Winter Quarter 2014

Atmospheric Sciences 532: Atmospheric Radiation I

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office hours to be arranged

COURSE OUTLINE

1. Introduction.
   - Composition and thermal structure of Earth's atmosphere
   - Vertical distribution of greenhouse gases
   - Solar and terrestrial radiation spectra
   - Distribution of solar radiation with season and latitude
2. Fundamentals of radiation
   - Radiation nomenclature and units: radiance, irradiance, intensity, flux, absorption coefficients, emissivity, optical depth, Beer's law
   - Radiative transfer equation
   - Blackbody radiation laws: Planck, Kirchhoff, Stefan-Boltzmann, Wien, Rayleigh-Jeans
   - Local thermodynamic equilibrium (LTE); non-LTE. Einstein relations, statistical equilibrium equation
   - Solution of longwave radiative transfer equation (Schwarzschild's equation)
   - Radiative equilibrium temperature distribution
   - Describe models for project
3. Absorption and emission of radiation by gases
   - Kinetic theory of gases
   - Molecular energy levels; electronic, vibrational, rotational transitions.
   - Spacing of lines.
   - Spectra of carbon dioxide, ozone, and water vapor. Water-vapor continuum.
   - Line shapes: natural, Doppler, pressure (collision) broadening.
   - Absorption by non-overlapping Lorentz lines: equivalent width
4. Absorption by bands of spectral lines.
   - Frequency-averaging of transmission. Band models; k-distributions
   - Pressure-averaging of transmission.
   - Angular-averaging of transmission. Exponential integrals, diffusivity factor
5. Applications
   - Radiation and climate
   - Remote sensing

ASSIGNMENTS
Homework: approximately 8 problem sets. 65%
Term project, 35%

The term project is to use an existing longwave radiative-transfer model to compute infrared radiation fluxes and cooling rates in the atmosphere. The model will be used to examine the effects of changing temperature and humidity profiles, and the vertical distribution of greenhouse gases (CO_2, O_3, CH_4, . . .) and the effect of clouds at various heights.

***TEXTBOOK** to purchase*

Petty, G.W., 2006: A First Course in Atmospheric Radiation. Sundog Publishing.

***TEXTBOOKS** (on reserve in Engineering Library)*

Thomas, G.E., and K. Stamnes, 1999: Radiative Transfer in the Atmosphere and Ocean. Cambridge Univ. Press.

Liou, K.N., 2002: An Introduction to Atmospheric Radiation, second edition. Academic Press.

Bohren, C.F., and E.E. Clothiaux, 2006: Fundamentals of Atmospheric Radiation. Wiley.

Houghton, J.T., 2002: The Physics of Atmospheres, third edition. Cambridge Univ. Press.

***REFERENCE BOOKS** (also on reserve in Engineering Library)*

Barrow, G.M., 1962: Introduction to Molecular Spectroscopy. McGraw-Hill.

Goody, R.M., and Y. Yung, 1989: Atmospheric Radiation, second edition. Oxford Univ. Press.

Menzel, D.H. (Ed.), 1966: Selected Papers on the Transfer of Radiation. Dover.

Paltridge, G.W., and C.M.R. Platt, 1976: Radiation Processes in Meteorology and Climatology. Elsevier.

Sears, F.W., and G.L. Salinger, 1975: Thermodynamics, Kinetic Theory, and Statistical Thermodynamics. Addison-Wesley.

BARROW, 1962: INTRODUCTION TO MOLECULAR SPECTROSCOPY

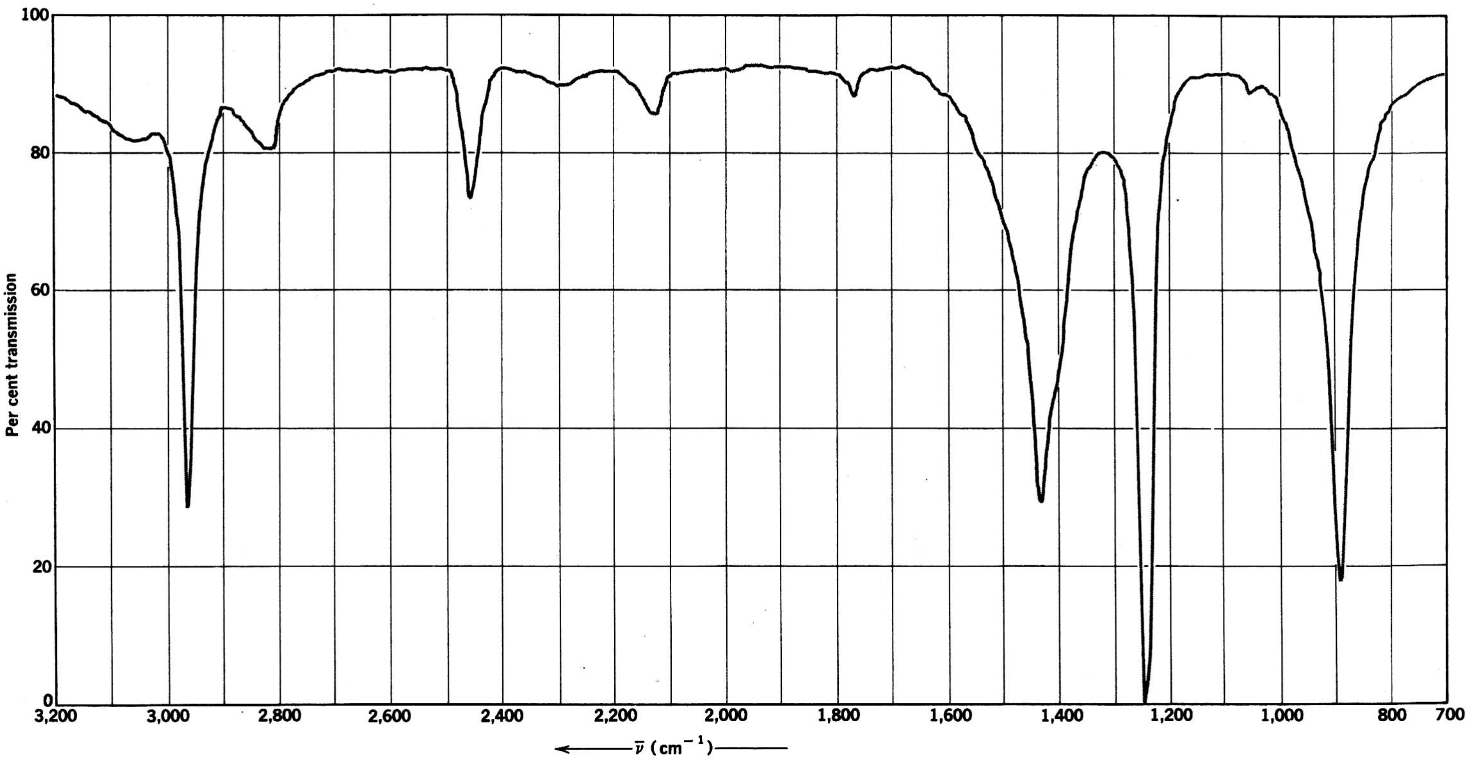


FIG. 7-1*a* The infrared spectrum of CH_3I as a liquid.

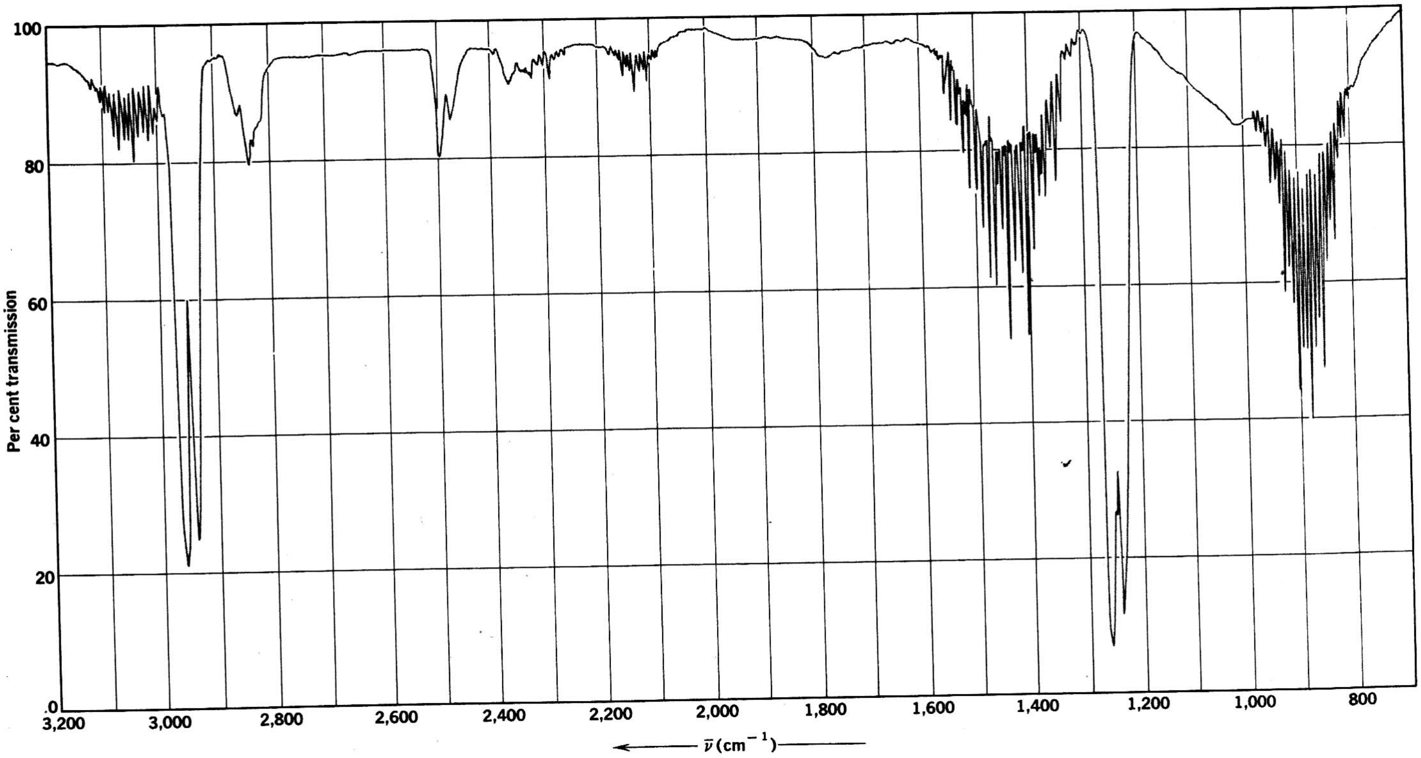


FIG. 7-1*b* The infrared spectrum of CH_3I as a vapor.

BOHREN & CLOTHIAUX 2006

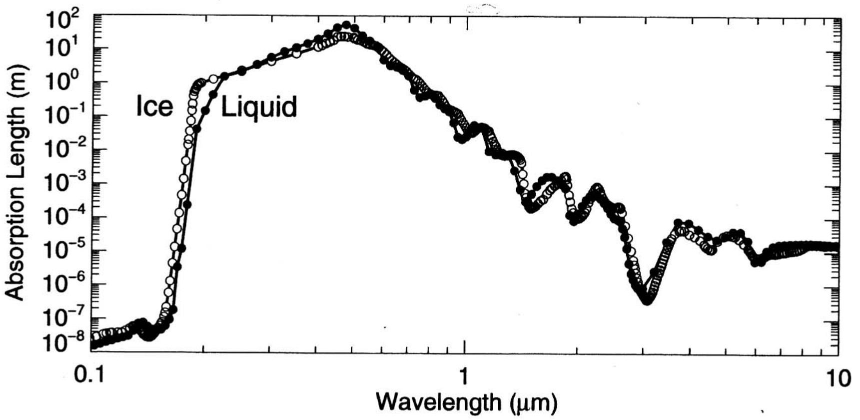
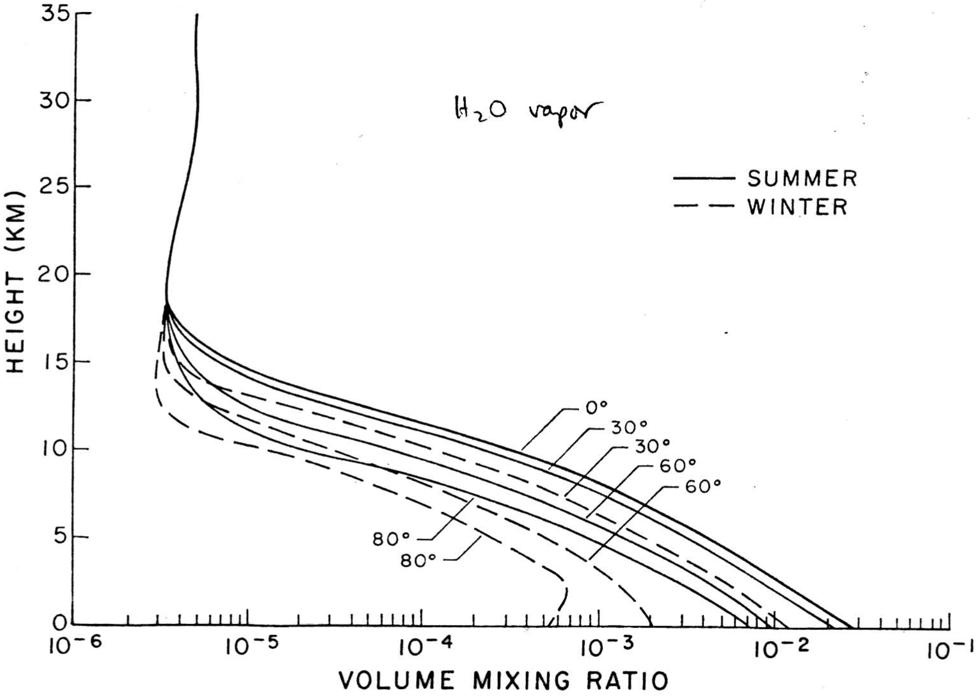
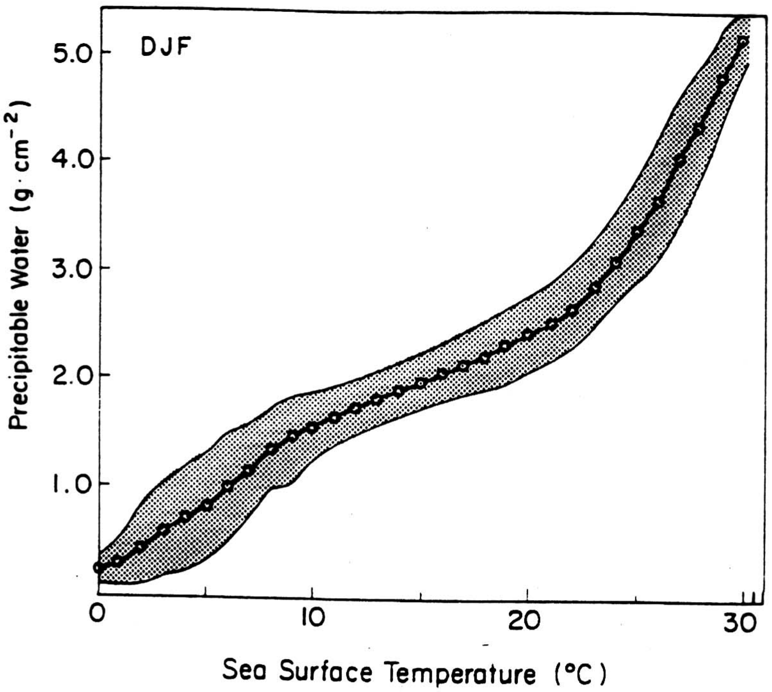


Figure 2.2: Absorption length (inverse absorption coefficient) of pure ice and liquid water from UV to IR. The data for liquid water were taken from Querry *et al.* (1991), those for ice from Warren (1984).

Atmospheres of the Inner Planets

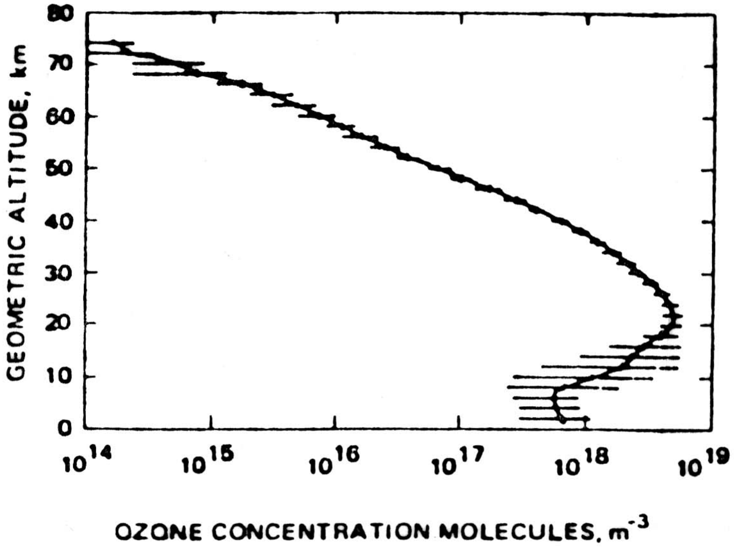
	Mercury	Venus	Earth	Mars
Atmospheric pressure at surface	~0	90 atm.	1 atm = 1013 millibars (mb)	0.007-0.010 atm. (7-10 mb) Varies with season
Surface air Temperature (K)	100 night 600 day	750	Mean 288 Range 184-330	Mean 216 Range 140-300
Major gases	-	CO_2 97%	N_2 78% O_2 21%	CO_2 95%
Minor gases	-	N_2 2%	Ar 1%	Ar 1.6% N_2 2%
Radiatively important gases ("greenhouse gases")	-	CO_2	H_2O water CO_2 carbon dioxide O_3 ozone CH_4 methane N_2O nitrous oxide	CO_2 H_2O
Notes		Covered with clouds of H_2SO_4	Radiatively important gases are not the major gases.	Pressure varies because CO_2 condenses out on polar caps.





GRAEME L. STEPHENS

JOURNAL OF CLIMATE, Vol. 3, No. 6, June 1990



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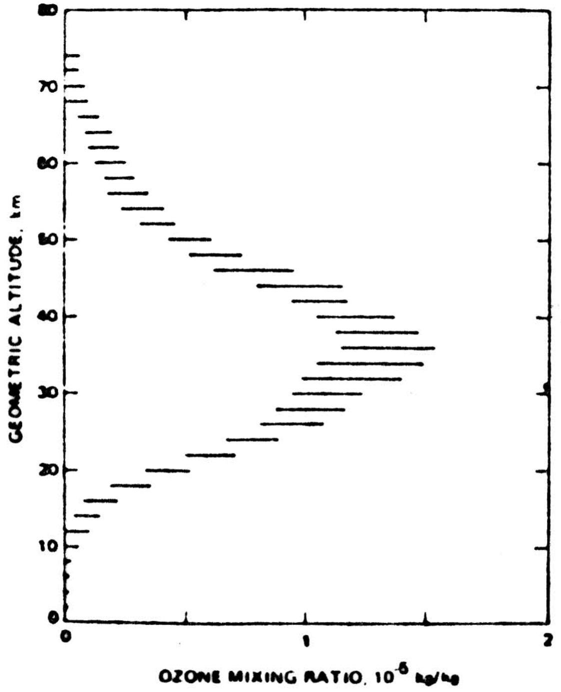
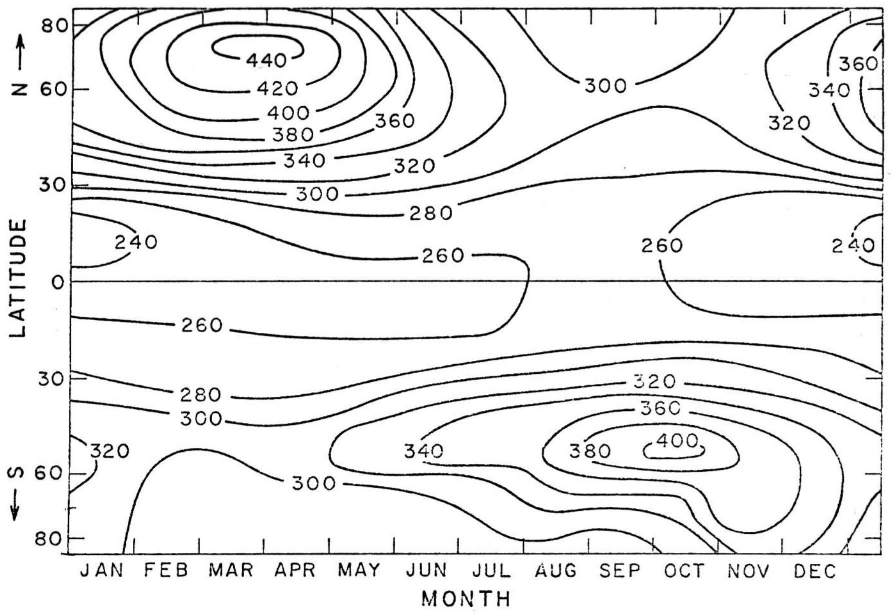


10^{-5} kg /kg

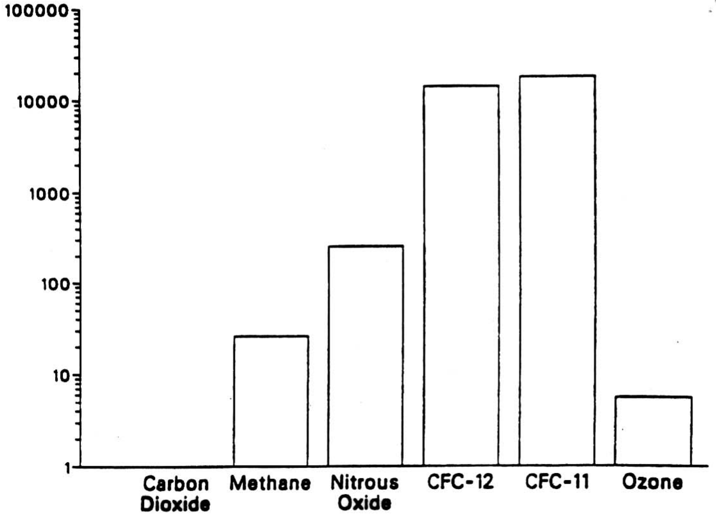


Latitude-Season Cross Section of Total Ozone (1957-1975)

"Dobson Units": milli-centimeters STP. Divide by 100 to get mm STP.

