve is called the equivalent width.**

Transmission in Spectrally-Complex Media:

Transmission in an Isolated Line (2)

Figure 18 illustrates what happens when a medium having a Lorentz profile is illuminated by a collimated beam, which has a flat, or ‘white’ spectrum:

- For small optical depths ($\tau(\tilde{\nu}) = \mathcal{S}u\Phi(\tilde{\nu}) = k(\tilde{\nu})u \ll 1$ for all $\tilde{\nu}$) the radiation at each wavenumber will be attenuated: shape of the absorption line $\propto \Phi(\tilde{\nu})u$.
- For larger u , the exponential in Eq. 66 will begin to be important, and the absorption will no longer be proportional to the optical depth.

The **mean beam absorptance** and **mean beam transmittance** for the spectral line are defined as:

$$\langle \alpha_b \rangle \equiv 1 - \langle \mathcal{T}_b \rangle \equiv \frac{1}{\Delta\tilde{\nu}} \int_{\Delta\tilde{\nu}} d\tilde{\nu} \alpha_b(\tilde{\nu}) = \frac{1}{\Delta\tilde{\nu}} \int_{\Delta\tilde{\nu}} d\tilde{\nu} [1 - e^{-\tau(\tilde{\nu})}] \equiv \frac{W}{\Delta\tilde{\nu}}. \quad (69)$$

The product $W = \langle \alpha_b \rangle \Delta\tilde{\nu} = \int_{\Delta\tilde{\nu}} d\tilde{\nu} [1 - e^{-\tau(\tilde{\nu})}]$ (defined here in units of wavenumber) is called the **equivalent width**: *the area between the horizontal line and the curve* in Fig. 19, which is **equal to the area of a rectangle with complete absorption inside, and zero absorption outside**.

Transmission in Spectrally-Complex Media: Transmission in an Isolated Line (3)

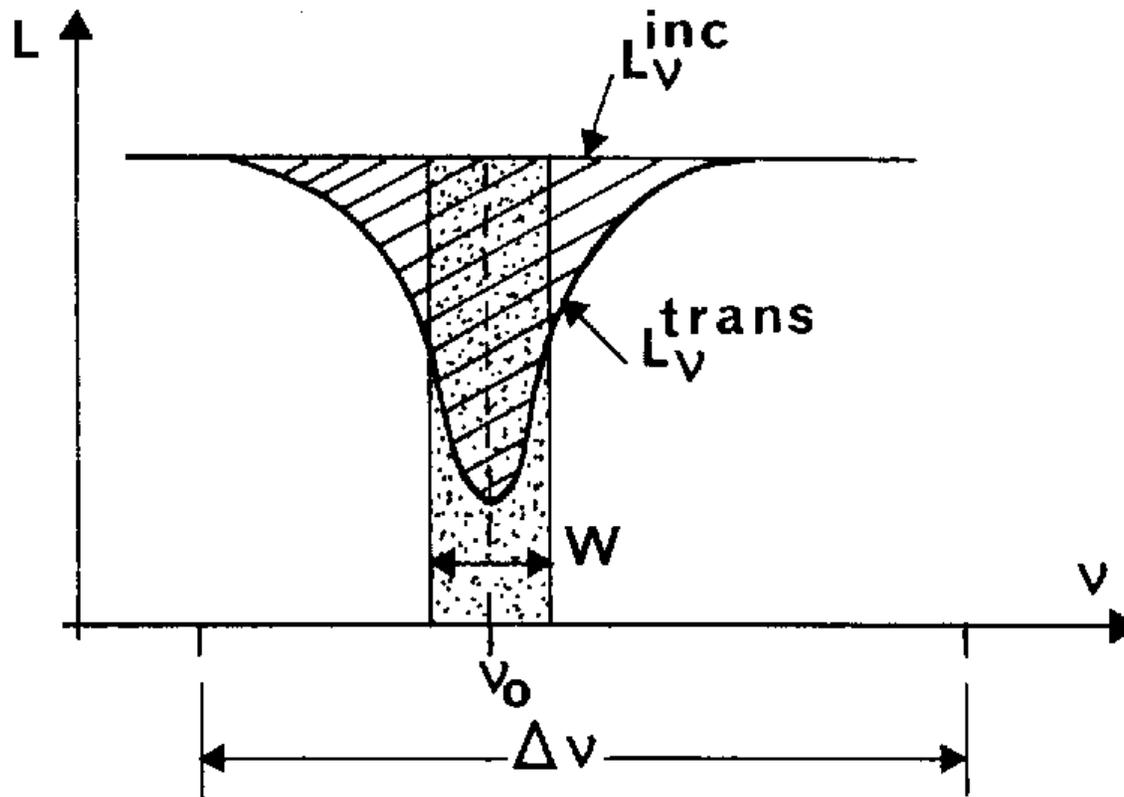


Figure 19: Schematic diagram illustrating the equivalent width. The dotted rectangular area is equal to the hatched area and represents the total energy absorbed in the line.

Transmission in Spectrally-Complex Media: Isolated Lorentz line (1)

Suppose the spectral profile is given by the Lorentz profile:

$$\Phi_L(\tilde{\nu}) = \frac{\alpha_L}{\pi[(\tilde{\nu} - \tilde{\nu}_0)^2 + \alpha_L^2]} \quad (70)$$

where α_L is the Lorentz half-width [cm^{-1}]. Setting $x \equiv (\tilde{\nu} - \tilde{\nu}_0)/\Delta\tilde{\nu}$, $y \equiv \alpha_L/\Delta\tilde{\nu}$, and introducing the dimensionless mass path $\tilde{u} \equiv \mathcal{S}u/2\pi\alpha_L$, we find that Eq. 69 [$\tau(\tilde{\nu}) = \mathcal{S}u\Phi(\tilde{\nu}) = ku$, where $k = \mathcal{S}\Phi(\tilde{\nu})$]:

$$\langle \alpha_b \rangle \equiv 1 - \langle \mathcal{T}_b \rangle \equiv \frac{1}{\Delta\tilde{\nu}} \int_{\Delta\tilde{\nu}} d\tilde{\nu} \alpha_b(\tilde{\nu}) = \frac{1}{\Delta\tilde{\nu}} \int_{\Delta\tilde{\nu}} d\tilde{\nu} [1 - e^{-\mathcal{S}u\Phi(\tilde{\nu})}]$$

for the mean beam absorptance becomes:

$$\langle \alpha_b(u) \rangle = \int_{-\infty}^{+\infty} dx \left[1 - \exp\left(-\frac{2\tilde{u}y^2}{x^2 + y^2}\right) \right]. \quad (71)$$