Spring 1991

Carbon Dioxide Information Analysis Center



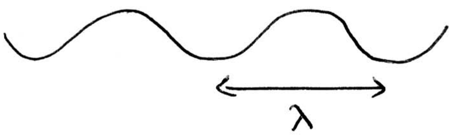
Global-warming effect of greenhouse gases relative to CO_2, from *A Fossil Energy Perspective*

ATMS 532 notes to insert after p. 6.

EM radiation is described as waves or particles.

wave

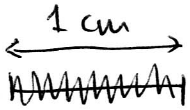
travels at the speed of light $c = 3 \times 10^8$ m/sec (in vacuum)



wavelength λ

frequency ν $\quad \nu = \frac{c}{\lambda}$ cycles per sec, Hertz (Hz)

wavenumber $\bar{\nu}$ $\quad \bar{\nu} = \frac{1}{\lambda}$ number of waves per cm.



e.g. if $\bar{\nu} = 400 \text{ cm}^{-1}$

then wavelength is $\frac{1}{400}$ cm $= 25\ \mu m$.

$$\bar{\nu}(\text{cm}^{-1}) = \frac{10\,000}{\lambda\ (\mu m)}$$

cultural differences in describing the spectrum:

UV	photon energy (eV)
vis, IR	wavelength (nm, μm)
IR	$\bar{\nu}$ (cm^{-1})
microwave radiowave	ν (MHz, GHz)

particle

When EM radiation interacts with matter (by absorption, emission, scattering), it is always absorbed, emitted, or scattered in discrete units (quanta) of energy called <u>photons</u>.

Energy of a photon $E = h\nu$

$\uparrow$ Planck's constant 6.63×10^{-34} J·s

So to compute the energy of EM radiation we can count the number of photons in each frequency-interval.

<u>Radiation can be</u>

- coherent (e.g. laser) or
- incoherent: no systematic phase relation between emitters

- polarized or
- unpolarized

Radiation emitted by Sun is <u>incoherent</u> and <u>unpolarized</u>.
But it can become partly polarized by interaction with Earth's atmosphere and surface

Radiation energy varies with

- location (x, y, z)
- angle (θ, ϕ) at any location
- frequency (ν) or wavelength (λ)
- polarization

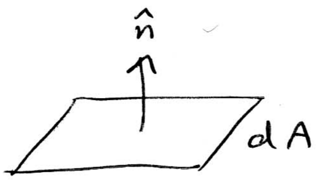
Energy : Joules = J

Power : Watt = J/sec.

Power per unit area $(W m^{-2})$ is called "flux" ("irradiance")

Radiation terminology

$$\text{Radiation energy}\left\{\begin{array}{l}\text{crossing}\\ \text{incident on}\\ \text{emitted from}\\ \text{reflected from}\end{array}\right\}\text{a unit area in unit time, irrespective of direction.}$$



Q Energy

A area

t time

① "Flux" (actually a flux-density) is

$$F = \frac{d^2 Q^{\rightarrow \text{Joules}}}{\underbrace{dA}_{m^2}\;\underbrace{dt}_{\text{sec}}} \qquad (W m^{-2}) \qquad (1)$$

where d^2Q is the energy crossing surface dA between time t and $t + dt$.

(Also called "irradiance" E)

6d

② Spectral flux :

flux per unit interval of wavelength or frequency.

$$F_\lambda = \frac{d^3Q}{dA\,dt\,d\lambda} \quad \left[W m^{-2} (\mu m)^{-1} \right]$$

$$F_\nu = \frac{d^3Q}{dA\,dt\,d\nu} \quad \begin{bmatrix} W m^{-2} Hz^{-1} \text{ if } \nu \text{ in Hz} = sec^{-1} \\ W m^{-2} (cm^{-1})^{-1} \text{ if } \nu \text{ in } cm^{-1} \end{bmatrix}$$

Total flux

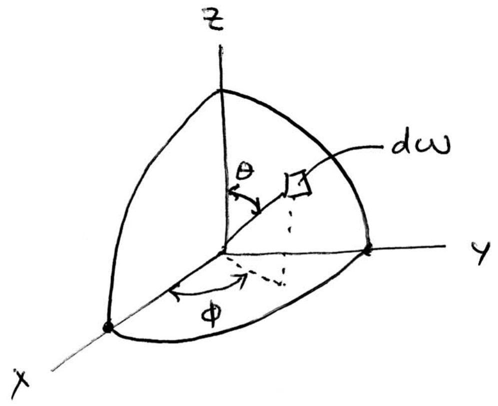
$$F = \int_0^\infty F_\lambda \, d\lambda = \int_0^\infty F_\nu \, d\nu$$

To convert from F_λ to F_ν : (they are different units)

$$\nu = \frac{c}{\lambda} \quad \text{so} \quad d\nu = -c\lambda^{-2} d\lambda$$

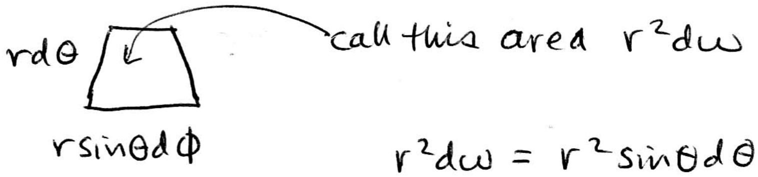
$$\text{or} \quad d\ln\nu = -d\ln\lambda$$

Geometry of a sphere (radius r)



z = vertical direction (zenith)
θ = zenith angle
ϕ = azimuth angle.
$d\omega$ = area element on surface of unit-sphere.
(element of "solid angle")

Area-element on surface of radius r:



$$r^2 d\omega = r^2 \sin\theta \, d\theta \, d\phi$$

$$d\omega = \sin\theta \, d\theta \, d\phi$$

Area of sphere $= 4\pi r^2$
Area of unit sphere $= 4\pi$

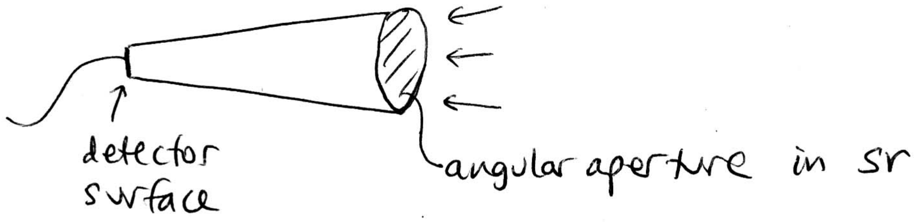
Total solid angle of a sphere:

$$\int_{\text{sphere}} d\omega = \int_0^{2\pi} \int_0^{\pi} \sin\theta \, d\theta \, d\phi = 4\pi \text{ "steradians" (sr)}$$

Any solid angular field of view is given in sr.

6f

A radiation detector with narrow field-of-view:



How big is steradian:

Steradian is ~ 1 radian × 1 radian

1 radian = 57°

4π sr = 12.6 sr to cover the sphere

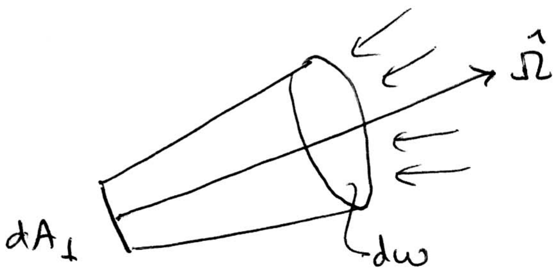
sphere = 4π sr = 41,260 "square degrees"

Distribution of radiation energy with angle

Define a direction vector $\hat{\Omega} = (\theta, \phi)$ (unit vector)

and an area element $dA_\perp$ perpendicular to $\hat{\Omega}$

and a solid angle element $d\omega$ centered on $\hat{\Omega}$.



③ Intensity I (Radiance L)

Intensity $I(\hat{\Omega})$ is the radiation energy dQ traveling in a direction within the solid angle element $d\omega$ centered on $\hat{\Omega}$, crossing unit area $\perp$ to $\hat{\Omega}$ in unit time.

$$I(\hat{\Omega}) = \frac{d^3Q}{dA_\perp \, dt \, d\omega} \qquad W m^{-2} sr^{-1}$$

④ Spectral intensity (spectral radiance)

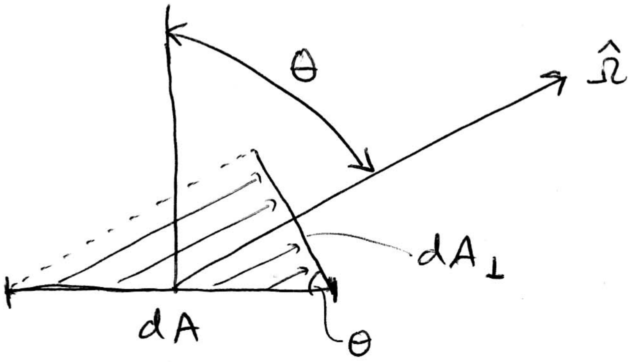
$$I_\lambda = \frac{dI}{d\lambda} \qquad W m^{-2} sr^{-1} \mu m^{-1}$$

$$I_\nu = \frac{dI}{d\nu} \qquad W m^{-2} sr^{-1} Hz^{-1}$$

or $W m^{-2} sr^{-1} (cm^{-1})^{-1}$

Relation of intensity to flux (radiance to irradiance)

Intensity is defined from the point of view of the detector; i.e. referred to a surface perpendicular to the direction of view $\hat{\Omega}$. To express it in terms of a different surface (such as a horizontal surface), that surface must be projected onto the perpendicular surface:



All radiation crossing dA, traveling in direction $\hat{\Omega}$, passes through a smaller area ⊥ the direction of travel.

$$dA_\perp = \cos\theta \, dA .$$

So $$I = \frac{d^3Q}{dA_\perp \, dt \, d\omega} = \frac{d^3Q}{\cos\theta \, dA \, dt \, d\omega} \quad (\mathrm{Wm^{-2}sr^{-1}})$$

Recall $$F = \frac{d^2Q}{dA\,dt} . \quad \text{so} \quad \frac{dF}{d\omega} = \frac{d^3Q}{dA\,dt\,d\omega}$$

so $$I = \frac{dF}{\cos\theta \, d\omega}$$

or $$F = \int I(\theta, \phi) \cos\theta \, d\omega$$

6i

Separate the upward and downward fluxes, so the integral goes over one hemisphere. E.g. for the upward flux $F\uparrow$:

$$F\uparrow = \int_{\Delta} I \cos\theta \, d\omega$$

$$= \int_0^{2\pi}\int_0^{\pi/2} I(\theta,\phi) \underbrace{\cos\theta}_{\mu} \underbrace{\sin\theta d\theta}_{-d\mu} d\phi$$

If I is independent of ϕ (azimuthally symmetric), common in thermal IR :

$$F\uparrow = 2\pi \int_0^1 I(\theta)\mu \, d\mu$$

Special case of I independent of μ in one hemisphere (e.g. upward emission from an isotropic emitter) :

$$F\uparrow = 2\pi I \underbrace{\int_0^1 \mu \, d\mu}_{1/2} = \pi I$$

units: $\mathbf{F}$ Wm^{-2}

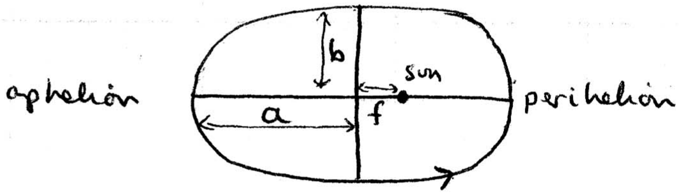
I $Wm^{-2}sr^{-1}$

π sr

DISTRIBUTION of SOLAR RADIATION as determined by

GEOMETRY OF EARTH'S ORBIT.

I Planetary orbits are ellipses.



a = semimajor axis

b = semi minor axis

f = distance from center to focus. Sun is at one focus.

$$a^2 = f^2 + b^2$$

Define eccentricity $e \equiv f/a$.

($e = 0$ for a circle)

closest approach of planet to sun (perihelion) $= a - f = a(1-e) = r_p$

greatest distance of planet from sun (aphelion) $= a + f = a(1+e) = r_a$

	Earth	Mars
now	$e = 0.0175$	$e = 0.093$

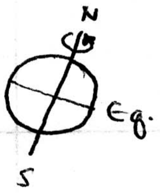
$$\text{extreme values} \begin{cases} e = 0 \\ e = 0.073. \end{cases}$$

Eccentricity varies over 10^5-year time scales due to gravitational pull of other planets.
(mainly Jupiter and Earth's moon)

II Rotation of planet.

The axis of rotation joins the North and South poles.

The circumference of the planet halfway between N, S poles is the equator.



The rotation rate is Ω.

$$\Omega = 2\pi \frac{\text{radians}}{\text{day}} = 360 \frac{\text{degrees}}{\text{day}} = 15 \frac{\text{degrees}}{\text{hour}} \text{ for earth.}$$

period of rotation is	24	hours	for earth
	24.5	hours	Mars
	10	hours	Jupiter

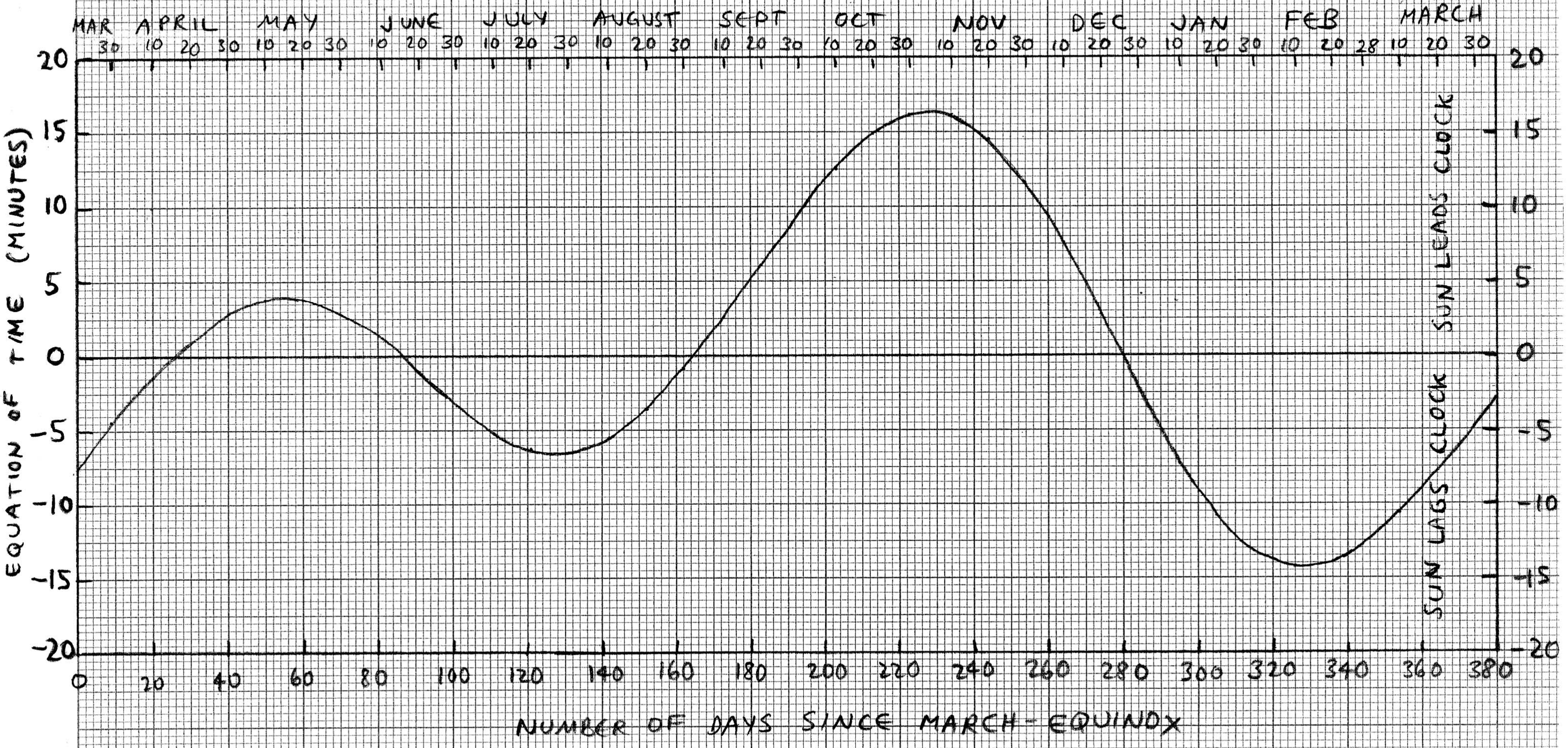
Rotation rate determines day-night cycle of insolation
and determines circulation of atmosphere.

The length of a solar day is the time from local solar noon on one day to local solar noon on the next day. "Local solar noon" is the time that the earth-sun line intersects our longitude circle. Local sun time is the time of a clock that reads 12:00 at local solar noon.

The length of a solar day, averaged over a year, is 24 hours. Particular solar days deviate from this by up to 30 seconds, depending on time of year, because the earth's axis is tilted and because the orbit is elliptical.

EQUATION OF TIME (SUN TIME − MEAN SUN TIME)

from STRAHLER 1975: PHYSICAL GEOGRAPHY page 83.



Cumulative deviations of solar day from 24 hours cause local suntime to deviate from mean solar time; this difference is called the "equation of time". Clock time differs from mean solar time because of the use of standard time ZONES.

There are 24 time zones, each covering 15° of longitude
($24 \times 15^\circ = 360^\circ$)

eg.

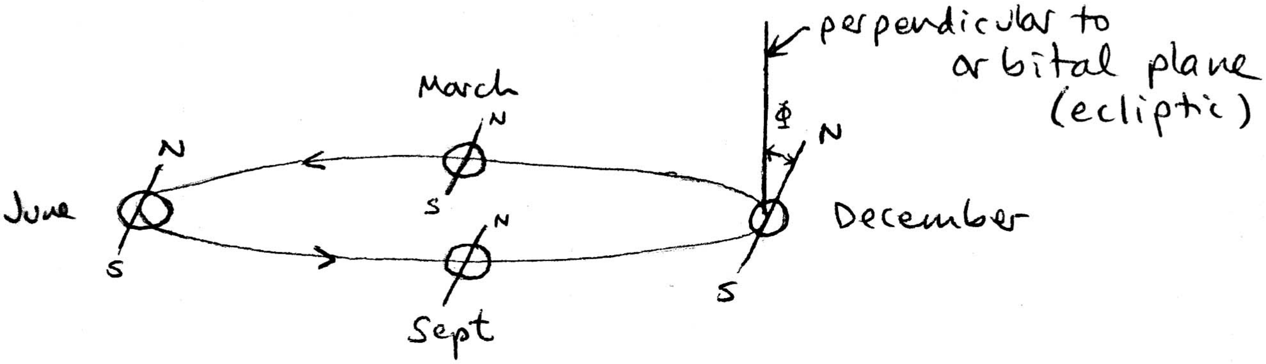
time zone	standard (central) longitude
GMT (UT)	0°
GMT+1	15° E
GMT-8	120° W

Longitude of Seattle is 122° W so Seattle is in the "120°W" time zone or the "GMT-8" time zone.

Noon GMT is 4 AM in Seattle.

II' Relation of rotation axis to the orbital plane.

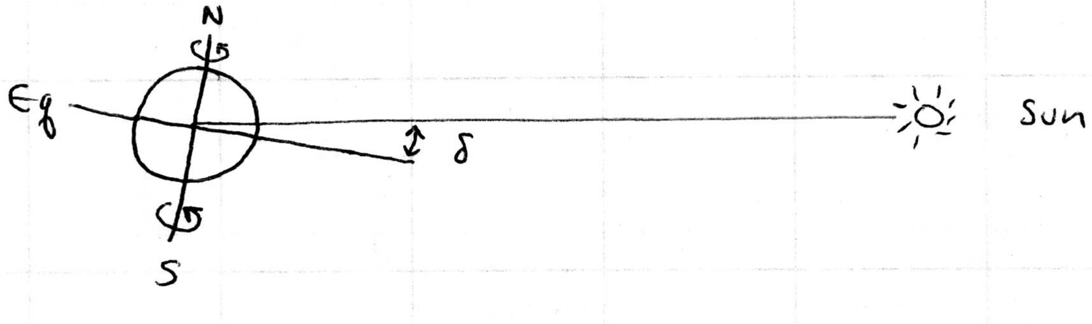
"Tilt" angle Φ is the angle between the axis of rotation and the perpendicular to the orbital plane. This tilt is responsible for the seasons.



For **Earth**, Φ varies in the range 22°-24.5°, on a 40,000-year cycle. It is now 23.5° and decreasing.

For **Mars**, Φ is now 23.9°. It varies between 15° and 35°.

Because the tilt remains constant over the year, the angle between the earth-sun line and the earth's equator varies between +23.5° and −23.5°. This angle is called the declination. δ



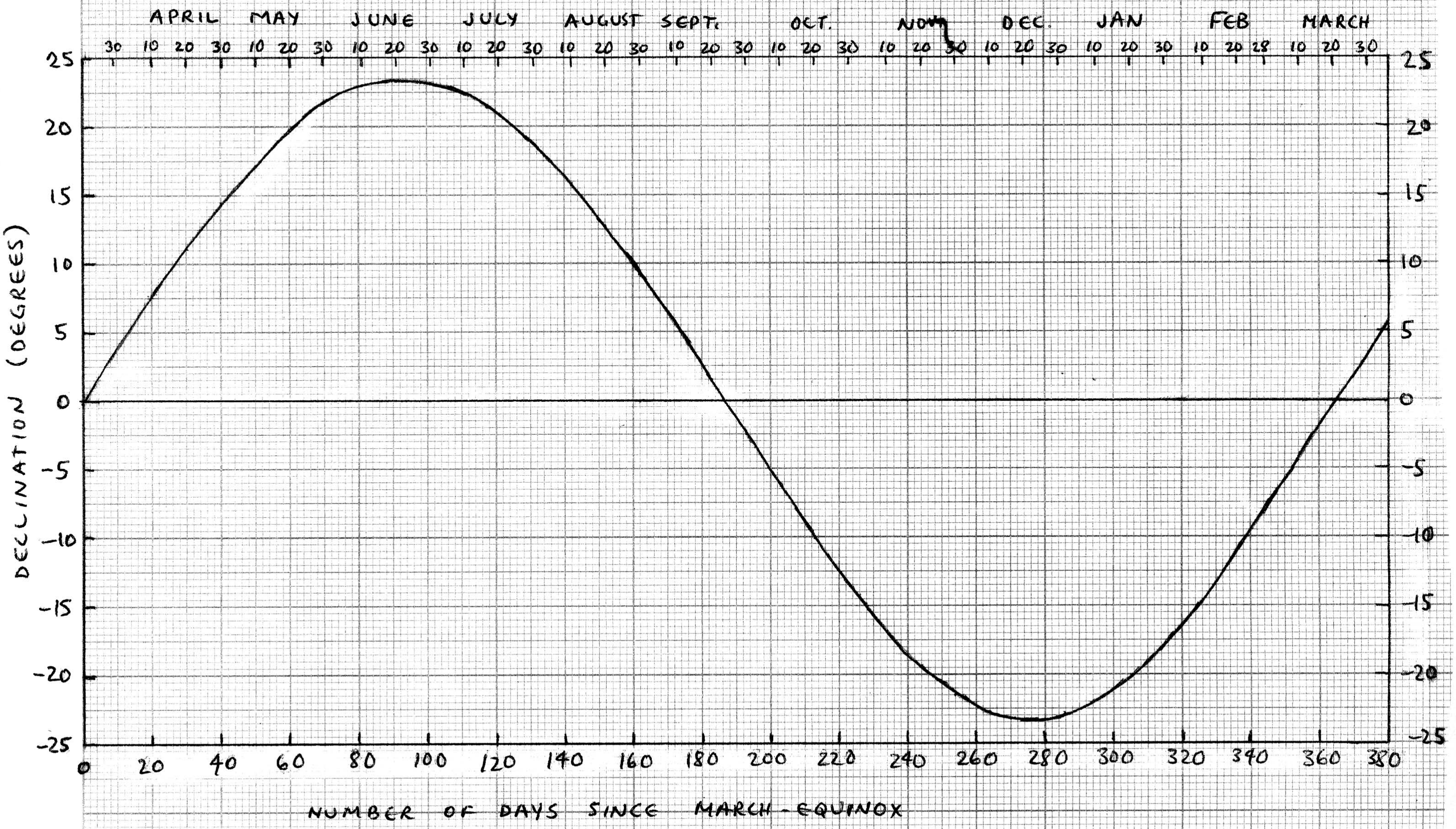
Declination thus also is the latitude where solar beam is vertical at noon.

The time of year when $\delta = 0°$ is called "equinox"

The time of year when $\delta = \pm 23.5°$ is called "solstice".

time of year	declination	sun is vertical at what latitude Φ
June solstice (21 June)	+23.45°	23.45°N (Tropic of Cancer)
September equinox (23 Sept)	0°	0°N (Equator)
December solstice (22 Dec)	−23.45°	23.45°S (Tropic of Capricorn)
March equinox (21 March)	0°	0°N (Equator)

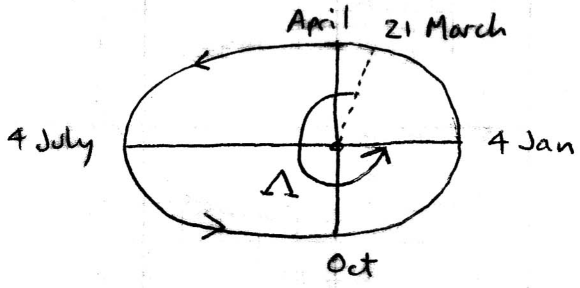
STRAHLER, 1975: PHYSICAL GEOGRAPHY page 83



IV Phase of season relative to position on elliptical orbit

"relative longitude of perihelion" Λ

Draw the earth's orbit, looking down on the north pole of the orbit:



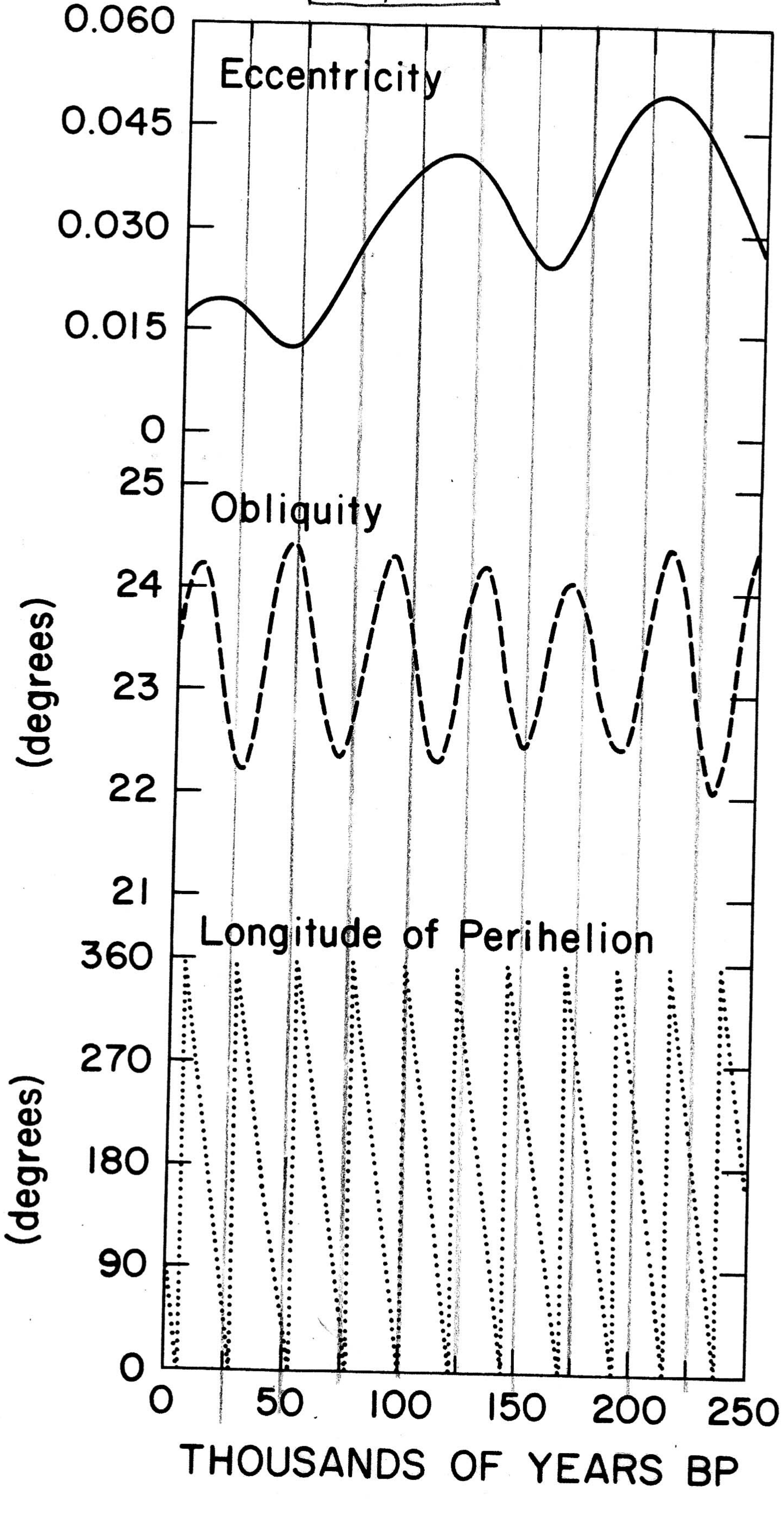
Λ is the angle in degrees from March-equinox (Hartmann's convention) to the time of perihelion.

Now $\Lambda \approx 282°$

Time of perihelion varies throughout the year, with a period about 20,000 years.

⑮

EARTH



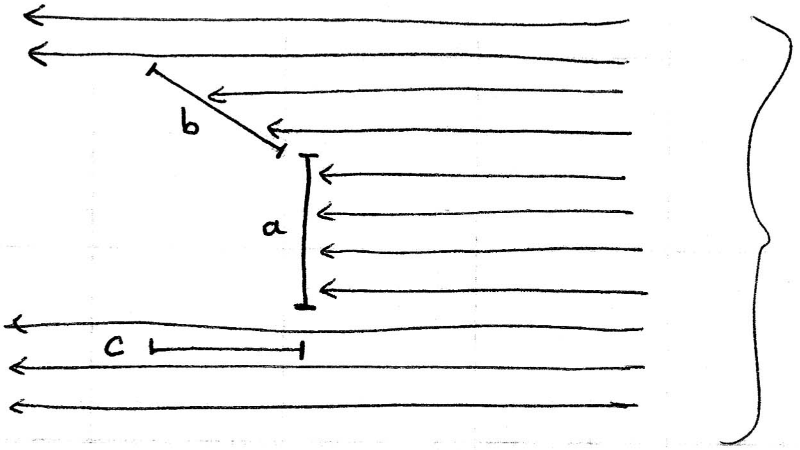
(angle from September-equinox)

B. Radiation received on a surface.

The rate of energy received by a flat surface* of 1 m^2 oriented perpendicular to the solar beam is equal to the solar constant, 1370 Wm^{-2} $= S_0$

* at the top of earth's atmosphere, at the mean earth-sun distance.

A tilted surface receives less than this:

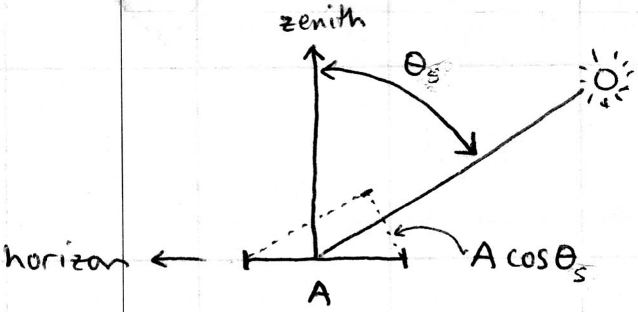


Surface a is perpendicular to the sun and intercepts S_0.

Surface b is tilted 60° and intercepts $\frac{1}{2} S_0$

Surface c is tilted 90° and intercepts zero.

Define the solar zenith angle θ_s as the angle from local vertical (or "zenith") down to the solar beam.



Project the surface onto a plane perpendicular to the solar beam. The area A (m^2) projects to a smaller area A cos θ_s (m^2).

All the sunlight that passes through this projected area is also incident on area A.

The power incident on the projected area is

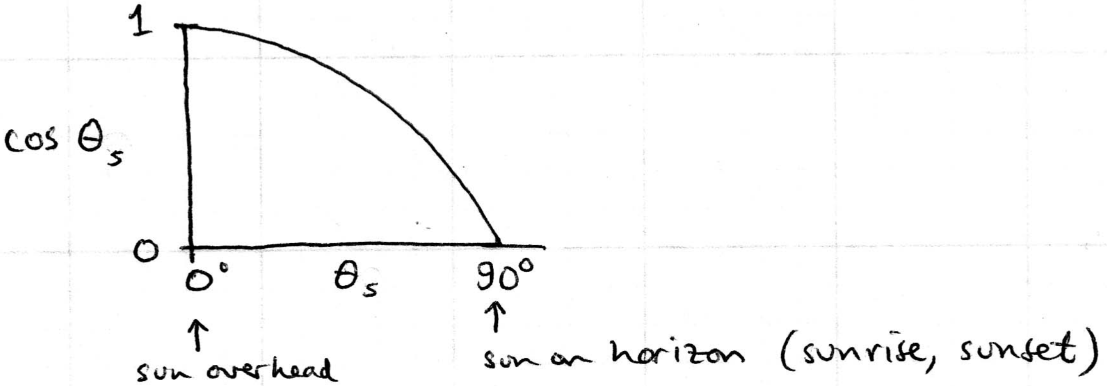
(solar constant) x (area)

$$(S_0 \ \underline{W m^{-2}}) \times (A \cos\theta_s \ \underline{m^2}) = S_0 A \cos\theta_s \ \underline{\text{watts}}.$$

This energy is distributed over area A, which therefore receives <u>insolation</u> (also called <u>irradiance</u>, radiation flux)

$$F = \frac{S_0 A \cos\theta_s \ \text{watts}}{A \quad m^2} = \underline{S_0 \cos\theta_s \quad W m^{-2}}$$

So the flux received on a horizontal surface at the top of the atmosphere is $S_0 \cos\theta_s \ W m^{-2}$



Most earth-surfaces are not ⊥ the solar beam.

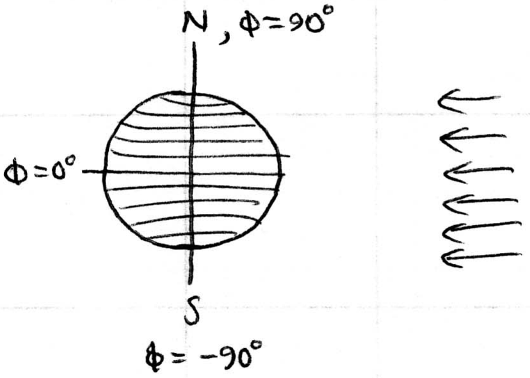
The solar beam is vertical only at one point on earth at any particular time. This point is always somewhere between latitudes 23.5°N and 23.5° S ie in the "<u>tropics</u>".

① eg at equinox, at noon.

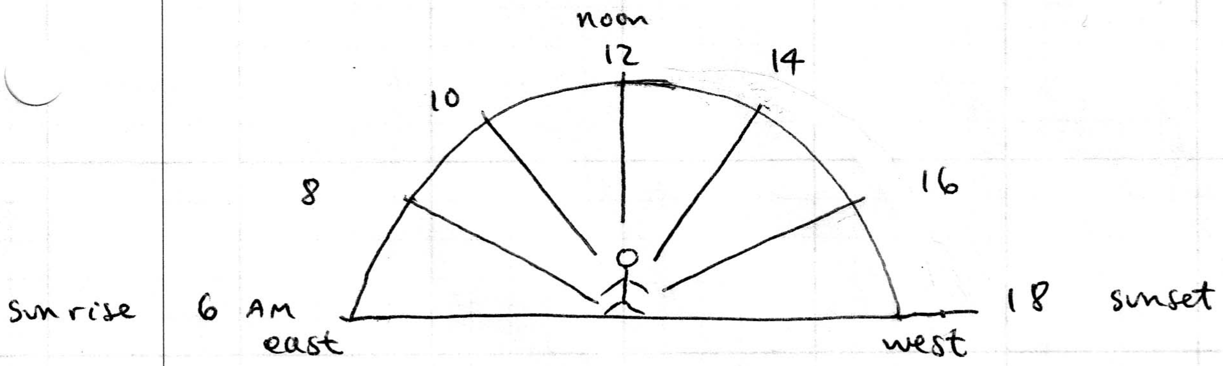
$\theta_s = 90°$ at poles

$\theta_s = \phi$ elsewhere

where ϕ = latitude.