This integral can be evaluated in closed form:

$$\langle \alpha_b(u) \rangle = 2\pi y \tilde{u} e^{-\tilde{u}} [I_0(\tilde{u}) + I_1(\tilde{u})] \equiv 2\pi y L(\tilde{u}). \quad (72)$$

$L(\tilde{u}) = \tilde{u}e^{-\tilde{u}} [I_0(\tilde{u}) + I_1(\tilde{u})]$, called the **Ladenburg-Reiche function**, is expressed in terms of **Bessel functions**, I_n ($n = 0, 1$).

Transmission in Spectrally-Complex Media: Isolated Lorentz line (2)

First, let $\tilde{u} \ll 1$, the **weak-line limit**. Then $L(\tilde{u}) \approx \tilde{u}$ and:

$$\langle \alpha_b(u) \rangle \approx 2\pi y \tilde{u} = \frac{\mathcal{S}u}{\Delta\tilde{\nu}} \propto u \quad (\tilde{u} \ll 1). \quad (73)$$

Equation 73 tells us that in this optically thin limit, the **linear regime**, the mean beam absorptance is directly proportional to the column mass of absorbing molecules^{††} – **independent of the line broadening mechanism**.

In the **strong-line limit** $\tilde{u} \gg 1$, we can ignore the y^2 term in the denominator of Eq. 71 in comparison to x^2 :

$$\langle \alpha_b(u) \rangle \approx \int_{-\infty}^{+\infty} dx [1 - \exp(-2\tilde{u}y^2/x^2)] = 2y\sqrt{2\pi\tilde{u}} = \frac{2}{\Delta\tilde{\nu}}\sqrt{\mathcal{S}\alpha_L u} \propto \sqrt{u}. \quad (74)$$

This **square-root** or **saturated regime**, verified by numerous spectroscopic experiments, should be contrasted with the exponential **Extinction Law**, $1 - \langle \alpha_b \rangle = \exp(-ku)$, where $k = \mathcal{S}\Phi(\tilde{\nu})$ is a constant: *The departure of absorption from an exponential behavior is the most important mathematical complication of non-grayness.*

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^{††}In this limit, the exponential **Extinction Law** implies: $1 - \langle \alpha_b \rangle = \exp(-ku) \approx 1 - ku \implies \langle \alpha_b \rangle \propto u$.

Transmission in Spectrally-Complex Media: The Elsasser Band Model (1)

Consider a band with equally spaced lines. Imagine that the mass path is large enough to be in the **square-root regime**, but the **widths** of the absorption lines are **small** compared to the line separation:

- As the mass path increases, the effect of line overlap becomes substantial because of absorption in the far wings. Then the mean absorptance cannot continue to grow like \sqrt{u} :
- A further increase in u can produce only a small increase in mean absorptance, and eventually it comes to a halt as the entire band becomes “blacked-out.”
- These effects are described in the highly idealized **Elsasser band model**, which *approximates a band with a periodic pattern of lines of equal strength and of equal width.*
- At a given wavenumber $\tilde{\nu}$, it is necessary to consider that **all lines** in the band **contribute to the absorption** at that wavenumber.

Transmission in Spectrally-Complex Media: The Elsasser Band Model (2)

The Elsasser band assumes an **infinite** number of lines, all separated by the line spacing δ . For Lorentzian lines the mass absorption coefficient is written as:

$$\alpha_m(\tilde{\nu}) = \sum_{n=-\infty}^{n=+\infty} \frac{\mathcal{S}}{\pi} \frac{\alpha_L}{[(\tilde{\nu} - n\delta)^2 + \alpha_L^2]}. \quad (75)$$

Elsasser showed that this function is mathematically identical to the following periodic function of wavenumber:

$$\alpha_m(\tilde{\nu}) = \frac{\mathcal{S}}{\delta} \frac{\sinh(2\pi y)}{\cosh(2\pi y) - \cos 2\pi x} \quad (76)$$

where $x \equiv \tilde{\nu}/\delta$ and $y \equiv \alpha_L/\delta$. We may then evaluate the expression for the mean transmittance by averaging with respect to $x = \tilde{\nu}/\delta$ from $x = -1/2$ to $x = +1/2$ ($2\pi x \in [-\pi, \pi]$), that is, from the wavenumber of minimum absorption to maximum absorption, and back again. The beam transmittance is [Eq. 69: $\langle \mathcal{T}_b \rangle = \frac{1}{\Delta\tilde{\nu}} \int_{\Delta\tilde{\nu}} d\tilde{\nu} e^{-\tau(\tilde{\nu})}$, $\tau(\tilde{\nu}) = \mathcal{S}u\Phi(\tilde{\nu}) = 2\pi\alpha_L\tilde{u}\Phi(\tilde{\nu})$]

$$\langle \mathcal{T}_b(y, u) \rangle = \int_{-1/2}^{+1/2} dx \exp \left[-\frac{2\pi\tilde{u}y \sinh(2\pi y)}{\cosh(2\pi y) - \cos 2\pi x} \right]. \quad (77)$$