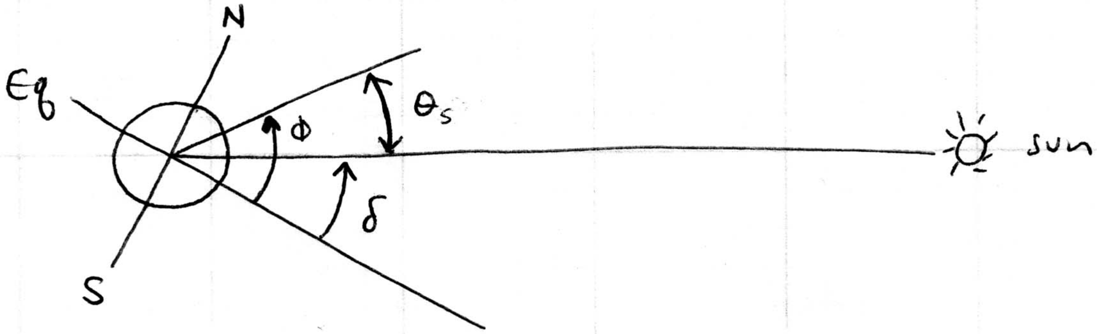


② eg at equator at equinox. (21 March, 23 Sept.)



local sun time	θ_s	$\cos\theta_s$	irradiance at Top of Atmosphere (T.O.A.)
6	90	0	0
8	60	0.5	$S_0/2$
9	45	0.71	$0.71 S_0$
12	0	1	S_0
18	90	0	0

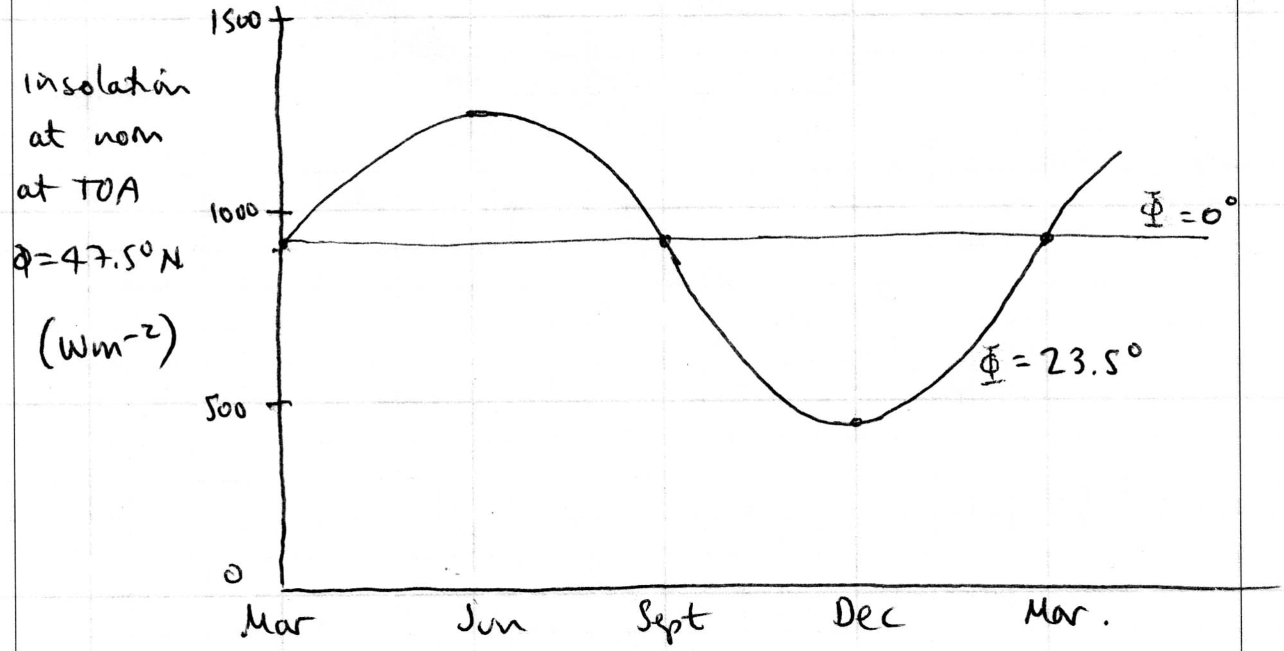
③ eg. noon, not equinox, not equator. At latitude ϕ



$\theta_s = |\phi - \delta|$ gives zenith angle at noon.

Seattle, $\phi = 47.5°$.

time	δ	θ_s	insolation at TOA
noon 21 June	23.5	$47.5 - 23.5 = 24°$	$1370 \cos 24 = 1252\ \mathrm{Wm^{-2}}$
noon 22 Dec	−23.5	$47.5 + 23.5 = 71°$	$1370 \cos 71 = 446$ "
noon 21 Mar, 23 Sep	0	47.5°	$1370 \cos 47.5 = 926$ "



A. Solar zenith angle for any latitude, date, and hour

Define : θ_s , ϕ, δ, h

① θ_s = zenith angle (0° to 90°). Angle between vertical and sun.

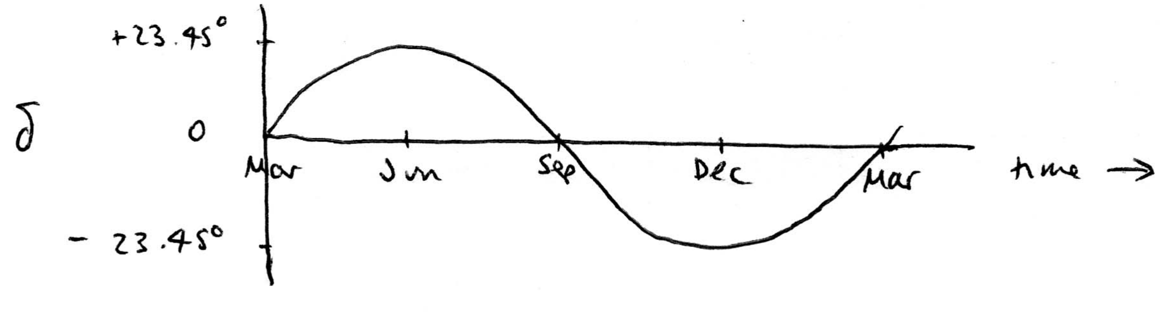
② ϕ = latitude (+90° to −90°) negative in S. Hemisphere.

North Pole $\phi = +90°$
Equator $\phi = 0$
South Pole $\phi = -90°$

③ δ = declination = angle between { plane of equator / earth-sun line

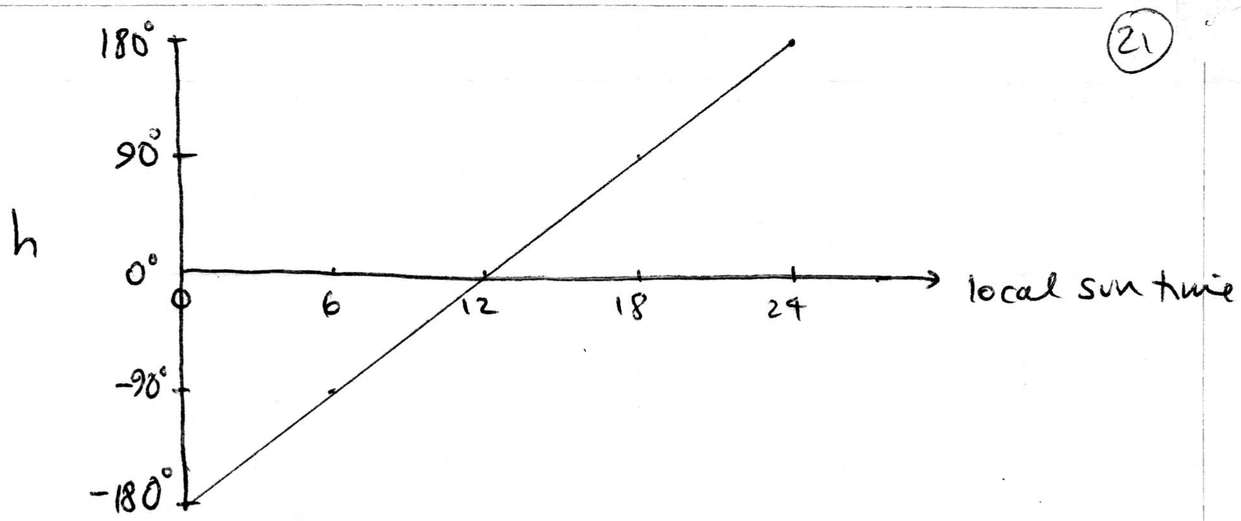
(+23.45° to −23.45°)

21 June $\delta = +23.45°$
21 March, 23 Sep $\delta = 0°$
22 Dec $\delta = -23.45°$



④ h = hour-angle: the angle through which the earth must turn to bring our longitude directly under the sun. (−180° to +180°, negative in morning).

h is zero at local noon and increases 15° every hour after noon.



so $\boxed{h = 15\,(t-12)}$

where h is hour-angle in <u>degrees</u>
and t is local sun time in hours.

or $\boxed{h = \frac{2\pi}{24}(t-12)}$ where h is in <u>radians</u>

⑤ with these definitions, Hartmann (Appendix A1) shows that

$$\boxed{\cos\theta_s = \sin\phi\,\sin\delta + \cos\phi\,\cos\delta\,\cos h} \qquad (1)$$

B. Time of sunrise and sunset

Now define H = half-day length, in degrees.

so $h = \begin{cases} +H & \text{at sunset} \\ -H & \text{at sunrise} \end{cases}$

At sunrise & sunset, $\theta_s = 90°$; $\cos\theta_s = 0$

Put $\cos\theta_s = 0$ in (1) and solve for h, and set it equal to H :

$$\boxed{\cos H = -\tan\phi \tan\delta} \ * \qquad (2)$$

C. Instantaneous flux of solar radiation at TOA , F (Wm^{-2})

$$F = S_o \left(\frac{\bar{r}_{es}}{r_{es}}\right)^2 \cos\theta_s \qquad (3)$$

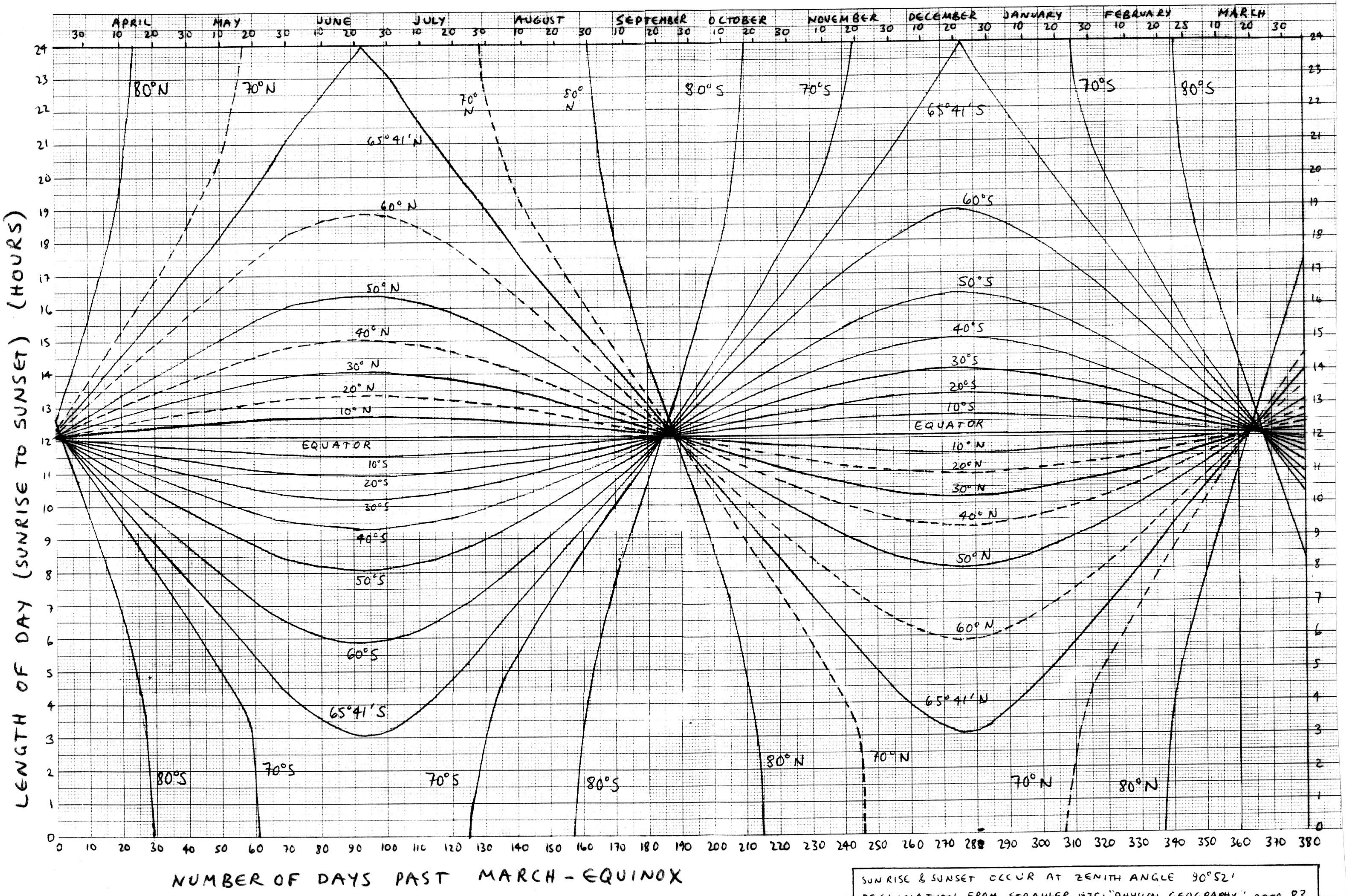
where S_o = solar constant for mean earth-sun distance = 1370 Wm^{-2}

r_{es} = earth-sun distance

$\bar{r}_{es}$ = mean earth-sun distance

θ_s = solar zenith angle.

* Eq. (2) does not work in polar summer or winter when daylength is 0 or 24 hours.



SUNRISE & SUNSET OCCUR AT ZENITH ANGLE 90°52'
DECLINATION FROM STRAHLER, 1975: "PHYSICAL GEOGRAPHY" page 83
DRAWN BY S. WARREN, APRIL 1986

D. Total radiation received over the course of a day, E (J m^{-2})

$$E = \int_{\text{sunrise}}^{\text{sunset}} F\,dt \qquad \text{where } t = \text{time (hours)}$$

[Change variables from t to h.

$$\frac{dh}{dt} = \Omega \text{, the rotation rate.}$$

$$\Omega = \frac{2\pi}{24} \text{ radians per hour} = 15 \text{ degrees per hour}$$
$$= 2\pi/86400 \text{ radians per second.}$$

[360 degrees = 2π radians]]

so
$$E = \frac{1}{\Omega} \int_{-H}^{H} F\,dh$$

$$= \frac{1}{\Omega} S_0 \left(\frac{\overline{r}_{es}}{r_{es}}\right)^2 \int_{-H}^{H} \left[\sin\phi \sin\delta + \cos\phi \cos\delta \cos h\right] dh$$

$$\boxed{E = \frac{2}{\Omega} S_0 \left(\frac{\overline{r}_{es}}{r_{es}}\right)^2 \left[H \sin\phi \sin\delta + \sin H \cos\phi \cos\delta\right]} \qquad (4)$$

where $\begin{cases} E \text{ is in Joules/m}^2 \\ H \text{ is in } \underline{\text{radians}} \end{cases}$; Ω is in radians per second

E. Average solar flux over the course of a day (24 hours or 86400 sec)

$$\overline{F} = \frac{E}{86400} \qquad \text{W m}^{-2}$$

$$\boxed{\overline{F} = \frac{S_0}{\pi} \left(\frac{\overline{r}_{es}}{r_{es}}\right)^2 \left[H \sin\phi \sin\delta + \sin H \cos\phi \cos\delta\right]} \qquad (5)$$

Hartmann

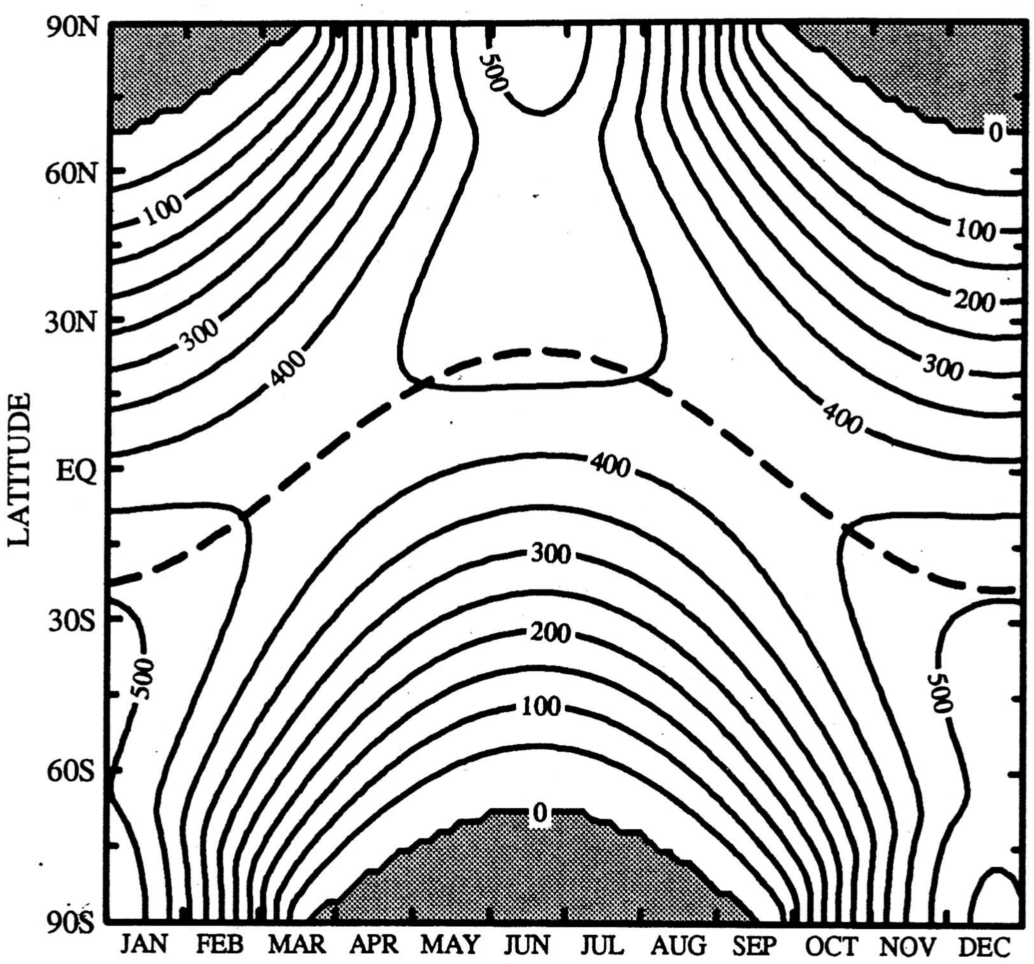


Fig. 2.6 Contour graph of the daily average insolation at the top of the atmosphere as a function of season and latitude. The contour interval is 50 W m^{-2}. The heavy dashed line indicates the latitude of the subsolar point at noon.

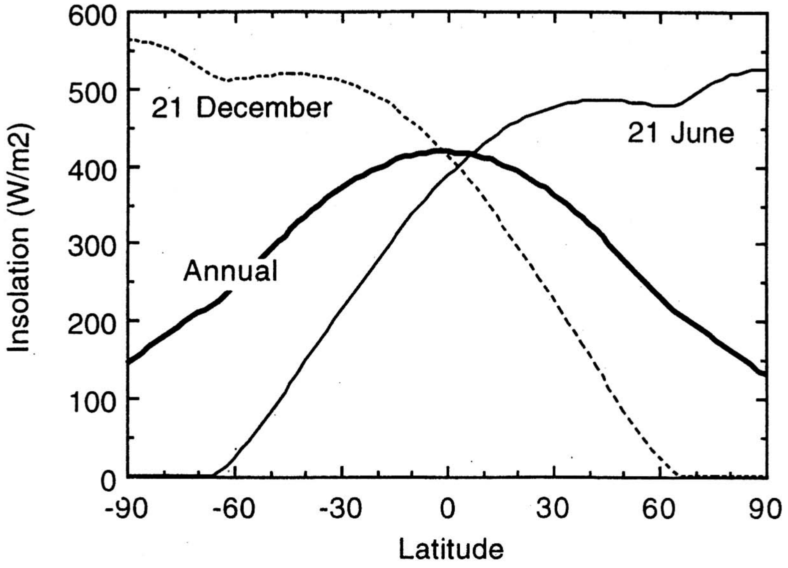


Fig. 2.7 Annual-mean and solstice insolation as functions of latitude.