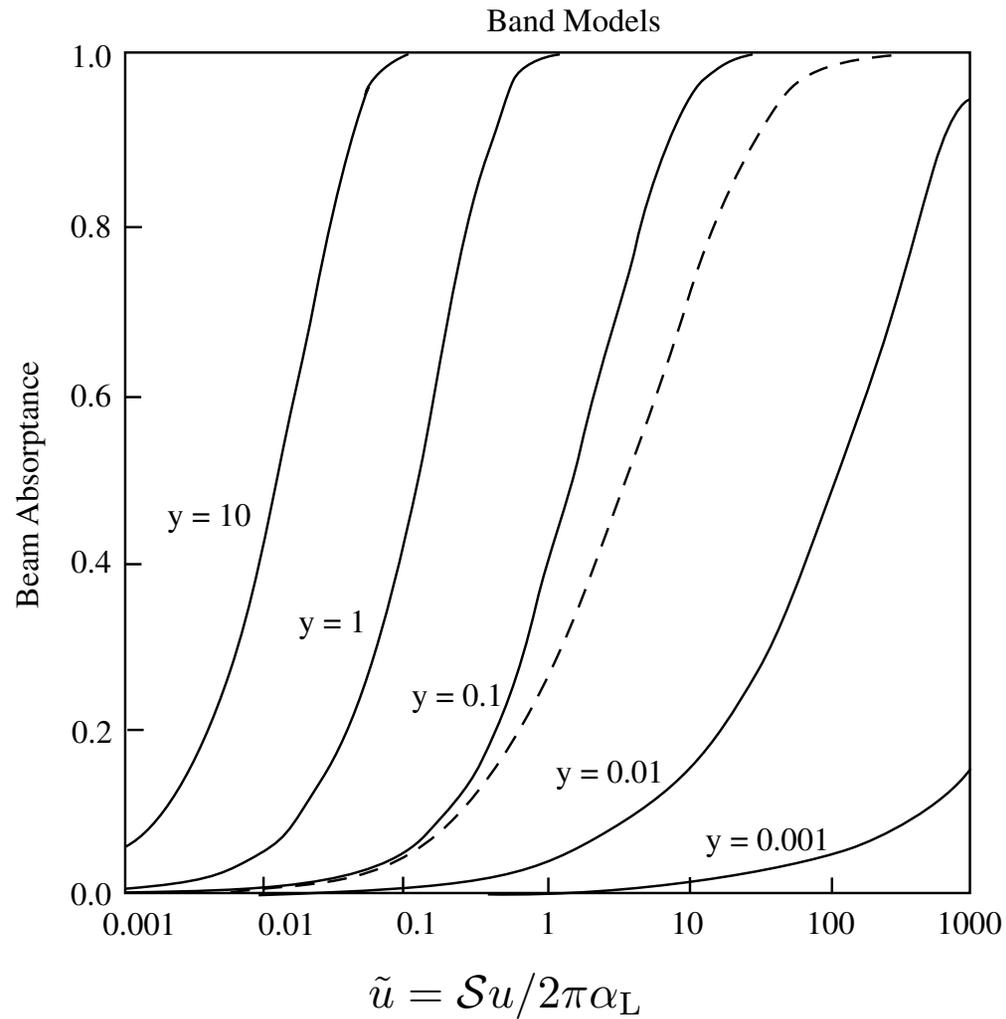


Figure 20: Mean beam absorbance, $\langle \alpha_b(y, u) \rangle$, versus absorber amounts \tilde{u} for the Lorentz-Elsasser model Eq. 77, solid lines) and the random-Lorentz-Malkmus model (shown only for $y = 0.1$, Eq. 89, dashed line). Each curve applies to a particular value of $y = \alpha_L / \Delta\tilde{\nu}$, the *grayness parameter*. For $y \gg 1$, the absorbance obeys the *Extinction Law* for a gray-absorbing medium.

Transmission in Spectrally-Complex Media: The Elsasser Band Model (3)

The beam absorptance for the Elsasser model, $\langle \alpha_b(y, u) \rangle = 1 - \langle \mathcal{T}_b(y, u) \rangle$, is plotted in Fig. 20 versus the dimensionless mass path $\tilde{u} \equiv \mathcal{S}u/2\pi\alpha_L$ for a variety of y -values; $y = \alpha_L/\Delta\tilde{\nu} = \alpha_L/\delta$ can be thought of as a **grayness parameter**:

- For small y , the behavior of the mean absorption departs radically from monochromatic absorption – at small \tilde{u} , only the line-centers absorb, and most radiation passes through the medium between the lines.
- For larger y , the regions between the lines begin to absorb strongly as the lines become saturated, thus accounting for the more pronounced dependence on \tilde{u} .
- For large y ($y \geq 10$), the lines completely overlap and the beam transmittance may be shown to be given by $\exp(-2\pi y\tilde{u}) = \exp(-\mathcal{S}u/\alpha_L)$, the **gray** limit.
- Another asymptotic region is the strong-line limit ($\tilde{u} \gg 1$) for which it may be shown that $\langle \alpha_b \rangle \approx \text{erf}[\pi y\sqrt{2\tilde{u}}]$, where erf denotes the **error function**.

Few bands in nature resemble the regular array visualized by Elsasser. However, this model has played an important role in the historical development of the subject.

Transmission in Spectrally-Complex Media: Distributed Line Radiances (1)

Real absorption spectra reveal that:

- line strengths are distributed over a wide range of values; and
line separations are also far from a constant, as assumed in the Elsasser model.

We first consider the situation of **an array of non-overlapping lines**. If we use an averaging interval which contains a large number of lines of varying strength:

- it is possible to define a continuous distribution function of line strengths, $p(\mathcal{S})$, such that the number of lines with strengths between \mathcal{S} and $\mathcal{S} + d\mathcal{S}$ is $p(\mathcal{S})d\mathcal{S}$.