25a

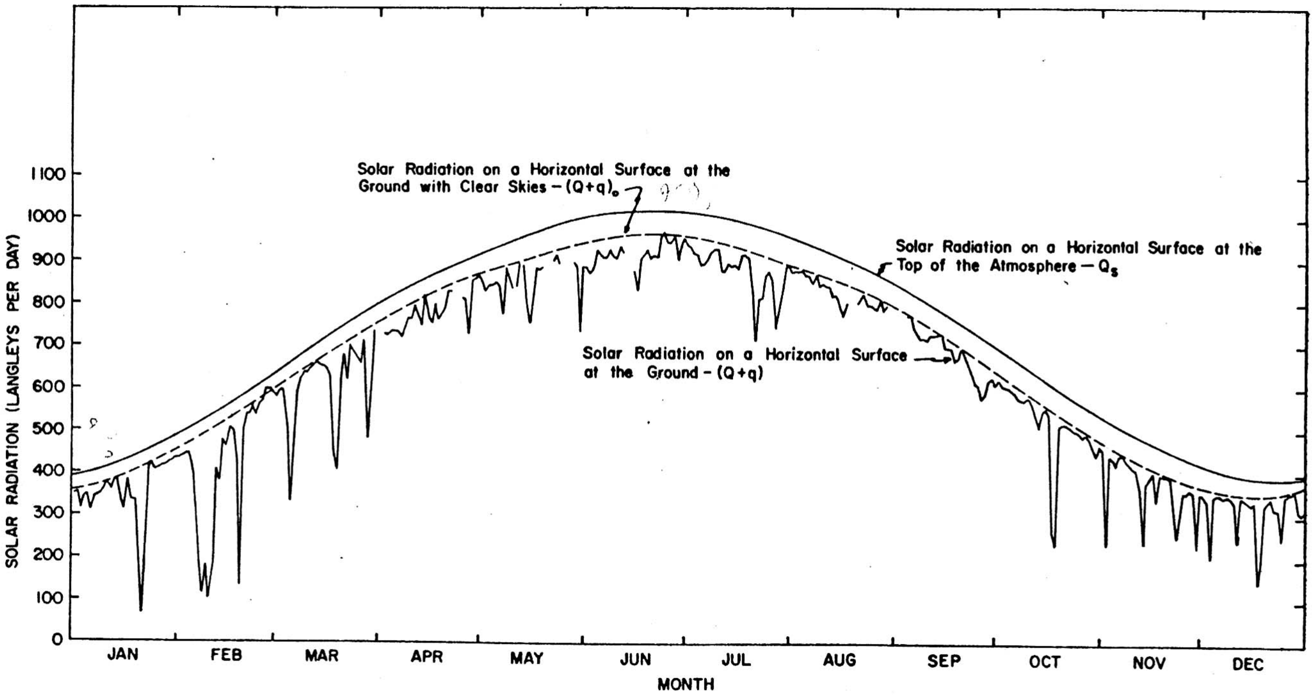


FIG. 11.—Solar radiation on a horizontal surface at the top of the atmosphere, Q_s, at the ground, $Q + q$, and at the ground with clear skies, $(Q + q)_0$, at Inyokern, California (35°39′N, 117°49′W), during 1962.

SELLERS 1965,

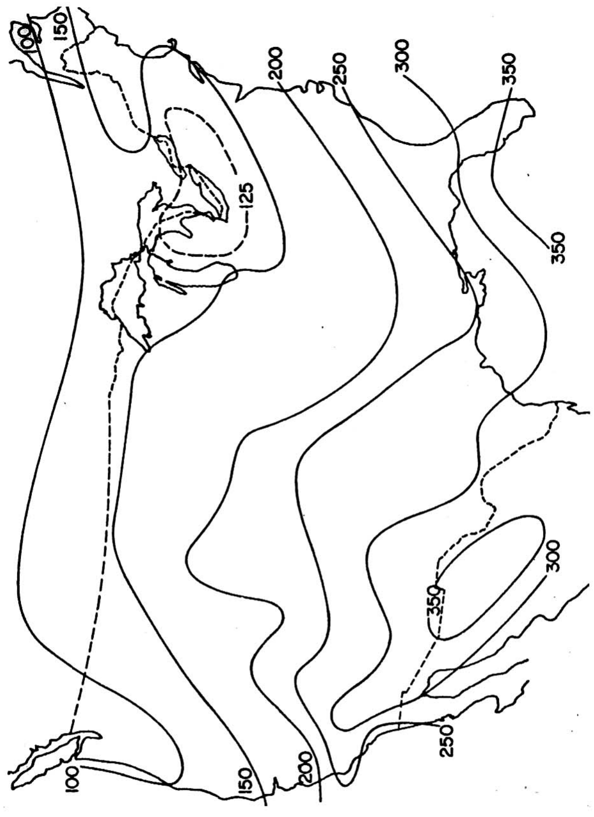


FIG. 9.—The average solar radiation on a horizontal surface at the ground in January in the United States. The units are langleys per day.

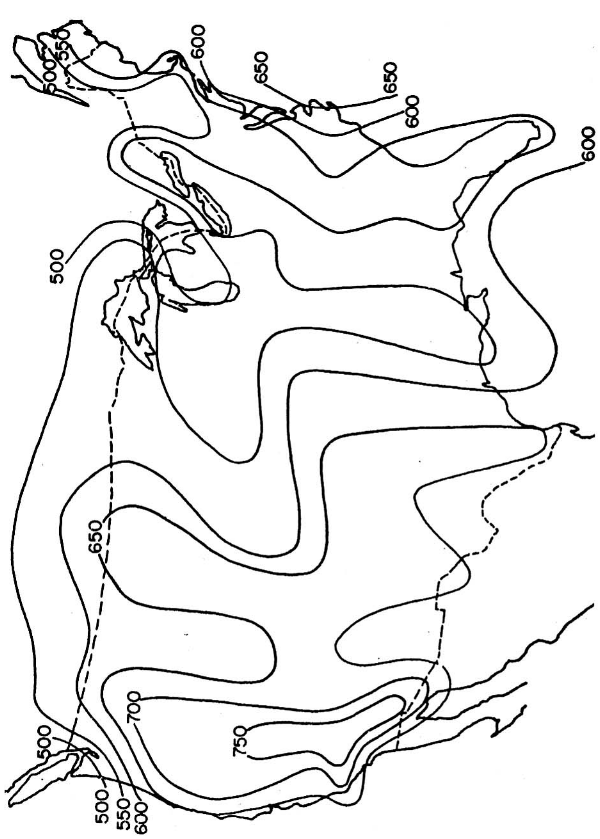


FIG. 10.—The average solar radiation on a horizontal surface at the ground in July in the United States. The units are langleys per day.

1 ly/day = 0.484 Wm^{-2}

SELLERS 1965

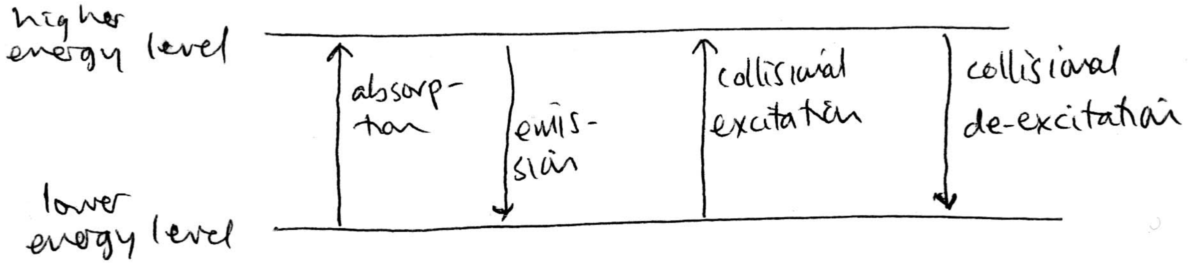
Interaction of Radiation with Matter

Working definitions:

*1. **Absorption:*** A photon is destroyed. Its energy is distributed by collisions into other forms of energy (vibrational, rotational, etc.). The frequency of subsequently *emitted* radiation is independent of the frequency of the absorbed photon. [Assuming collision-dominated; i.e. that frequency of collisional transitions is much greater than frequency of radiation-induced transitions. This is the assumption of "local thermodynamic equilibrium".]

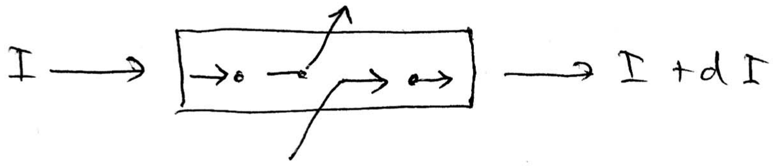
*2. **Scattering:*** The photon changes direction but not frequency.

*3. **Emission**:* A photon is created. The molecule emitting the photon loses internal energy (vibrational, rotational, etc.) equivalent to the energy of the photon.



*4. **Extinction:*** All processes that remove photons from a beam of light. Extinction is the sum of scattering-out and absorption.

5. A beam of light passing through a medium can be:
Depleted by *scattering*-out-of-the-beam and by *absorption.*
Augmented by *scattering*-into-the-beam and by *emission.*



Interaction of radiation with Earth's surface and atmosphere

Absorption of solar radiation	Mostly at surface, some in atmosphere
Scattering (reflection) of solar radiation	Mostly by clouds, some at surface
Emission of infrared radiation	Surface, clouds, and atmospheric gases

Sears & Salinger 1975.

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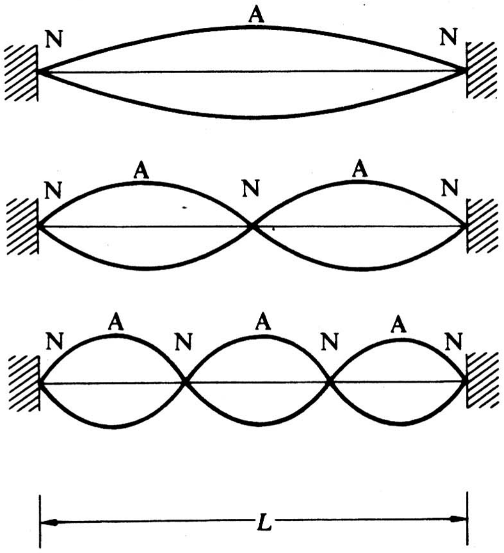

Fig. 11–1 Three of the possible stationary waves in a stretched string fixed at both ends.

the reader will have to take them on faith or refer to texts devoted to this subject. In any event, as far as the methods of *statistics* are concerned, it is enough to know that quantized energy states *exist*.

In quantum mechanics, also known as wave mechanics, the general method of attacking a problem is to set up and (hopefully) solve an equation known as Schrödinger's* equation. In many problems, this equation is exactly analogous to the wave equation describing the propagation of transverse waves in a stretched string, fixed at both ends. As is well known, the string can vibrate in a steady state in any one of a number of stationary waves, three of which are shown in Fig. 11–1. That is, there may be a node N at each end and an antinode A at the center, or there may be a node at the center as well as at the ends, with antinodes midway between the nodes, and so on. The important result is that there is always an *integral number* of antinodes in the steady-state modes of vibration; one antinode in the upper diagram, two in the next, and so on. The distance between nodes (or antinodes) is one-half a wavelength, so if L is the length of the string, the wavelengths λ of the possible stationary waves are

$$\lambda_1 = 2L, \qquad \lambda_2 = \frac{1}{2}\,2L, \qquad \lambda_3 = \frac{1}{3}\,2L, \quad \text{etc.};$$

or in general

$$\lambda_j = \frac{1}{n_j}\,2L,$$

---

* Erwin Schrödinger, Austrian physicist (1887–1961).

13–2 THE DEBYE THEORY OF THE SPECIFIC HEAT CAPACITY OF A SOLID

The simple Einstein theory assumes that all atoms of a solid oscillate at the same frequency. Nernst and Lindemann* found empirically that the agreement between theory and experiment could be improved by assuming two groups of atoms, one oscillating at a frequency ν and the other at a frequency 2ν. This idea was extended by Born,† von Karman,‡ and Debye, who considered the atoms, not as isolated oscillators all vibrating at the same frequency, but as a system of coupled oscillators having a continuous spectrum of natural frequencies.

---

* Frederick A. Lindemann, First Viscount Cherwell, British physicist (1886–1957).

† Max Born, German physicist (1882–1970).

‡ Theodor von Kármán, Hungarian engineer (1881–1963).

As a simple example of coupled oscillators, suppose we have two identical particles connected by identical springs, as in Fig. 13–2. If both particles are given equal initial velocities in the same direction, as indicated by the upper arrows, the particles will oscillate in phase with a certain frequency ν_1. If the initial velocities are equal and opposite, as indicated by the lower arrows, the particles will oscillate out of phase but with a different frequency ν_2. If the initial velocities have arbitrary values, the resultant motion is a superposition of two oscillations of frequencies ν_1 and ν_2. The system is said to have two *natural frequencies*.

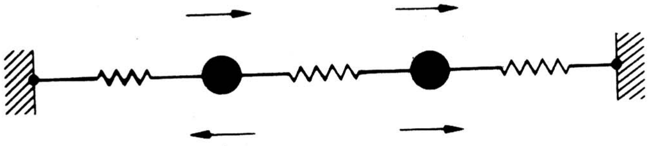

Fig. 13–2 Coupled oscillators.

Now suppose that the number of particles (and springs) is increased. It is no great task to calculate the natural frequencies when the number is small, but as the number is increased there are too many simultaneous equations to be solved. It turns out, however, that if there are N particles in the chain, the system will have N natural frequencies, whatever the value of N.

Now extend these ideas to three dimensions. A simple model of a crystal consists of a three-dimensional array of particles connected by springs, and such an array has $3N$ natural frequencies. Because of the impossibility of calculating these frequencies when N is as large as the number of molecules in a macroscopic crystal, Debye assumed that the natural frequencies of the atoms of a crystal would be the same as the frequencies of the possible stationary waves in a crystal if the crystal were a *continuous elastic solid*. This is a standard problem in the theory of elasticity, and we shall outline its solution without giving details. The procedure is closely analogous to that described in Section 11–2, except that we are now dealing with *real* elastic waves and not with the mathematical waves of wave mechanics.

As explained in Section 11–2, an elastic string of length L fixed at both ends, can oscillate in a steady state in any mode for which the wavelength λ is given by

$$\lambda = \frac{2L}{n},$$

where $n = 1, 2, 3, \ldots$, etc.

The fundamental equation of any sort of wave motion states that the speed of propagation c equals the product of the frequency ν and the wavelength λ:

$$c = \nu\lambda.$$

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It follows that for any frequency ν, the number n is

$$n = \frac{2L}{c}\nu$$

and

$$n^2 = \frac{4L^2}{c^2}\nu^2.$$

The theory of elasticity leads to the result that the natural frequencies of stationary waves in an elastic solid in the form of a cube of side length L are given by the same equation except that the possible values of n^2 are

$$n^2 = n_x^2 + n_y^2 + n_z^2,$$

where n_x, n_y, and n_z are positive integers that can have the values 1, 2, 3, . . . , etc.

To find the number of waves in any frequency interval, or the *frequency spectrum*, we proceed in the same way as in Section 12–1 and Fig. 12–1. Let the numbers n_x, n_y, and n_z be laid off on three mutually perpendicular axes. Each triad of values determines a point in n-space, with corresponding values of n and of ν. Let $\mathscr{G}$ represent the total number of possible frequencies, up to and including that corresponding to some given n. This is equal to the number of points within an octant of a sphere of radius n, the volume of which is $(\pi/6)\,n^3$, and since $n = (2L/c)\nu$,

$$\mathscr{G} = \frac{4\pi}{3}\frac{L^3}{c^3}\nu^3.$$

But L^3 is the volume V of the cube, and it can be shown that regardless of the shape of the solid we can replace L^3 with V. Then

$$\mathscr{G} = \frac{4\pi}{3}\frac{V}{c^3}\nu^3. \tag{13–4}$$

However, three types of elastic waves can propagate in an elastic solid: a longitudinal or compressional wave (a sound wave) traveling with speed c_l, and two transverse or shear waves polarized in mutually perpendicular directions and traveling with a different speed c_t. The total number of possible stationary waves having frequencies up to and including some frequency ν is therefore

$$\mathscr{G} = \frac{4\pi}{3}V\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)\nu^3. \tag{13–5}$$

According to the Debye theory Eq. (13–5) can also be interpreted as describing the number of linear *oscillators* having frequencies up to and including the frequency ν. Thus, to be consistent with the notation of Section 12–2, $\mathscr{G}$ in Eq. (13–5) should be replaced by $\mathscr{N}$ and

$$\mathscr{N} = \frac{4\pi}{3}V\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)\nu^3. \tag{13–6}$$

13–3 BLACKBODY RADIATION

The thermodynamics of blackbody radiation was discussed in Section 8–7 and we now consider the statistical aspects of the problem. The radiant energy in an evacuated enclosure whose walls are at a temperature T is a mixture of electromagnetic waves of all possible frequencies from zero to infinity, and it was the search for a theoretical explanation of the observed energy distribution among these waves that led Planck to the postulates of quantum theory.

To apply the methods of statistics to a batch of radiant energy, we consider the waves themselves as the "particles" of an assembly. Each wave can be considered a particle called a *photon* and the assembly can be described as a *photon gas.* Because the photons are indistinguishable and there is no restriction on the number per energy state, the assembly obeys the Bose-Einstein statistics.

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The problem is very similar to that of a phonon gas discussed in the preceding section. The number of photons in the enclosure cannot be considered an independent variable and the B-E distribution function reduces to the simpler form,

$$\Delta\mathcal{N}_\nu = \frac{\Delta\mathcal{G}_\nu}{\exp(h\nu/kT) - 1}.$$

There is, however, a difference in the expression for the degeneracy $\Delta\mathcal{G}_\nu$. As we showed in the preceding section, the degeneracy of a macrolevel, in an assembly of waves (or photons) is equal to the possible number $\Delta\mathcal{G}_\nu$ of stationary waves in the frequency interval from ν to $\nu + \Delta\nu$. Let us return to Eq. (13-5),

$$\mathcal{G} = \frac{4\pi}{3}\frac{V}{c^3}\nu^3,$$

where $\mathcal{G}$ is the number of stationary waves with frequencies up to and including ν. Electromagnetic waves are purely transverse and there can be *two* sets of waves, polarized in mutually perpendicular planes and both traveling with the speed of light c. Also, since empty space has no structure, there is no upper limit to the maximum possible frequency. Then interpreting $\mathcal{G}$ as the total number of possible energy states of all frequencies up to and including ν, we have

$$\mathcal{G} = \frac{8\pi}{3}\frac{V}{c^3}\nu^3.$$

The degeneracy $\Delta\mathcal{G}_\nu$ is therefore

$$\Delta\mathcal{G}_\nu = \frac{8\pi V}{c^3}\nu^2\,\Delta\nu,$$

and the number of waves (or photons) having frequencies between ν and $\nu + \Delta\nu$ is

$$\Delta\mathcal{N}_\nu = \frac{8\pi V}{c^3}\frac{\nu^2}{\exp(h\nu/kT) - 1}\Delta\nu. \qquad (13\text{-}20)$$

The energy of each wave is $h\nu$, and after dividing by the volume V, we have for the energy per unit volume, in the frequency range from ν to $\nu + \Delta\nu$, or the *spectral energy density* $\Delta\mathbf{u}_\nu$,

$$\Delta\mathbf{u}_\nu = \frac{8\pi h}{c^3}\frac{\nu^3}{\exp(h\nu/kT) - 1}\Delta\nu. \qquad (13\text{-}21)$$

This equation has the same *form* as the experimental law (Planck's law) given in Section 8-7, and we now see that the experimental constants c_1 and c_2 in Eq. (8-50) are related to the fundamental constants h, c, and k, by the equations

$$c_1 = \frac{8\pi h}{c^3}, \qquad c_2 = \frac{h}{k}. \qquad (13\text{-}22)$$

When numerical values of h, c, and k are inserted in these equations, the calculated values of c_1 and c_2 agree exactly with their experimental values, within the limits of experimental error.

At a given temperature T, and at high frequencies for which $h\nu \gg kT$, the exponential term is large; we can neglect the 1; and

$$\Delta \mathbf{u}_\nu \simeq \frac{8\pi h}{c^3} \nu^3 \exp(-h\nu/kT)\, \Delta\nu. \tag{13–23}$$

An equation of this form had been derived by Wien* before the advent of quantum theory and it is known as *Wien's law*. It is in good agreement with experiment at high frequencies but in very poor agreement at low frequencies.

However, at low frequencies for which $h\nu \ll kT$, $[\exp(h\nu/kT) - 1]$ is very nearly equal to $h\nu/kT$ and

$$\Delta \mathbf{u}_\nu \simeq \frac{8\pi kT}{c^3} \nu^2\, \Delta\nu. \tag{13–24}$$

This equation had been derived by Rayleigh† and Jeans,‡ also before the quantum theory, and had been found to agree with experiment at low, but not at high, frequencies. That it cannot be correct in general can be seen by noting that as the frequency becomes very high, the predicted energy density approaches infinity. (This result is sometimes referred to as the "ultraviolet catastrophe.")

It is interesting to note that Planck's first approach to the problem was purely empirical. He looked for an equation having a mathematical form such that it would reduce to the Wien equation when $h\nu/kT$ was large, and to the Rayleigh-Jeans equation when $h\nu/kT$ was small. He found that Eq. (13–21) had this property, and his search for a theoretical explanation of the equation led to the development of quantum theory.

Figure 13–5 shows graphs of the dimensionless quantity $\dfrac{\Delta \mathbf{u}_\nu}{\Delta\nu}\left(\dfrac{c^3h^2}{8\pi k^3T^3}\right)$, plotted as a function of the dimensionless quantity $h\nu/kT$. The solid curve is a graph of Planck's law, and the dotted curves are, respectively, graphs of the Rayleigh-Jeans law, applicable when $h\nu \ll kT$, and of Wien's law, applicable when $h\nu \gg kT$.