For a single line:

$$\langle \alpha_b(u) \rangle = \frac{1}{\Delta\tilde{\nu}} \int_{\Delta\tilde{\nu}} d\tilde{\nu} [1 - e^{-\mathcal{S}u\Phi(\tilde{\nu})}].$$

Hence, in the limit of an infinite number of lines, the mean beam absorptance becomes:

$$\langle \alpha_b(u) \rangle = \int_0^\infty d\mathcal{S} p(\mathcal{S}) \int_{\Delta\tilde{\nu}} \frac{d\tilde{\nu}}{\Delta\tilde{\nu}} \{1 - \exp[-\mathcal{S}u\Phi(\tilde{\nu})]\}. \quad (78)$$

Transmission in Spectrally-Complex Media: Distributed Line Radiances (2)

Several analytic line-strength distributions are in use. Three of the most common are:

$$\textit{Exponential Distribution: } p(\mathcal{S}) = (1/\bar{\mathcal{S}}) \exp(-\mathcal{S}/\bar{\mathcal{S}}) \quad (79)$$

$$\begin{aligned} \textit{Godson Distribution: } p(\mathcal{S}) &= \bar{\mathcal{S}}/(\mathcal{S}_{max}\mathcal{S}) & (\mathcal{S} < \mathcal{S}_{max}) \\ p(\mathcal{S}) &= 0 & (\mathcal{S} > \mathcal{S}_{max}) \end{aligned} \quad (80)$$

$$\textit{Malkmus Distribution: } p(\mathcal{S}) = (1/\mathcal{S}) \exp(-\mathcal{S}/\bar{\mathcal{S}}), \quad (81)$$

where the average line strength is defined as:

$$\bar{\mathcal{S}} = \int_0^\infty d\mathcal{S} \mathcal{S} p(\mathcal{S}). \quad (82)$$

These distributions are normalized so that $\int_0^\infty d\mathcal{S} p(\mathcal{S}) = 1$. An additional distribution is the trivial one in which all values of \mathcal{S} collapse to a single value:

- the **δ -function distribution**, $p(\mathcal{S}) = \delta(\mathcal{S} - \bar{\mathcal{S}})$,

an example of which is the Elsasser band model.

Transmission in Spectrally-Complex Media:

Distributed Line Radiances (3)

Example 1: Absorptance in a Lorentz-Exponential Model

To illustrate the usefulness of the analytic \mathcal{S} -distributions, we derive an analytic expression for the beam absorptance. Assuming the exponential distribution (Eq. 79), and interchanging orders of integration in Eq. 78, we can carry out the inner integration analytically

$$\langle \alpha_b(u) \rangle = \frac{1}{\Delta\tilde{\nu}} \int_{\Delta\tilde{\nu}} d\tilde{\nu} \int_0^\infty \frac{d\mathcal{S}}{\bar{\mathcal{S}}} e^{-s/\bar{\mathcal{S}}} [1 - e^{-su\Phi(\tilde{\nu})}] = \frac{1}{\Delta\tilde{\nu}} \int_{\Delta\tilde{\nu}} d\tilde{\nu} \frac{\bar{\mathcal{S}}u\Phi(\tilde{\nu})}{1 + \bar{\mathcal{S}}u\Phi(\tilde{\nu})}. \quad (83)$$

Adopting a Lorentz profile for $\Phi(\tilde{\nu})$, Eq. 70: $\Phi_L(\tilde{\nu}) = \frac{\alpha_L}{\pi[(\tilde{\nu}-\tilde{\nu}_o)^2 + \alpha_L^2]}$, we may integrate analytically to obtain ($\tilde{u} = \bar{\mathcal{S}}u/2\pi\alpha_L$ and $y = \alpha_L/\Delta\tilde{\nu}$)

$$\langle \alpha_b(u) \rangle = \frac{\bar{\mathcal{S}}u/\Delta\tilde{\nu}}{\sqrt{1 + \bar{\mathcal{S}}u/\pi\alpha_L}} = \frac{2\pi y\tilde{u}}{\sqrt{1 + \tilde{u}/2}}. \quad (84)$$

To proceed further, we need to determine the numerical values for the parameters $\bar{\mathcal{S}}$ and $\bar{\mathcal{S}}/\alpha_L$. Both can be determined by requiring that the results match the accurate asymptotic expressions in the strong- and weak-line limits.

Transmission in Spectrally-Complex Media: Distributed Line Radiances (4)

Example 2: Absorptance in a Lorentz-Malkmus Model

Using the Malkmus distribution, Eq. 81:

$$p(\mathcal{S}) = (1/\mathcal{S}) \exp(-\mathcal{S}/\bar{\mathcal{S}})$$

we proceed as in Example 1, by interchanging orders of integration. The result for the beam absorptance is

$$\langle \alpha_b(u) \rangle = \frac{1}{\Delta\tilde{\nu}} \int_{\Delta\tilde{\nu}} d\tilde{\nu} \ln[1 + \bar{\mathcal{S}}\Phi(\tilde{\nu})u]. \quad (85)$$

Assuming a Lorentz profile: $\Phi(\tilde{\nu}) = \Phi_L(\tilde{\nu}) = \frac{\alpha_L}{\pi[(\tilde{\nu}-\tilde{\nu}_0)^2 + \alpha_L^2]}$, we integrate analytically to obtain ($\tilde{u} \equiv \mathcal{S}u/2\pi\alpha_L$):

$$\langle \alpha_b(u) \rangle = \frac{\pi\alpha_L}{2\Delta\tilde{\nu}} \left[\sqrt{1 + 4\bar{\mathcal{S}}u/\pi\alpha_L} - 1 \right] = (\pi y/2) [\sqrt{1 + 8\tilde{u}} - 1]. \quad (86)$$

Note that Eqs. 84 and 86 are *not* valid when lines overlap.

Transmission in Spectrally-Complex Media: Random Band Model (1)

In some irregular spectral bands (e.g. water vapor), the line positions appear to vary randomly over the spectrum: the **statistical, random, or Goody-Meyer band model** becomes useful.

Let the band interval of width $\Delta\tilde{\nu}$ consist of n lines of average separation δ , so that $\Delta\tilde{\nu} = n\delta$, and assume that the line positions are **uncorrelated**. Then:

- the transmission of the band can be written in terms of the products of the individual line transmittances, $\langle \mathcal{T}_i \rangle$ and absorptances $\langle \alpha_i \rangle$:

$$\langle \mathcal{T}_b \rangle = \langle \mathcal{T}_1 \rangle \langle \mathcal{T}_2 \rangle \cdots \langle \mathcal{T}_n \rangle = \left[\frac{1}{\Delta\tilde{\nu}} \int_{\Delta\tilde{\nu}} d\tilde{\nu} \int_0^\infty d\mathcal{S} p(\mathcal{S}) e^{-\mathcal{S}u\Phi(\tilde{\nu})} \right]^n = \left[1 - \frac{\langle \alpha_b \rangle}{n} \right]^n. \quad (87)$$

Taking the limit $n \rightarrow \infty$, and noting that $(1 - x/n)^n \rightarrow e^{-x}$, we find:

$$\langle \mathcal{T}_b(u) \rangle = e^{-\langle \alpha_b(u) \rangle}. \quad (88)$$

This result says that *the beam transmittance of randomly-placed overlapping lines is equal to the exponential of (minus) the non-overlapped single-line beam absorptance.*

Transmission in Spectrally-Complex Media: Random Band Model (2)

Applying this result to the Lorentz-Malkmus band model (Eq. 86):

$\langle \alpha_b(u) \rangle = \frac{\pi\alpha_L}{2\Delta\tilde{\nu}} \left[\sqrt{1 + 4\mathcal{S}u/\pi\alpha_L} - 1 \right] = (\pi y/2) [\sqrt{1 + 8\tilde{u}} - 1]$, we find:

$$\langle \mathcal{T}_b(u) \rangle = \exp \left[- \frac{\pi\alpha_L}{2\Delta\tilde{\nu}} \left\{ \sqrt{1 + \frac{4\mathcal{S}u}{\pi\alpha_L}} - 1 \right\} \right] = e^{-(\pi y/2)(\sqrt{1+8\tilde{u}}-1)} \quad (89)$$

where $y \equiv \alpha_L/\delta$ and $\tilde{u} \equiv \mathcal{S}u/2\pi\alpha_L$.

- Eq. 89 fits laboratory data and transmission “data” calculated from LBL calculations with very good accuracy. In particular: it better accounts for the weak lines (f. ex. in the H₂O 6.3 μm band) than does the random-exponential model.
- The curve of growth for this model is shown in Fig. 20 for $y = 0.1$ (dashed line) in order to compare with the Elsasser model. Note that for this value of y , the random model yields more transmission (less absorption) for all optical depths.
- The enhanced transmission is due to the occasional wide gap occurring in the random model that is not present in regular-array models. The **random-Malkmus model** (Eq. 89) is one of the **best** all-round analytic band models.

MODTRAN: A moderate resolution band model (1)

This computer code was devised to:

- be efficient, user-friendly, upgradeable, well maintained, and readily available to the community;
- provide the user with the means to quickly evaluate atmospheric transmittance for a large variety of user-specified atmospheric conditions.

The curve of growth^{‡‡} is modeled by MODTRAN as arising from

- n_s identical strong lines of strength S_s , and
- n_w identical weak lines of strength $S_w \leq S_s$.

Moment equations of the true and pseudo distributions are matched to determine the temperature-dependent line strengths and their number:

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^{‡‡}The increase in spectral bin integrated absorptivity (one minus transmittance) as a function of molecular column amount, see Fig. 20.

MODTRAN: A moderate resolution band model (2)

$$n_s S_s^{1/3} + n_w S_w^{1/3} = \sum_{J=1}^N \mathcal{S}_J^i(T)^{1/3} \quad n_s S_s^{2/3} + n_w S_w^{2/3} = \sum_{J=1}^N \mathcal{S}_J^i(T)^{2/3} \quad (90)$$

$$n_s S_s + n_w S_w = \sum_{J=1}^N \mathcal{S}_J^i(T) \quad n_s S_s^{4/3} + n_w S_w^{4/3} = \sum_{J=1}^N \mathcal{S}_J^i(T)^{4/3}. \quad (91)$$

Traditional absorption coefficient $\langle \frac{S}{d} \rangle$ and line spacing $\langle \frac{1}{d} \rangle$ band model parameters are stored on a grid of temperatures:

$$\left\langle \frac{S}{d} \right\rangle_s = \frac{n_s S_s}{\Delta \tilde{\nu}}; \quad \left\langle \frac{1}{d} \right\rangle_s = \frac{n_s}{\Delta \tilde{\nu}}; \quad \left\langle \frac{S}{d} \right\rangle_w = \frac{n_w S_w}{\Delta \tilde{\nu}}; \quad \left\langle \frac{1}{d} \right\rangle_w = \frac{n_w}{\Delta \tilde{\nu}}.$$

\mathcal{S}_J^i is the line strength of the J^{th} line of a specific molecule in wavenumber bin i at temperature T :

- The line strengths \mathcal{S}_J^i are scaled from the HITRAN database using $\mathcal{S}_i = \mathcal{S}_{i0} \left(\frac{T_0}{T}\right)^m \exp\left[-\frac{E_i''}{k_B}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$ with a reference temperature of 296 K.
- In versions of MODTRAN prior to MODTRAN5, $\Delta \tilde{\nu}$ was 1.0 cm^{-1} . In MODTRAN5 and MODTRAN6, the band model parameters were reformulated to increase the resolution to 0.1 cm^{-1} , and user-specified bandwidth options of 0.1, 1.0, 5.0, or 15.0 cm^{-1} are available.