The total energy density $\mathbf{u}_\nu$, including all frequencies, can now be found by summing $\Delta\mathbf{u}_\nu$ over all values of ν from zero to infinity, since there is no limit to the maximum value of ν. Replacing the sum with an integral, we have

$$\mathbf{u}_\nu = \frac{8\pi h}{c^3} \int_0^\infty \frac{\nu^3}{\exp(h\nu/kT) - 1}\, d\nu;$$

---

* Wilhelm Wien, German physicist (1864–1928).

† John W. Strutt, Lord Rayleigh, English physicist (1842–1919).

‡ Sir James H. Jeans, English mathematician (1877–1946).

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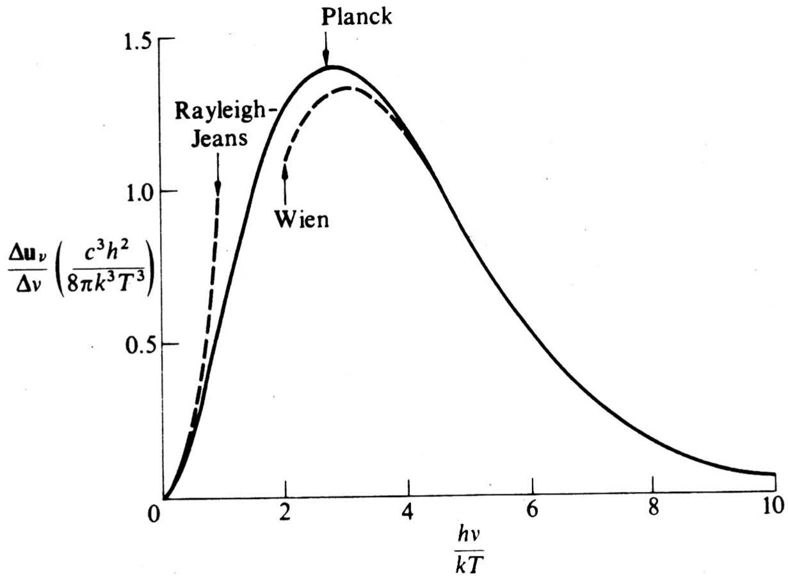


Fig. 13–5 Graphs of Planck's law, Wien's law, and the Rayleigh-Jeans law.

or, if we define a dimensionless variable $x = h\nu/kT$,

$$\mathbf{u}_\nu = \frac{8\pi k^4}{c^3h^3}T^4\int_0^\infty \frac{x^3\,dx}{\exp(x) - 1}\,.$$

The value of the definite integral is $\pi^4/15$, so

$$\mathbf{u}_\nu = \frac{8\pi^5k^4}{15c^3h^3}T^4 = \sigma T^4, \tag{13–25}$$

where

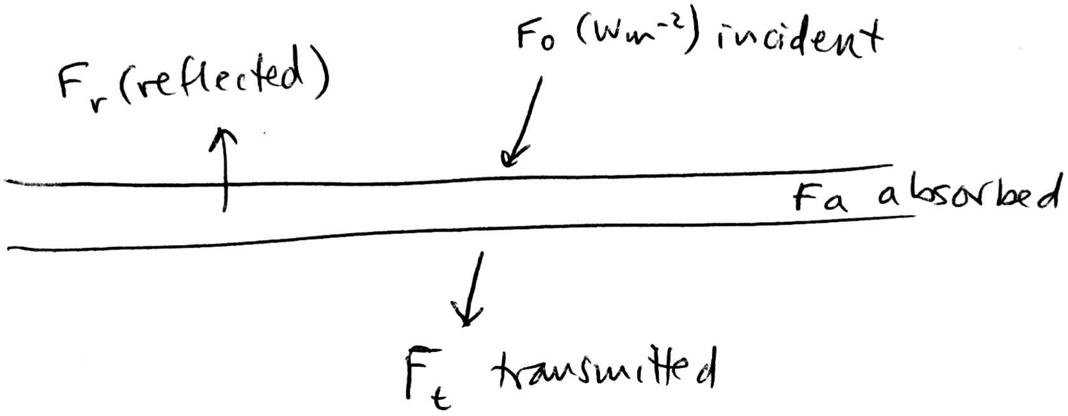
$$\sigma = \frac{8\pi^5k^4}{15c^3h^3}\,. \tag{13–26}$$

Equation (13–25) is the same as *Stefan's law* (Eq. (8–54)); and when the values of k, c, and h are inserted in Eq. (13–26), the calculated and experimental values of σ agree exactly, within the limits of experimental error.

Thus quantum theory and the methods of statistics provide a theoretical basis for the form of Planck's law, and relate the experimental constants c_1, c_2, and σ to the fundamental constants h, c, and k. Expressions for the internal energy, the entropy, and the Helmholtz and Gibbs functions of blackbody radiant energy were derived by the principles of thermodynamics in Section 8–7 and need not be repeated here. It will be recalled that the Gibbs function $G = 0$, which might also have been taken as a justification for setting $\mu = 0$ in the B-E distribution function.

Radiative properties of non-black materials

Consider a radiation flux F_o incident on one side of a horizontally homogeneous slab of some material (like a stratus cloud, or the ozone layer, or a snowpack). What can happen to that radiation we will classify into three categories: reflected, absorbed, transmitted.



In steady state, these rates F_o, F_r, F_a, and F_t are constant in time, and

$F_o = F_r + F_a + F_t$ (conservation of energy).

Define ratios:

transmittance (transmissivity)	$t = F_t / F_o$
reflectance (reflectivity, albedo)	$r = F_r / F_o$
absorptance (absorptivity)	$a = F_a / F_o$

so $F_o = rF_o + aF_o + tF_o$,

and $\boldsymbol{r + a + t = 1}$.

These ratios vary with wavelength. They are all fractions between 0 and 1.

For an ***opaque*** surface: $t = 0$; $r + a = 1$

For a ***blackbody***: $a = 1$; $r = t = 0$

Emission from non-black materials

Let I_λ be the emission rate from an object (which may be non-black) at wavelength λ at temperature T.
Let $a(\lambda)$ be the absorptance of the object.
Let B_λ be the emission rate from a blackbody at the same temperature at wavelength λ.

Define ***emittance (emissivity)***: $\varepsilon_\lambda \equiv I_\lambda / B_\lambda$

Kirchhoff's law: $\boldsymbol{\varepsilon_\lambda = a_\lambda}$

Kirchhoff's law is derived under conditions of thermal equilibrium, but it is more generally valid in a *collision-dominated* system; i.e. in which the rate of collisional excitation is much greater than the rate of absorption of photons.

So $I_\lambda = a_\lambda B_\lambda$. Since $a_\lambda \leq 1$, an object in thermal equilibrium cannot emit more than a blackbody.

For a blackbody, $a = e = 1$.

For an opaque surface: $a_\lambda + r_\lambda = 1$,
so $\varepsilon_\lambda + r_\lambda = 1$

Proof (by thermodynamics)

(a) For the case a_λ independent of λ ("grey").

Consider two infinite parallel opaque walls facing each other. Start them both at temperature T, then disconnect them so that they are not in thermal contact. Let Wall 1 be a blackbody. Wall 2 is not black; it has absorptance $a_2 < 1$; its emissivity ε_2 is unknown. To find ε_2 we consider the energy budget of Wall 2:

Flux emitted by Wall 1: $F = \sigma T^4$

Flux absorbed by Wall 2 = (absorptance) × (incident flux)

$= a_2 \sigma T^4$

Flux emitted by Wall 2 $= \varepsilon_2 \sigma T^4$.

Heating rate of Wall 2 (W m^{-2}) = gain - loss

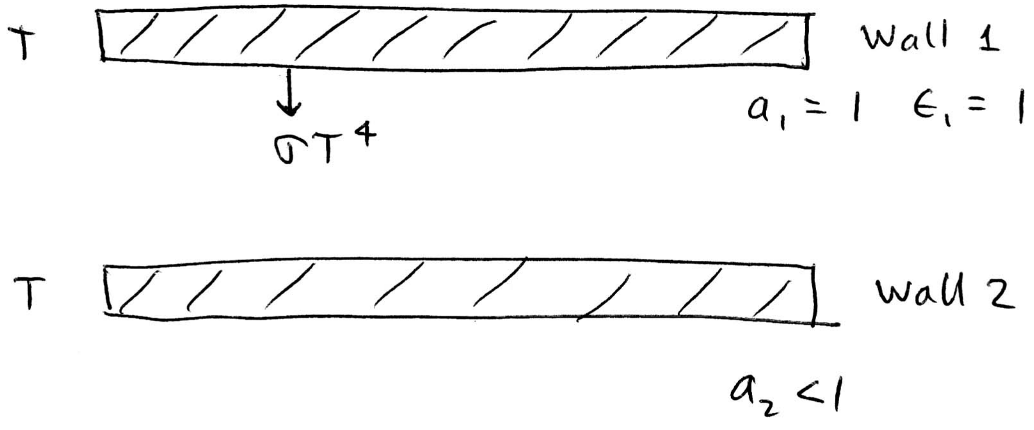
= flux absorbed - flux emitted

$= a_2 \sigma T^4 - \varepsilon_2 \sigma T^4$

$= (a_2 - \varepsilon_2) \sigma T^4$.

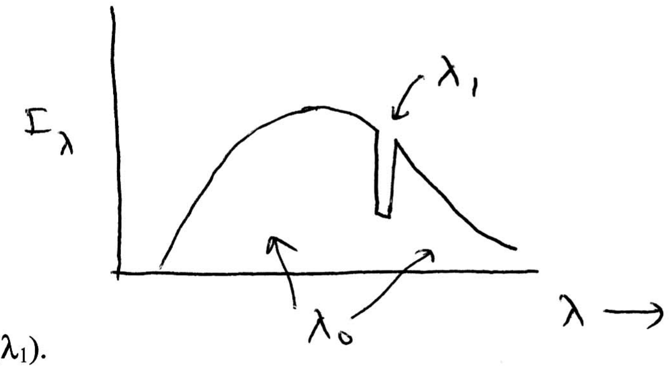
If the heating rate is not zero then the wall is changing temperature; e.g. if $\varepsilon_2 < a_2$ then Wall 2 heats while Wall 1 cools, in violation of the second law of thermodynamics. Therefore the heating rate is zero:

$0 = (a_2 - \varepsilon_2) \sigma T^4$, and $\mathbf{a_2 = \varepsilon_2}$.



(b) Proof for *a* varying with λ, to show that $\varepsilon_\lambda = a_\lambda$ at each wavelength.

Wall 1 is still black; Wall 2 is black at all wavelengths except a narrow wavelength range at λ_1. Call all the remaining wavelengths λ_o. Emission from Wall 2 looks like this:



So $a(\lambda_o) = \varepsilon(\lambda_o) = 1$. We now must find $\varepsilon(\lambda_1)$.

Emitted by Wall 1: $F_1 = \pi I_1$; $I_1 = B(\lambda_1) + \int B(\lambda_0) d\lambda_0$.

Emitted by Wall 2: $I_2 = \varepsilon(\lambda_1) B(\lambda_1) + \int B(\lambda_0) d\lambda_0$.

Energy budget of Wall 2: absorbed = emitted

$$\pi\left[a(\lambda_1)B(\lambda_1) + \int B(\lambda_0)d\lambda_0\right]I_2 = \pi\left[\varepsilon(\lambda_1)B(\lambda_1) + \int B(\lambda_0)d\lambda_0\right]$$

So $a(\lambda_1) = \varepsilon(\lambda_1)$, or $\mathbf{a_\lambda = \varepsilon_\lambda}$.

Now we can see why a cavity emits as a blackbody. Suppose the walls are half-black: $a=0.5$, $r=0.5$, $\varepsilon=0.5$. Then each wall *emits* half of the Planck function but also *reflects* half, so the total radiation emerging from the surface is the Planck function.

Notes:

1. In general *a* depends on angle, so Kirchhoff's law must be qualified:

$a(\lambda, \theta, \phi) = \varepsilon(\lambda, \theta, \phi)$. For opaque surfaces, $a = 1 - r$, so $\varepsilon(\lambda, \theta, \phi) = 1 - r(\lambda, \theta, \phi)$.

2. The validity of Kirchhoff's law does not depend on thermal equilibrium but rather only on "local thermodynamic equilibrium (LTE), the condition that the collisional lifetime of an energy level is much less than the radiational lifetime. This ensures that the populations of states is in accord with the Boltzmann distribution and is required for the temperature to be defined.

Reference: E.A. Milne, 1930, *Thermodynamics of the Stars*, pp. 79-82. Reprinted by Menzel, 1966, *Selected Papers on the Transfer of Radiation* (pub. Dover).

Radiative lifetimes $\tau_r = A_{21}^{-1}$
for vibrational transitions:
H_2O 6.3-μm τ_r~0.1 sec.
CO_2 15-μm τ_r~0.4 sec.
O_3 9.6-μm τ_r~0.1 sec.

Collisional lifetimes $\tau_c = c_{21}^{-1}$
at $T = 0°C, p = 1$ bar:
For vibrational transitions 10^{-6} - 10^{-5} sec.
For rotational transitions $\tau_c < 10^{-6}$ sec.

But τ_c is proportional to 1/p, so whereas $\tau_r \sim 10^4\ \tau_c$ at sea level, $\tau_r \sim \tau_c$ at $p \sim 10^{-4}$ bar (z = 70 km).

LTE breaks down at different altitudes for different gases, and at different altitudes for different frequencies for the same gas.

Local Thermodynamic Equilibrium (LTE)

In LTE we can assume

(1) Maxwell-Boltzmann velocity distribution

(2) Boltzmann distribution of excited states

(3) Emission = $\varepsilon_\nu B_\nu$

"Local" thermodynamic equilibrium means that the temperature may vary with location, but if it varies slowly with distance then the velocity distribution and the distribution of excited states is given by the *local* temperature.

A consequence of LTE is that the emitted radiation spectrum is independent of the absorbed radiation spectrum.

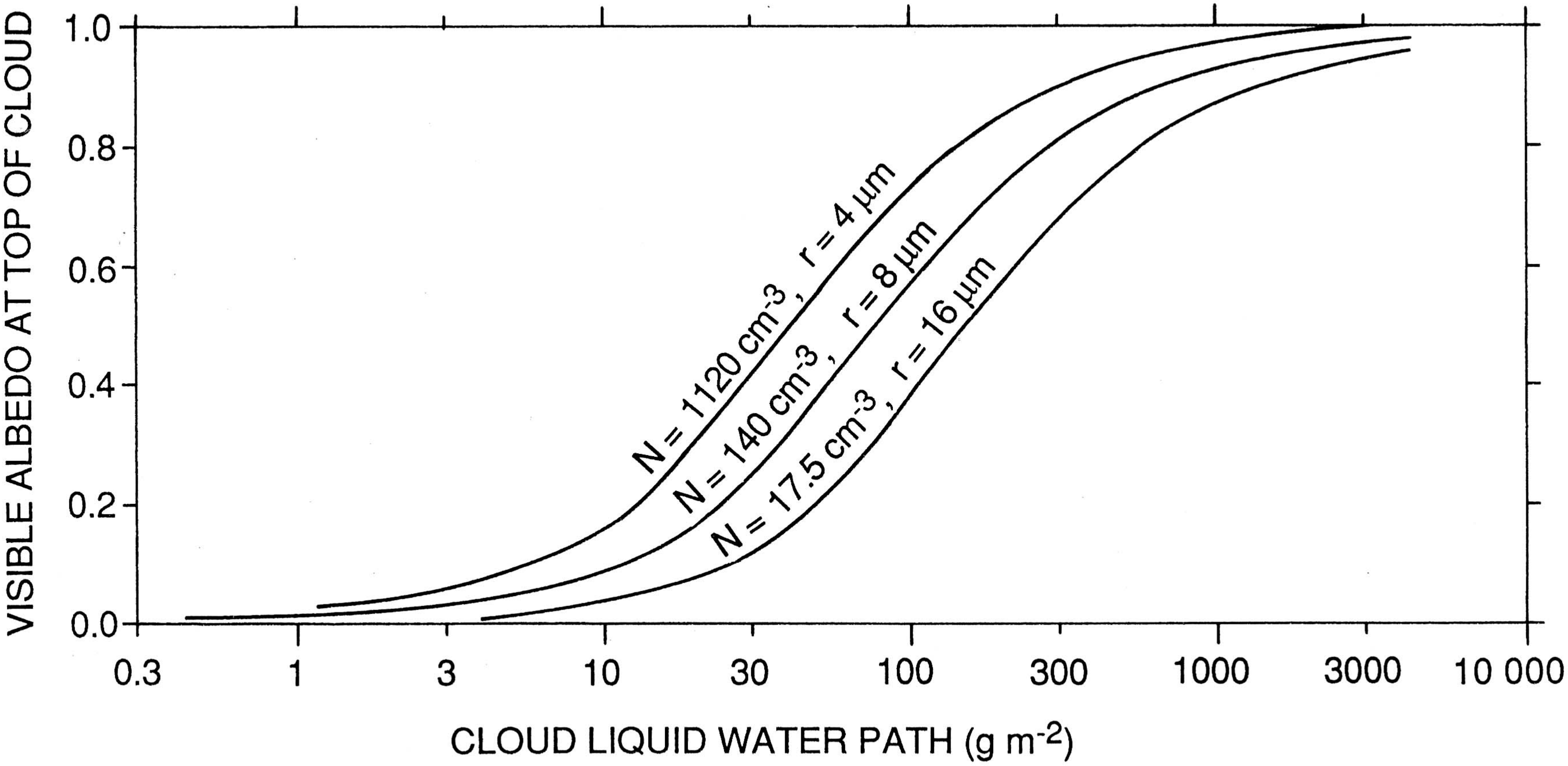


Fig. 2 Albedo at top of cloud as a function of liquid water path for three different number densities (*N*) of CCN corresponding to three different average droplet radii (*r*). The calculation is for visible wavelengths at which the cloud is nonabsorbing and for an overhead sun (elevation angle 90°). For a typical maritime cloud liquid water content of 0.3 g m^{-3}, a cloud of thickness 1 km has LWP = 300 g m^{-2}. [Modified from Fig. 12.6 of Twomey (1977).]

Radiative transfer equation.

$$dI = -\text{losses} + \text{gains}$$

$$= dI_a + dI_{so} + dI_{em} + dI_{si}$$

Subscripts

a	absorption
s	scattering
e	extinction
em	emission
si	scattering-in
so	scattering-out

$$\left.\begin{aligned} dI_{so} &= -\beta_s I\,ds \\ dI_a &= -\beta_a I\,ds \end{aligned}\right\} -\beta_e I\,ds$$

Absorptance of path ds:

$$\frac{-dI_a}{I} = \beta_a\,ds$$

By Kirchhoff's law, absorptance = emissivity

$$\text{so} \quad \epsilon = \beta_a\,ds$$

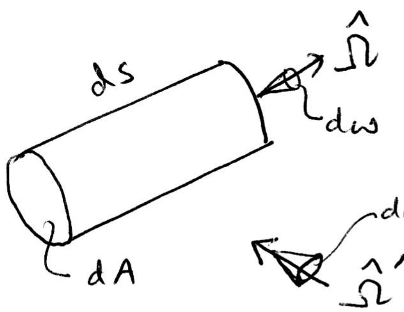
$$\therefore \quad dI_{em} = \epsilon B = \beta_a B\,ds.$$

Put this into r.t.e.:

$$dI = -\beta_e I\,ds + \beta_a B\,ds + dI_{si} \qquad (1)$$

Now derive the gain due to scattering-in:
It's related to the scattering-out loss of intensity from other directions.

volume element $= ds\, dA$
(where dA is $\perp \hat{\Omega}$)



Definition of intensity:

$$\text{Intensity} = \frac{dQ}{dA\, dt\, d\omega} \qquad (2)$$

Intensity lost by scattering-out is

$$dI_{so} = -\beta_s\, ds\, I$$

Energy lost from $I(\hat{\Omega})$ by scattering-out (within volume element $ds\, dA$):

$$dQ_{so}(\hat{\Omega}) = dA\, dt\, d\omega\, dI_{so}(\hat{\Omega}) = -dA\, dt\, \beta_s\, ds \left[I(\hat{\Omega})\, d\omega \right] \qquad (3)$$

The same multiplier gives the energy loss from $I(\hat{\Omega}')\, d\omega'$ in this volume element (if β_s is independent of direction), because it encounters the same mass. Therefore:

$$dQ_{so}(\hat{\Omega}') = -dA\, dt\, \beta_s\, ds \left[I(\hat{\Omega}')\, d\omega' \right]$$

Then using (2):

$$dI_{so}(\hat{\Omega}')\, dA\, d\omega' = \frac{dQ_{so}(\hat{\Omega}')}{dt} = -dA\, \beta_s\, ds\, I(\hat{\Omega}')\, d\omega' \qquad (4)$$

This is the loss from the $\hat{\Omega}'$ beam by scattering within volume element $ds\, dA$. Some of this scattered radiation will go into the $\hat{\Omega}$ direction, according to the Phase Function.