MODTRAN: A moderate resolution band model (3)

Computation of the transmittance across a bin involves four steps:

1. The Voigt line shape of an “average” line is integrated over the $\Delta\tilde{\nu}$ [cm⁻¹] bandwidth (bin) interval.
2. If a bin contains more than one line of a given species, the **lines are assumed to be randomly distributed** with statistical overlap.
3. The contribution from lines with centers in nearby bins is calculated as a molecular “continuum” component.
4. The H-C-G approximation (see Appendix I, §I.1) is used to replace an inhomogeneous path with a homogeneous one by using average values for the band model parameters.

For a finite number of lines within a spectral interval $\Delta\tilde{\nu}$, the transmittance is:

$$\langle \mathcal{T}_b \rangle = \langle \mathcal{T}(S_s u, \alpha_L, \alpha_D) \rangle^{n_s} \langle \mathcal{T}(S_w u, \alpha_L, \alpha_D) \rangle^{n_w}, \quad (92)$$

where $\langle \mathcal{T}(S u, \alpha_L, \alpha_D) \rangle$ is the mixed Lorentz–Doppler single-line transmittance, computed with Doppler and line-strength weighted Lorentz spectral bin half-widths, α_D and α_L , respectively.

MODTRAN: A moderate resolution band model (4)

The single-line transmittances are computed from

$$\langle \mathcal{T}(Su, \alpha_L, \alpha_D) \rangle = \int_{\Delta\tilde{\nu}} d\tilde{\nu} \exp[-\mathcal{S}u\Phi_V(\tilde{\nu})], \quad (93)$$

where the Voigt profile $\Phi_V(\tilde{\nu})$ (see §3.3.3) is centered within the spectral bin.

Equation 92 works well with the narrow (0.1, 1.0, 5.0, or 15.0 cm^{-1}) MODTRAN spectral bins for the following reasons:

1. In much of the visible through IR spectral region, **a single molecular species is the dominant absorption** source.
2. Where overlap between strong molecular bands of two species does occur, H_2O is generally one of the species.
3. The H_2O transition frequency and line-strength distributions appear quite randomly within narrow spectral bins.

Therefore, **the correlation of H_2O absorption with the absorption from overlapping molecular species is well represented as random**. Furthermore, when moderate spectral resolution results are sought, **spectral averaging of the relatively fine resolution MODTRAN values tends to stochastically cancel statistical variations**.

MODTRAN: A moderate resolution band model (5)

For mixed Lorentz-Doppler absorption, the single-line equivalent width $\langle\alpha_b\rangle\Delta\tilde{\nu}$ is computed from:

$$\langle\alpha_b\rangle\Delta\tilde{\nu} = \Delta\tilde{\nu}[1 - \langle\mathcal{T}_b\rangle] = \int_{\Delta\tilde{\nu}} d\tilde{\nu} [1 - e^{-Su\Phi_V(\tilde{\nu})}] \quad (94)$$

where $\Phi_V(\tilde{\nu})$ is the Voigt profile.

- The contributions from lines located in the wing interval outside of a given bin but within $\pm 25 \text{ cm}^{-1}$ are computed separately.
- The MODTRAN6 code has been restructured towards a modular, object-oriented architecture to simplify upgrades.
- It includes **a line-by-line algorithm for high-resolution RT calculations** as well as algorithms to take into account the effects of aerosols and clouds.

MODTRAN: A moderate resolution band model (6)

Unfortunately, most band models are incompatible with the requirements for “quasi-monochromatic” treatment of multiple scattering. Thus:

- inclusion of multiple scattering requires the use of methods like the k -distribution approach (to be discussed next).
- The MODTRAN code, which has a “fixed-wavenumber” sampling, is assumed to be “quasi-monochromatic” and therefore automatically compatible with multiple scattering treatments.
- The original two-stream algorithm for multiple scattering in MODTRAN has been replaced by the more accurate DISORT algorithm (Chapter 9).
- This “quasi-monochromatic” treatment of multiple scattering in MODTRAN seems to work well.
- The MODTRAN code is far too “expensive” to use in global climate models, and is most suitable for one-dimensional models.
- However, it is a most valuable tool for testing of simpler, inexpensive radiative transfer codes developed for use in global climate models.

Spectral Mapping Transformations for Homogeneous Media: the k -distribution Method (1)

Despite a great deal of effort and mathematical ingenuity expended on band models over the past sixty years or so:

- they still have definite limitations, given the necessity in modern climate models to obtain irradiances and heating rates to 1% accuracy. BUT
- Fortunately, it is now possible to calculate these quantities by “brute-force” line-by-line (LBL) methods to 0.1% accuracy (assuming perfect spectroscopic parameters).
- Since the heating rates must be computed at nearly every grid point of a General Circulation Model (GCM), LBL calculations represent significant computational demands even on modern supercomputers. Thus:
- LBL results are most useful as a standard of comparison for less accurate, but much more efficient algorithms.
- An approach that has received much attention is the k -**distribution** and its associated **correlated k -distribution** method.

Spectral Mapping Transformations for Homogeneous Media: the k -distribution Method (2)

These methods:

- provides much better accuracy than the conventional band models, and yet require two to three orders of magnitude less computer time than LBL methods;
- can accommodate multiple scattering in a straightforward manner. An LBL calculation is needed to derive the parameters. BUT:
- since the simplified calculations are then repeated many times over, the cost-savings can be substantial.

Consider a spectral interval $\Delta\tilde{\nu} = \tilde{\nu}_1 - \tilde{\nu}_2$: large enough to contain a significant number (say > 20) of spectral lines, but small enough that the Planck function is essentially constant over $\Delta\tilde{\nu}$. The beam transmittance over a homogeneous mass path u is:

$$\langle \mathcal{T}_b(u) \rangle = \frac{1}{\Delta\tilde{\nu}} \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} d\tilde{\nu} e^{-k(\tilde{\nu})u} \quad (95)$$

where $k(\tilde{\nu}) = \mathcal{S}\Phi(\tilde{\nu})$ denotes the mass extinction coefficient, which is equal to the mass absorption coefficient for a purely-absorbing medium.

Spectral Mapping Transformations for Homogeneous Media: the k -distribution Method (3)

To compute $\langle \mathcal{T}_b(u) \rangle$ accurately using the above form would require:

- division of the spectral interval $\Delta\tilde{\nu}$ into sub-intervals $\delta\tilde{\nu}$ small enough so that $k(\tilde{\nu})$ is essentially constant.
- Such a fine division would require $\delta\tilde{\nu}$ to be $\approx 10^{-3} - 10^{-5} \text{ cm}^{-1}$, which requires a total of $\Delta\tilde{\nu}/\delta\tilde{\nu} \approx 10^4 - 10^6$ spectral points for a small part (say 10 cm^{-1}) of the spectrum, which:
- must be repeated over the entire band, for all absorption bands and over the full range of mass path u . Also:
- it must be repeated for the range of pressures and temperatures encountered in the atmosphere.
- Clearly, this kind of “frontal attack” is computationally prohibitive.

A more efficient approach involves a transformation of Eq. 95 based on the recognition that **the same value of $k(\tilde{\nu})$ is encountered many times over in the spectral interval $\Delta\tilde{\nu}$.**

Spectral Mapping Transformations for Homogeneous Media: the k -distribution Method (4)

If we were to combine, or bin, all the values of $k(\tilde{\nu})$ into groups, and perform the transmittance calculation only once for a given value of k , then

- we could eliminate all the redundancy of Eq. 95: $\langle \mathcal{T}_b(u) \rangle = \frac{1}{\Delta\tilde{\nu}} \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} d\tilde{\nu} e^{-k(\tilde{\nu})u}$.
- Furthermore: if we order the groups into monotonically increasing values of k , we will obtain a much-more “orderly” function $f(k)$ which has more desirable characteristics than the wildly varying $k(\tilde{\nu})$.

Choosing an interval Δk , which is suitably small, the k -**distribution** can be formally defined by the following grouping algorithm:

$$f(k) \equiv \frac{1}{\Delta\tilde{\nu}} \sum_{\ell=1}^M \left| \frac{d\tilde{\nu}}{dk} \right| W_{\ell}(k). \quad (96)$$

- Here $W_{\ell}(k)$ is the “window” function, equal to unity when $k_{min}^{\ell} \leq k \leq k_{max}^{\ell}$, and zero otherwise.
- M is the number of monotonically varying wavenumber sub-intervals in which the absorption coefficient switches from increasing to decreasing values.

Spectral Mapping Transformations for Homogeneous Media: the k -distribution Method (5)

- In the l th sub-interval, the absorption coefficient varies from k_{min}^l to k_{max}^l . The absolute value of the derivative is taken, because we want to count the value whether or not k is increasing or decreasing with wavenumber.

Note that k is considered to be a continuous variable.

Eq. 95: $\langle \mathcal{T}_b(u) \rangle = \frac{1}{\Delta\tilde{\nu}} \int_{\tilde{\nu}_1}^{\tilde{\nu}_2} d\tilde{\nu} e^{-k(\tilde{\nu})u}$ can then be rewritten as a finite sum:

$$\langle \mathcal{T}_b(u) \rangle \approx \sum_{j=1}^N \Delta k_j f(k_j) e^{-k_j u} \quad (97)$$

where N is the total number of monotonic sub-intervals over the entire range of k -values. In the limit of $\Delta k \rightarrow 0$ (assuming that the number of lines is always large within Δk), the above sum becomes an integral:

$$\langle \mathcal{T}_b(u) \rangle = \int_{k_{min}}^{k_{max}} dk f(k) e^{-ku} \quad (98)$$

where k_{min} and k_{max} are the minimum and maximum values of k over the entire spectral interval, $\Delta\tilde{\nu}$.

Spectral Mapping Transformations for Homogeneous Media: the k -distribution Method (6)

It is clear that if we sum $f(k)$ over all binned values of k , we should get unity, that is:

$$\sum_{j=1}^N f(k_j)\Delta k_j = 1, \quad \text{or for } \Delta k_j \rightarrow 0, \quad \int_{k_{min}}^{k_{max}} dk f(k) = 1. \quad (99)$$

If we sum the distribution up to some value of $k_n < k_{max}$, we may define the **cumulative k -distribution** as:

$$g(k_n) \equiv \sum_{j=1}^n f(k_j)\Delta k_j, \quad \text{or for } \Delta k_j \rightarrow 0, \quad g(k) = \int_0^k dk' f(k'). \quad (100)$$

We can now write Eqs. 97 and 98 as:

$$\langle \mathcal{T}_b(u) \rangle \approx \sum_{j=1}^N e^{-k_j u} \Delta g_j, \quad \text{or for } \Delta k_j \rightarrow 0, \quad \langle \mathcal{T}_b(u) \rangle = \int_0^1 dg e^{-k(g)u}. \quad (101)$$

Note that the upper limit of unity is consistent with g being a cumulative k -distribution, that is, the total number of k -values **smaller than k** .

Spectral Mapping Transformations for Homogeneous Media: the k -distribution Method (7)

Writing out Eq. 101 as:

$$\langle \mathcal{T}_b(u) \rangle \approx \Delta g_1 e^{-k_1 u} + \Delta g_2 e^{-k_2 u} + \dots + \Delta g_N e^{-k_N u} \quad (102)$$

we see that we have an approximation to the transmittance as a **weighted sum of monochromatic transmittances**.

- This approximation is known as the **exponential-sum fit transmittance** or ESFT approximation. Clearly:
- the EFST approximation reduces the non-gray problem to a finite number of gray problems for which we have many computational tools.
- If we knew the transmittance measured in the laboratory under low-spectral resolution, or had access to LBL calculations of $\langle \mathcal{T}_b(u) \rangle$, we could in principle perform a non-linear least-squares fit of Eq. 102 to the “data” to yield the “coefficients” of the fit $(\Delta g_1, \Delta g_2, \dots; k_1, k_2, \dots)$ at any desired accuracy.