Definition of Phase function $P(\hat{\Omega}', \hat{\Omega})$:

Given a photon that was incident from solid angle $d\omega'$ about $\hat{\Omega}'$ and has been scattered, then

$\frac{1}{4\pi} P(\hat{\Omega}', \hat{\Omega})\, d\omega$ is the probability that the photon will reappear in solid angle element $d\omega$ about $\hat{\Omega}$.

The average value of P is 1 : $\int_{4\pi} \frac{1}{4\pi} P(\hat{\Omega}', \hat{\Omega})\, d\omega = 1$.

Gain to $I(\hat{\Omega})$ due to scattering-in :

$dI_{si}(\hat{\Omega})\, dA\, d\omega$ energy gain in direction $\hat{\Omega}$ per unit time

$= \beta_s I(\hat{\Omega}')\, ds\, dA\, d\omega'$ energy scattered per unit time out of $\hat{\Omega}'$ in volume element $ds\, dA$ [from (4)]

$\times \frac{1}{4\pi} P(\hat{\Omega}', \hat{\Omega})\, d\omega$ probability (given scattering) of scattering from $\hat{\Omega}'$ into $\hat{\Omega}$.

Then integrate over all incoming angles $d\omega'$:

$$dI_{si}(\hat{\Omega})\, dA\, d\omega = \int_{4\pi} \beta_s I(\hat{\Omega}')\, ds\, dA\, d\omega' \frac{1}{4\pi} P(\hat{\Omega}, \hat{\Omega})\, d\omega$$

$$dI_{si}(\hat{\Omega}) = \beta_s\, ds \int_{4\pi} I(\hat{\Omega}') \frac{P(\hat{\Omega}', \hat{\Omega})}{4\pi}\, d\omega' \qquad (5)$$

Now put (5) into (1) :

Combining all losses and gains (Eqs 1, 5):

$$dI(\hat{\Omega}) = -\beta_e I(\hat{\Omega})\,ds + \beta_a B\,ds + \beta_s\,ds \int_{4\pi} I(\hat{\Omega}') \frac{P(\hat{\Omega}',\hat{\Omega})}{4\pi}\,d\omega'$$

$$\beta_e\,ds = d\tau_{path} \qquad \frac{\beta_s}{\beta_e} = \tilde{\omega} \qquad \frac{\beta_a}{\beta_e} = 1-\tilde{\omega}$$

$$\beta_s\,ds = \tilde{\omega}\,d\tau_{path}$$

$$\beta_a\,ds = (1-\tilde{\omega})\,d\tau_{path}$$

$$\frac{dI(\hat{\Omega})}{d\tau_{path}} = -I(\hat{\Omega}) + (1-\tilde{\omega})B + \tilde{\omega}\int_{4\pi} I(\hat{\Omega}') \frac{P(\hat{\Omega}',\hat{\Omega})}{4\pi}\,d\omega' \tag{6}$$

This is the integro-differential equation of radiative transfer (same as Petty Eq. 11.9 but with different sign convention for τ).

If $\beta_s = 0$ then $\tilde{\omega} = 0$ and

$$\frac{dI}{d\tau_{path}} = -I + B .$$

or

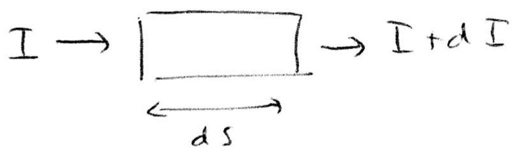
$$\boxed{\mu \frac{dI}{d\tau} = -I + B}$$

"Longwave" radiative-transfer equation.

Solution of

Radiative transfer equation for absorption & emission (no scattering) Schwarzschild's eqn. for longwave

Drop the subscript λ or ν.



① **Absorption.**

$$dI_{abs} = -\beta_a I\, ds.$$

Absorptance = fraction absorbed = $\frac{-dI}{I} = \beta_a ds$

② **Emission**

By Kirchhoff's law ($\epsilon = a$),

emissivity of the path ds is $\epsilon = \beta_a ds$

Intensity emitted from ds is $\epsilon \cdot B = \beta_a ds B(T(s))$

③ radiative transfer eq:

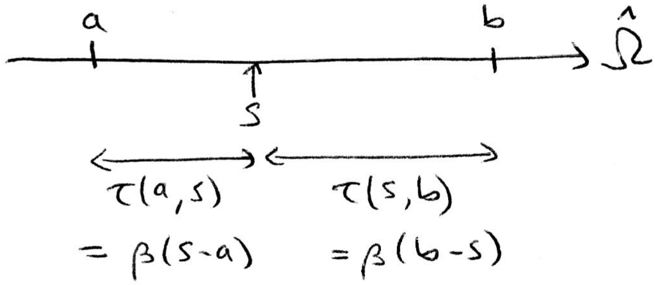
$$dI = -\underset{\substack{\text{absorption} \\ \text{(loss)}}}{\beta_a I\, ds} + \underset{\substack{\text{emission} \\ \text{(gain)}}}{\beta_a B\, ds} \qquad (1)$$

Now drop the subscript $\beta_a \to \beta$, but it means absorption.

$$\frac{1}{\beta}\frac{dI}{ds} = -I(s) + B(s) \qquad (2)$$

④ Solution of the r.t.e.,

Given $I(a)$ find $I(b)$. s is the variable of integration.
Measure τ along the path.



To solve (2), multiply by the integrating factor $e^{+\beta(s-a)}$

$$\underbrace{e^{\beta(s-a)} \frac{dI}{\beta ds}} = \underbrace{-e^{\beta(s-a)} I(s)} + e^{\beta(s-a)} B(s)$$

$$\frac{1}{\beta}\frac{d}{ds}\left[e^{\beta(s-a)} I(s)\right] = e^{\beta(s-a)} B(s)$$

Solve this differential equation by integrating.
Integrate along $\hat{\Omega}$ from $s=a$ to $s=b$:

$$\frac{1}{\beta}\left[e^{\beta(s-a)} I(s)\right]_{s=a}^{s=b} = \int_a^b e^{\beta(s-a)} B(s)\, ds$$

$$\frac{1}{\beta} e^{\beta(b-a)} I(b) = \frac{1}{\beta} I(a) + \int_a^b e^{\beta(s-a)} B(s)\, ds.$$

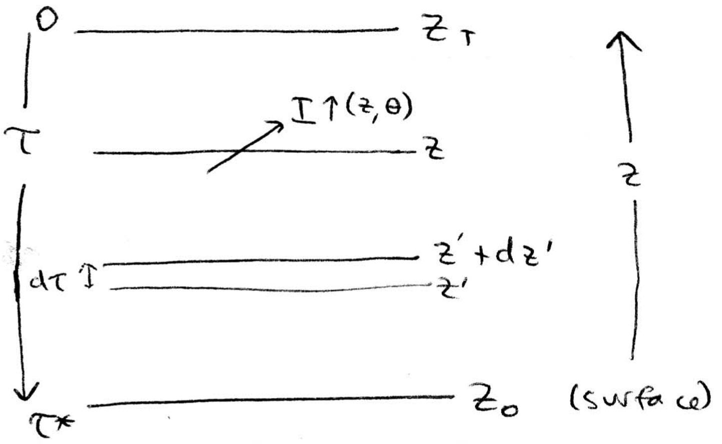
Now multiply through by $\beta e^{-\beta(b-a)}$ to get $I(b)$ on L.H.S.

$$I(b) = I(a)\, e^{-\beta(b-a)} + \int_a^b \beta\, \underbrace{e^{-\beta(b-a)}\, e^{\beta(s-a)}}_{e^{-\beta(b-s)}}\, B(s)\,ds$$

Rewriting in terms of τ (path) and $d\tau = \beta\, ds$:

$$I(b) = \underbrace{I(a)\, e^{-\tau(a,b)}}_{\text{attenuated incident beam}} + \underbrace{\int_{\tau(a)}^{\tau(b)} B(s)\, e^{-\tau(s,b)}\, d\tau}_{\substack{\text{contributions to } I \\ \text{from sources along the} \\ \text{path between } a \text{ and } b, \\ \text{attenuated along the} \\ \text{remaining distance to } b.}} \tag{3}$$

⑤ Now change variables for plane-parallel geometry:



Eq. (3) for upward intensity:

$I(s) \longrightarrow I\uparrow(z,\theta)$

$\tau \longrightarrow \tau/\mu$ (τ now measured vertically)

$a \longrightarrow z_0$

$$I\uparrow(z,\theta) = I\uparrow(z_0,\theta)\, e^{-\tau(z,z_0)/\mu} + \int_{\tau(z)}^{\tau(z_0)} B(z')\, e^{-\tau(z,z')/\mu}\, \frac{d\tau}{\mu} \tag{4}$$

Assume surface emissivity $= 1$

so $I(z_0,\theta) = B(T_g)$ where T_g = ground temp.

$$I\uparrow(z,\theta) = \underbrace{B(T_g)}_{\text{emission from surface}}\ \underbrace{e^{-\tau(z_0,z)/\mu}}_{\text{transmittance from surface to level } z} + \int_{\tau(z)}^{\tau(z_0)} \underbrace{B(T_{z'})}_{\text{Planck function at } z'}\ \underbrace{e^{-\tau(z,z')/\mu}}_{\text{transmittance from } z' \text{ to } z}\ \underbrace{\frac{d\tau}{\mu}}_{\text{emissivity of layer } dz'} \tag{5}$$

Emissivity of layer dz in direction θ:

$$\epsilon = \beta_a\, ds = \beta_a \frac{dz}{\mu} = \frac{d\tau}{\mu}$$

Change variable of integration from $d\tau$ to dz' :

$$-\frac{d\tau}{\mu} = \beta\,\frac{dz'}{\mu} .$$ Then (5) becomes :

$$I\uparrow(z,\theta) = B(T_g)\, e^{-\tau(z,z_0)/\mu} + \int_{z_0}^{z} B(T_{z'})\, e^{-\tau(z,z')/\mu}\, \beta\,\frac{dz'}{\mu} \qquad (6)$$

Eq(6) can be written in terms of transmittance from z' to z :

$$t(z,z',\theta) = e^{-\tau(z,z')/\mu} \quad \text{or} \quad t = e^{-\tau/\mu}$$

So $\frac{dt}{d\tau} = -\frac{1}{\mu}\, e^{-\tau/\mu}$. Also, $-d\tau = \beta\, dz$

$$\frac{dt}{dz} = \frac{dt}{d\tau}\frac{d\tau}{dz} = \frac{\beta}{\mu}\, e^{-\tau/\mu}$$. This appears in (6).

So (6) becomes.

$$I\uparrow(z,\theta) = B(T_g)\, e^{-\tau(z,z_0)/\mu} + \int_{z_0}^{z} B(T_{z'})\, \underbrace{\frac{dt}{dz'}}_{\text{Weighting function } W}\, dz' \qquad (7)$$

where t means $t(z,z',\theta)$

Eqs. (5) and (7) are solutions for I at any level z. Two levels of special interest are $z = z_0$ (surface) and $z = z_T$ (TOA).

Upward intensity at top of atmosphere (seen by satellite)

From (5), using τ as coordinate:

$$I\uparrow(\text{TOA}, \theta) = B(T_g)\, e^{-\tau^*/\mu} + \int_0^{\tau^*} B(\tau)\, e^{-\tau/\mu} \frac{d\tau}{\mu}$$

From (7), using z as coordinate:

$$I\uparrow(\text{TOA}, \theta) = B(T_g)\, e^{-\tau^*/\mu} + \int_{z_0}^{z_T} B(T_z) \underbrace{\frac{dt(z, z_T)}{dz}}_{\text{“}W\uparrow\text{”}} dz$$ (Petty 8.54)

Downward intensity at surface

Similarly

$$I\downarrow(z_0, \theta) = \int_0^{\tau^*} B(\tau)\, e^{-(\tau^*-\tau)/\mu} \frac{d\tau}{\mu}$$

or using z as coordinate:

$$I\downarrow(z_0, \theta) = \int_{z_0}^{z_T} B(T_z) \underbrace{\frac{dt(z_0, z)}{dz}}_{\text{“}W\downarrow\text{”}} dz$$ (Petty 8.53)

Exponential Integrals

Reference: Abramowitz & Stegun, "Handbook of Mathematical Functions", chapter 5 (contains Tables).

$$E_n(\tau) \equiv \int_1^\infty \frac{e^{-\tau x}}{x^n}\,dx$$

$$E_n(0) = \frac{1}{n-1} \qquad (n>1)$$

$$\frac{dE_n(\tau)}{d\tau} = -E_{n-1}(\tau)$$

Recursion:

$$E_{n+1}(\tau) = \frac{1}{n}\left[e^{-\tau} - \tau E_n(\tau)\right] \quad (n=1,2,3,\dots)$$

Asymptotic limit: $E_n(\tau) \rightarrow \frac{e^{-\tau}}{\tau}$ as $\tau \rightarrow \infty$

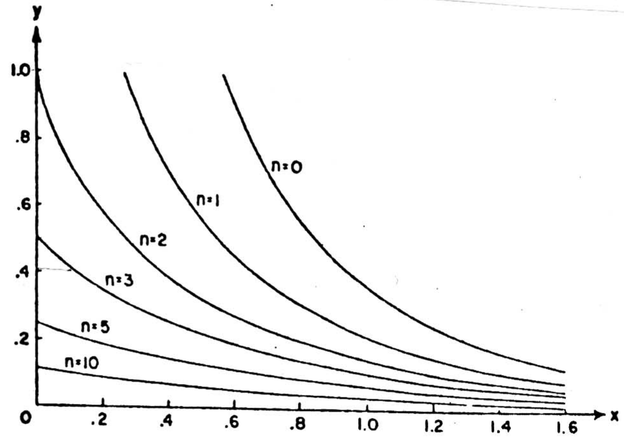
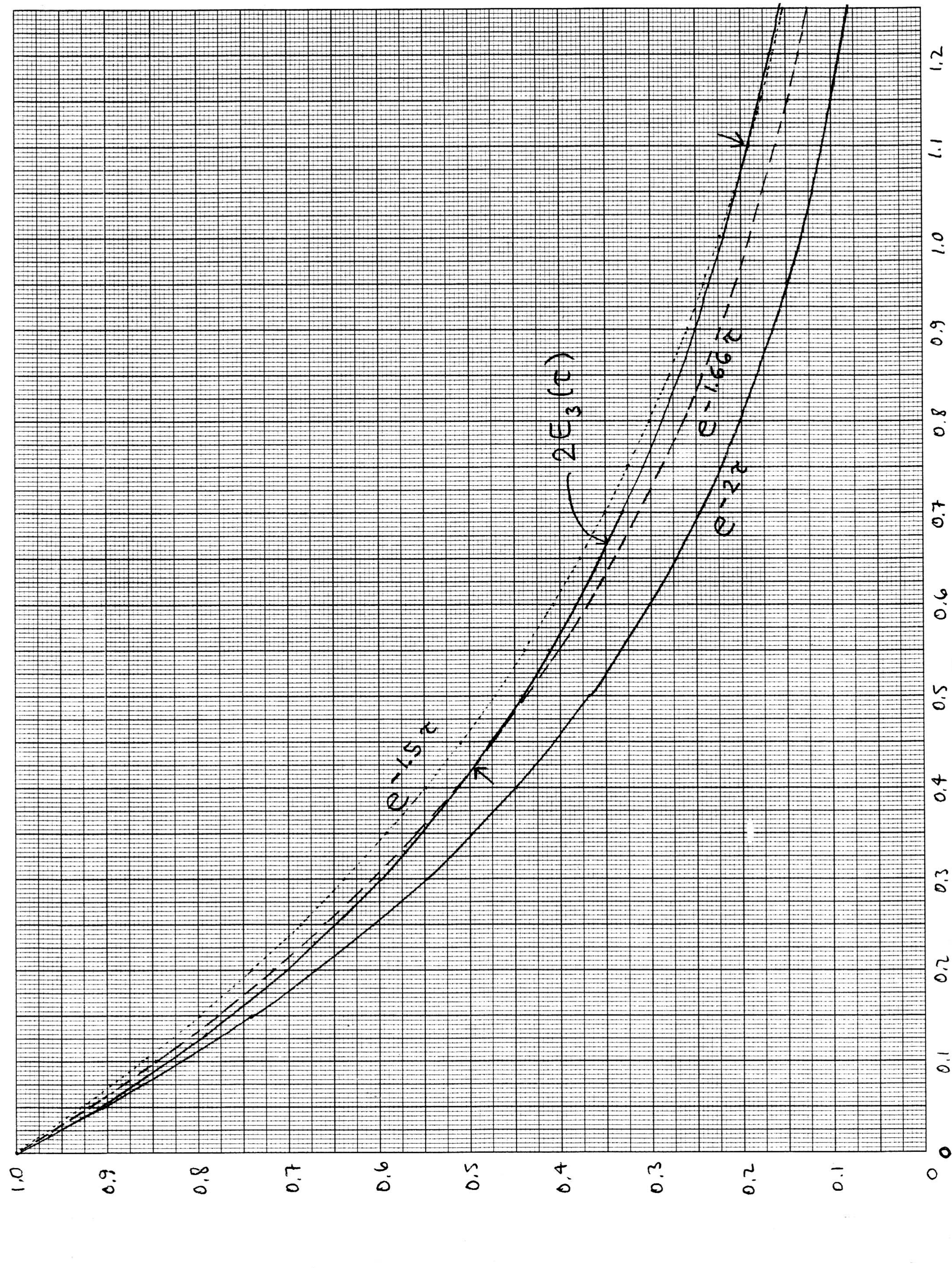
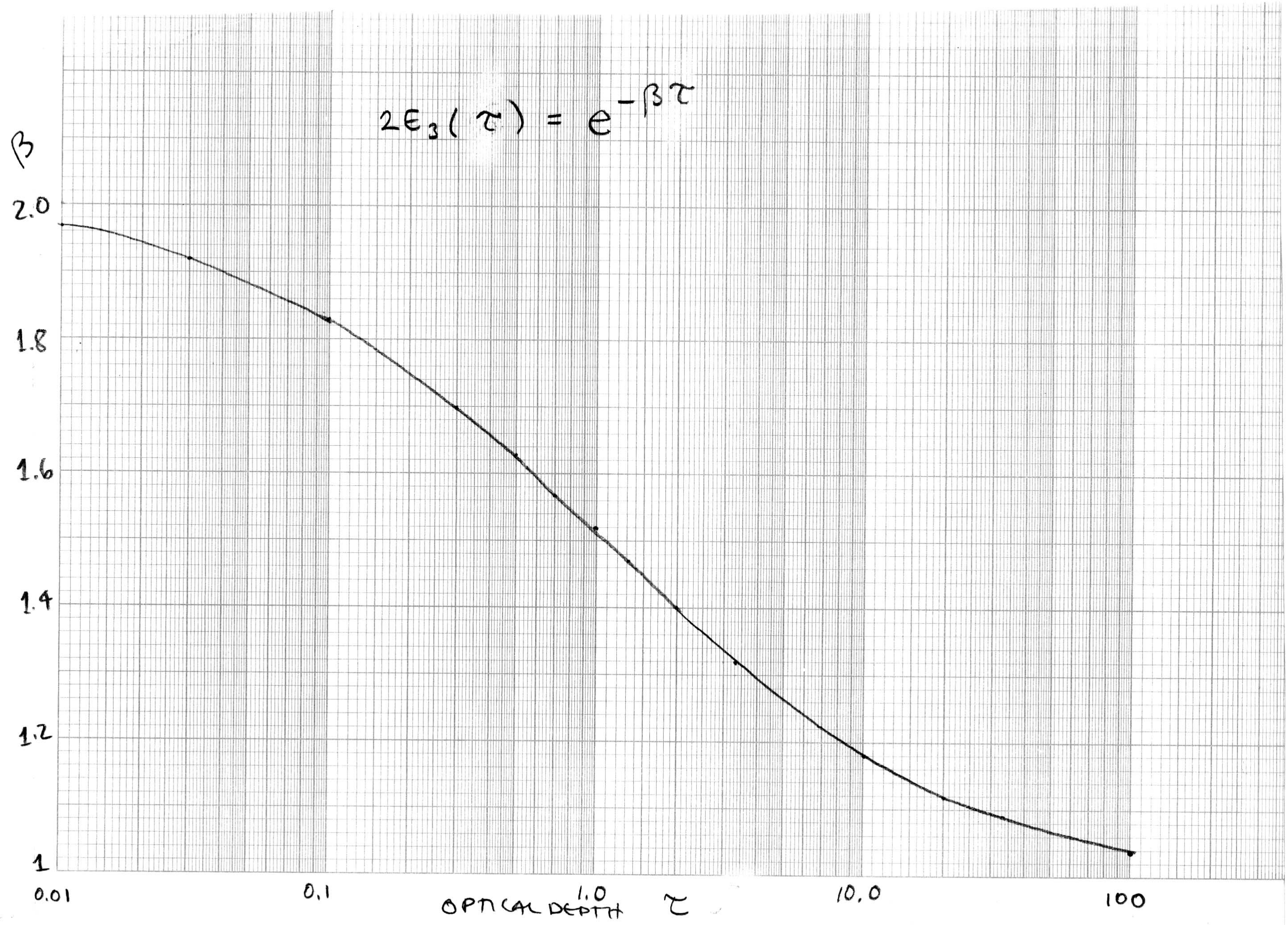
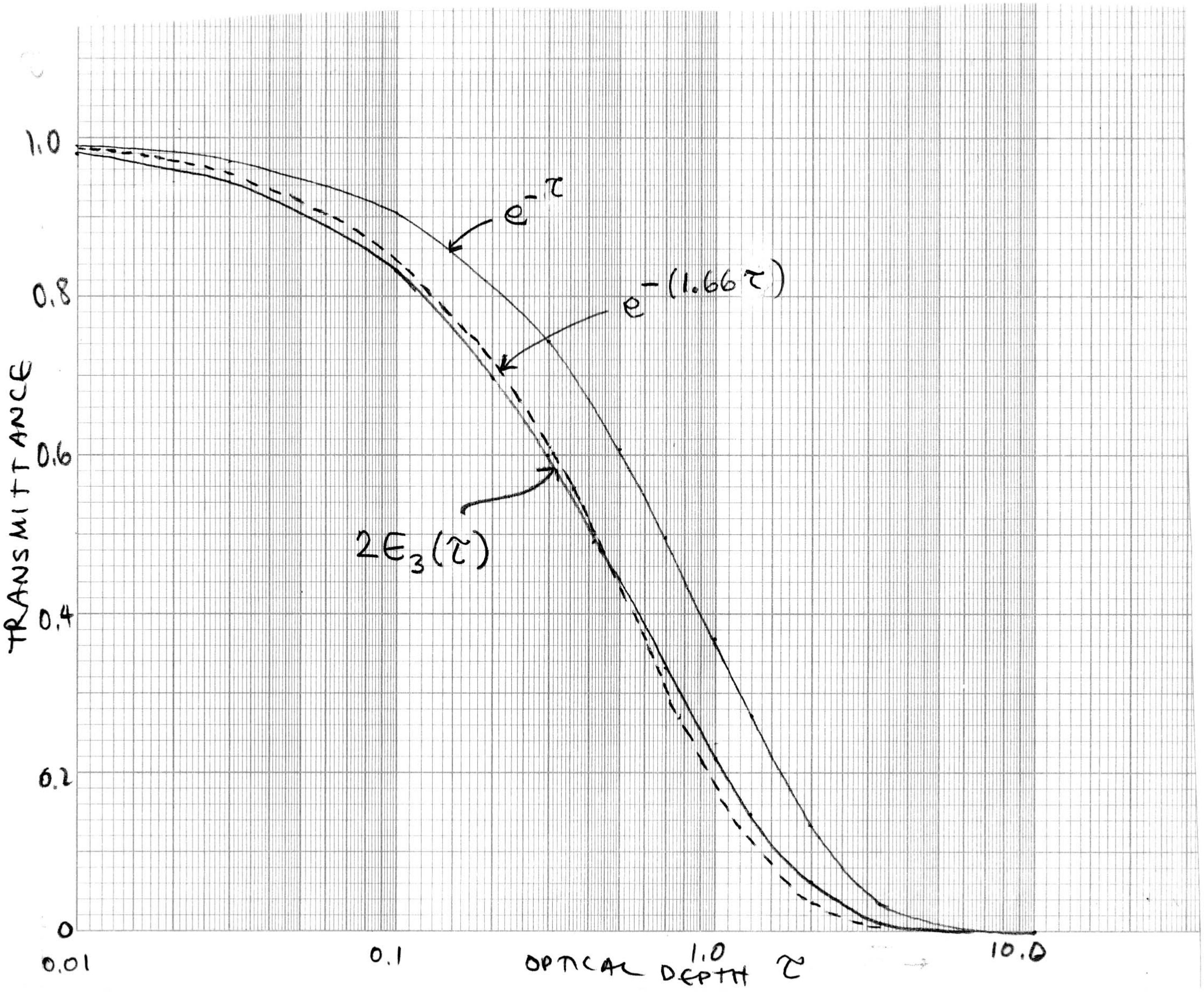