Unfortunately, this problem is mathematically ill-posed, and special analysis techniques must be applied for this method to be practical.

Spectral Mapping Transformations for Homogeneous Media: the k -distribution Method (7)

- Fortunately, the current availability of accurate synthetic absorption spectra (see Fig. 21) means that we can compute the k -distribution directly, and:
- the coefficients of the EFST approximation may be determined without least-squares fitting, simply by numerical integration.
- It is a straightforward, but time-consuming, task for the computer to construct sorted tables of absorption coefficients to derive $f(k)$ and $g(k)$ from say, a spectroscopic database (such as HITRAN).
- The **inverse k -distribution** $k(g)$ is also needed in order to perform spectral mapping.
- An “inverse table” of k versus g is easily constructed by computer methods.
- Examples of numerical determinations of $f(k)$, $g(k)$ and $k(g)$ are shown in Fig. 21.

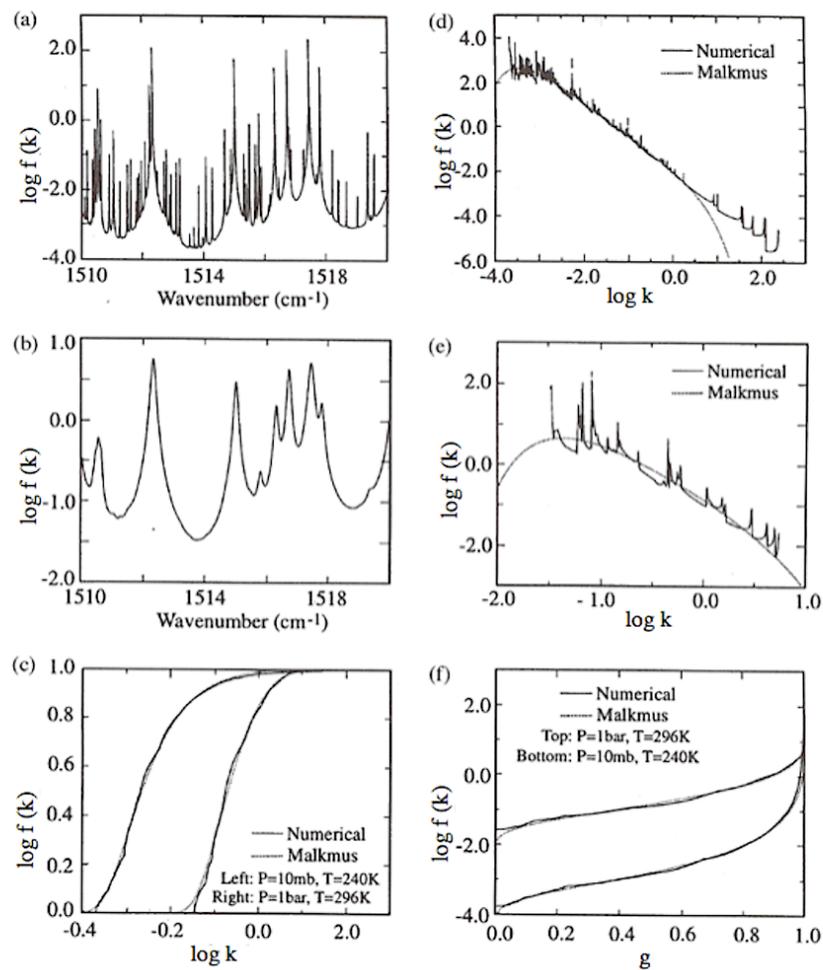


Figure 21: Absorption coefficient spectrum for the 1510–1520 cm^{-1} portion of the 6.3 μm water vapor band. (a) Line-by-line absorption coefficients for a pressure of 10 mbar and temperature 240 K and (b) for a pressure of 1 bar and temperature 296 K. The spectra utilize the HITRAN 1982 atmospheric line compilation and include 141 lines with absorption contributions from outside of the interval within a 5 cm^{-1} Lorentz wing cutoff limit. (c) Cumulative frequency distributions of the absorption coefficient spectra (a) and (b). (d) and (e) Absorption coefficient frequency distributions corresponding to absorption spectra in (a) and (b). (f) The k -distributions for the absorption coefficient spectra in (a) and (b). Malkmus band model equivalents, obtained to provide the best fit to line-by-line transmission, are shown by dashed lines.

Spectral Mapping Transformations for Homogeneous Media: k -distribution for the Malkmus band model

Can we derive analytic expressions for $f(k)$, given analytic band-model representations of $\langle \mathcal{T}_b(u) \rangle$? To this end we examine a limiting form of Eq. 98: $\langle \mathcal{T}_b(u) \rangle = \int_{k_{min}}^{k_{max}} dk f(k) e^{-ku}$ where we set the limits of integration on k equal to $(0, \infty)$:

$$\langle \mathcal{T}_b(u) \rangle = \int_0^\infty dk f(k) e^{-ku} = \mathcal{L}f(k) \quad (103)$$

where \mathcal{L} denotes the *Laplace transform*. We may find $f(k)$ provided the **inverse Laplace transform** of $\langle \mathcal{T}_b(u) \rangle$ exist:

$$f(k) = \mathcal{L}^{-1} \langle \mathcal{T}_b(u) \rangle. \quad (104)$$

The inverse transform exists in analytic form for the statistical-Malkmus model:

$$f(k) = (1/2)k^{-3/2} \sqrt{\mathcal{S}y/2\pi} \exp \left[(y/8) \left(2 - \frac{\mathcal{S}}{k} - \frac{k}{\mathcal{S}} \right) \right]. \quad (105)$$

If $y = 2\alpha_L/\Delta\tilde{\nu}$ is large, we have broad, overlapping lines: the distribution becomes gray ($k = \text{constant}$). If y is small, the line overlap is less: smaller k -values will appear in the absorption minimum (the spectral ‘window’) between adjacent lines. The cumulative distribution can also be determined in closed form (see Fig. 21).