FIGURE 5.2. $y = E_n(x)$
$n = 0, 1, 2, 3, 5, 10$


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
τ
$e^{-1.5\tau}$
$2E_3(\tau)$
$e^{-1.66\tau}$
$e^{-2\tau}$


$2E_3(\tau) = e^{-\beta\tau}$
β
2.0
1.8
1.6
1.4
1.2
1
0.01
0.1
1.0
10.0
100
OPTICAL DEPTH τ


1.0
0.8
0.6
0.4
0.2
0
TRANSMITTANCE
0.01
0.1
1.0
10.0
OPTICAL DEPTH τ
$e^{-\tau}$
$e^{-(1.66\tau)}$
$2E_3(\tau)$

RODGERS
& WALSHAW
1966
QJRMS 92, 67-92

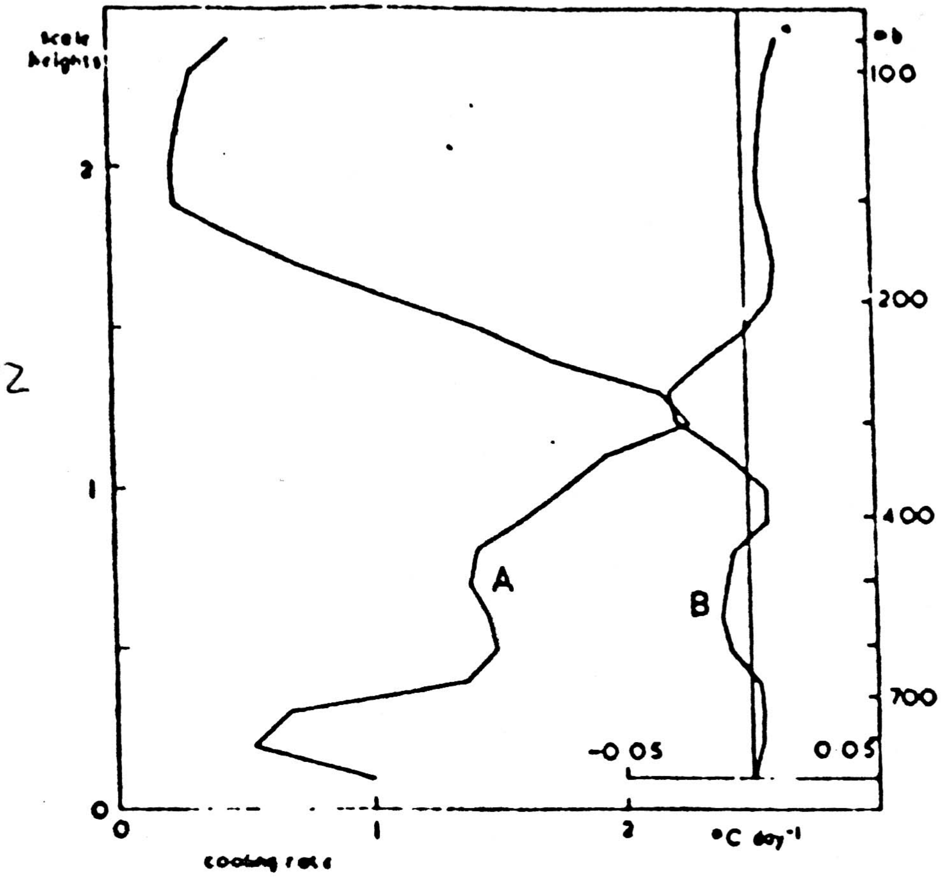


Figure 6. Accuracy of the diffuse approximation.

A : 'Exact' i.e. using the diffuse transmission function.

B : 'Exact' minus 'approximate.'

(Water vapour rotation band. Atmosphere T.1, Appendix B).

Radiative-Equilibrium Temperature Profile

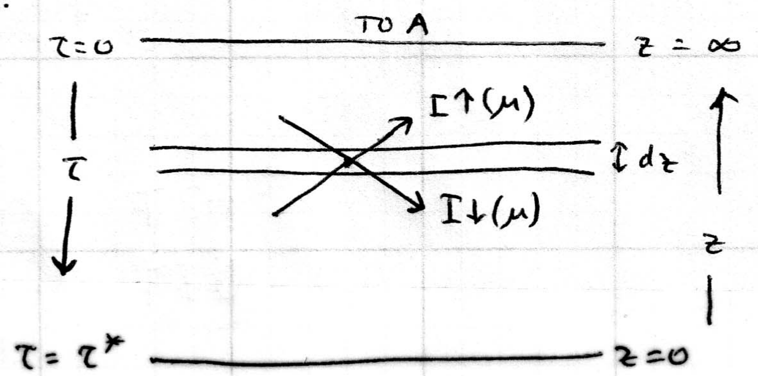
in multi-layer (or continuously-varying) atmosphere.

[following Houghton chapter 2.] uses Two-stream method.

Assume the atmosphere is transparent to solar radiation so the solar energy $\frac{S_0}{4}(1-A_p)$ is absorbed at the lower boundary, and in the atmosphere we need to compute only the transport of longwave radiation.

Model atmosphere is nonabsorptive in solar and "grey" in IR (i.e. k_{abs} independent of λ so τ indep. of λ); so we use spectrally-integrated intensities and fluxes.

Coordinates:



$d\tau = -k\rho\, dz$

Sign convention: μ is positive for both $I\uparrow$ and $I\downarrow$ $(0 \le \mu \le 1)$. Then

$$\mu \frac{dI\downarrow}{d\tau} = -\text{losses} + \text{gains}$$

$$\mu \frac{dI\uparrow}{d\tau} = +\text{losses} - \text{gains}$$ because increasing τ means moving backwards along the path.

so

$$\boxed{\mu \frac{dI\uparrow}{d\tau} = I\uparrow - B \qquad \mu \frac{dI\downarrow}{d\tau} = -I + B} \tag{1}$$

But for heating rates we need to integrate I over angle;
We need an equation for F not I; the "two-stream" approximation.

We can replace I by F in (1) <u>if</u>

we replace B by πB

and τ/μ by $\tau/\bar{\mu}$

$\frac{1}{\bar{\mu}} = 1.66$ is called the "diffusivity factor."

It is an average value of $\frac{1}{\mu}$ which corresponds to $\theta = 53°$.

So the analog of (1) for flux is

$$\left.\begin{aligned} \bar{\mu}\frac{dF\downarrow}{d\tau} &= -F\downarrow + \pi B \\ \bar{\mu}\frac{dF\uparrow}{d\tau} &= F\uparrow - \pi B \end{aligned}\right\} \quad (2)$$

These equations can be solved by adding and subtracting them:

$$\left.\begin{aligned} \bar{\mu}\frac{d(F\uparrow + F\downarrow)}{d\tau} &= F\uparrow - F\downarrow \\ \bar{\mu}\frac{d(F\uparrow - F\downarrow)}{d\tau} &= F\uparrow + F\downarrow - 2\pi B \end{aligned}\right\} \quad (3).$$

Following Houghton, define the abbreviations ψ and ϕ:

$\psi \equiv F\uparrow + F\downarrow$, twice the average flux

$\phi \equiv F\uparrow - F\downarrow$, the <u>net</u> flux (what's its sign?)

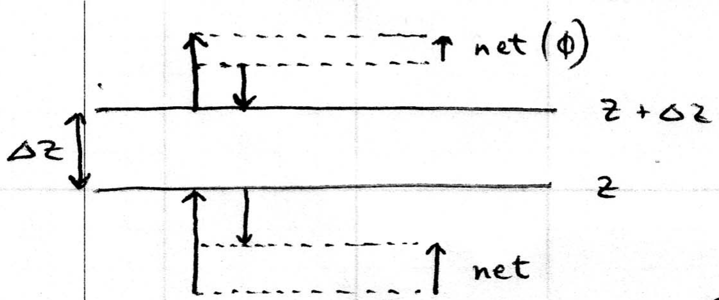
so $F\uparrow = \frac{\psi+\phi}{2}$ $\quad F\downarrow = \frac{\psi-\phi}{2}$

so (3) becomes

$$\begin{cases} \bar{\mu}\dfrac{d\psi}{d\tau} = \phi & (4) \\[2ex] \bar{\mu}\dfrac{d\phi}{d\tau} = \psi - 2\pi B & (5) \end{cases}$$

Now $\dfrac{d\phi}{d\tau} = 0$ for radiative equilibrium, as we illustrate next. i.e. net flux is a constant, independent of height.

The HEATING RATE of a layer Δz is given by the net effect of <u>four</u> fluxes.



$\phi(z+\Delta z) = F\uparrow(z+\Delta z) - F\downarrow(z+\Delta z)$

$\phi(z) = F\uparrow(z) - F\downarrow(z)$

$$\frac{d\phi}{dz} = \frac{d}{dz}(F\uparrow - F\downarrow)$$

$\dfrac{d\phi}{dz}$ is negative in this example, leading to heating.

Convert this <u>convergence-of-net-flux</u> $\dfrac{d\phi}{dz}$ into a <u>heating rate</u> $\dfrac{dT}{dt}$:

$$\rho_{air}\, C_p \frac{dT}{dt} = -\frac{d\phi}{dz} \qquad \text{(units W m}^{-3}\text{)}$$

where ρ_{air} is density of air ($g\ m^{-3}$)

C_p is heat capacity of air ($J\ g^{-1}\ deg^{-1}$)

$\dfrac{dT}{dt}$ is heating rate ($deg\ sec^{-1}$)

In radiative equilibrium $\frac{d\phi}{dz} = 0$.

[and $\frac{dT}{dt} = 0$ as well, if there are no other sources of heating.]

$$\frac{d}{dz}(F\uparrow - F\downarrow) = \frac{d\phi}{dz} = 0.$$

So $F\uparrow - F\downarrow = \Phi$ = <u>constant</u>.

The net flux is a constant, independent of z (or τ).

From (5):

$$\psi = 2\pi B \qquad (6)$$

or $\frac{F\uparrow + F\downarrow}{2} = \pi B$; i.e. πB is the average of $F\uparrow$, $F\downarrow$, as expected.

Substitute (6) into (4): $2\pi\bar{\mu}\frac{dB(\tau)}{d\tau} = \phi$.

Integrating, $B(\tau) = \frac{\phi}{2\pi\bar{\mu}}\tau + C_1$

Find the constant of integration C_1 by using the boundary condition at TOA ($\tau = 0$) where $B(0) = C_1$.

$F\downarrow(\text{TOA}) = F\downarrow(\tau = 0) = 0$; no downward IR at TOA.

So $\phi = \psi$ at TOA : $\psi(0) = \phi$

$C_1 = B(0) = \frac{\psi(0)}{2\pi} = \phi/2\pi$ from (6)

$$\text{So } B(\tau_F) = \frac{\phi}{2\pi}\left(\frac{\tau}{\bar{\mu}} + 1\right) \qquad (7)$$

$\therefore$ <u>B is linear in optical depth</u>.

[Contrast radiation transport to steady-state heat-conduction, which has <u>temperature</u> linear in depth.]

Now also evaluate ϕ, from the radiation balance at TOA.

At TOA $\quad F_\downarrow = 0$.

net IR out = net solar absorbed.

$$\phi = \frac{S_0}{4}(1-A_p) = \sigma T_e^4$$

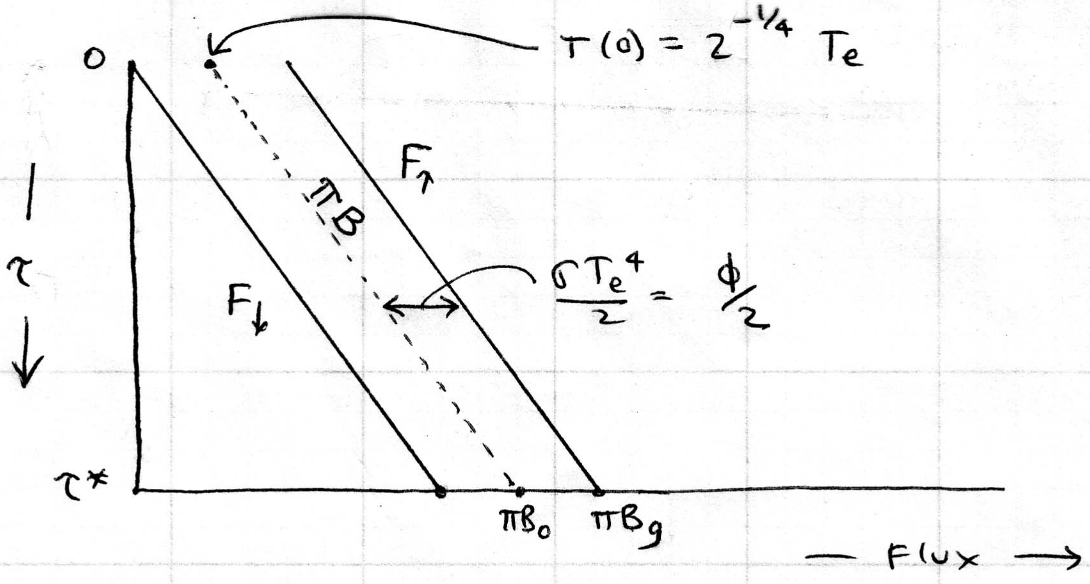
so $\frac{\phi}{2} = \frac{\sigma T_e^4}{2}$ and the system is solved. The results are

$$F_\uparrow = \pi B + \frac{\sigma T_e^4}{2} \qquad \text{from } F_\uparrow = \frac{\psi + \phi}{2}$$

$$F_\downarrow = \pi B - \frac{\sigma T_e^4}{2} \qquad \text{from } F_\downarrow = \frac{\psi - \phi}{2}$$

$$\pi B(\tau) = \sigma [T(\tau)]^4 = \frac{\sigma T_e^4}{2}\left(\frac{\tau}{\bar{\mu}} + 1\right) \qquad \text{from } (7)$$

$$\text{So } T(\tau) = T_e \left(\frac{\tau/\bar{\mu} + 1}{2}\right)^{1/4}$$

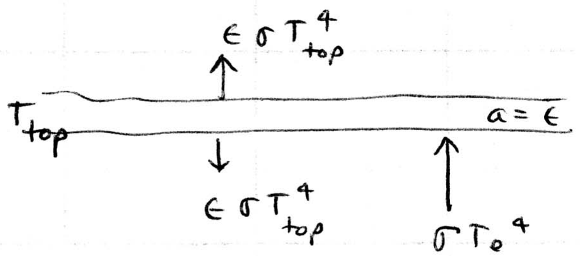


For a larger τ^* (thicker atmosphere), T_s would be larger.

Explanation of $T(0)$ and $T(\tau^*)$:

① **TOA** $\tau = 0$

Consider a thin layer of air at TOA.



$$\begin{bmatrix}\text{gain by}\\ \text{absorption}\end{bmatrix} = \begin{bmatrix}\text{loss by}\\ \text{emission}\end{bmatrix}$$

$$a \sigma T_e^4 = 2 \epsilon \sigma T_{top}^4$$

$$T_e^4 = 2 T_{top}^4$$

$$T_{top} = 2^{-1/4} T_e = 0.84 T_e$$

$$= 214 \text{ K} \approx T_{tropopause}$$

② **surface**.

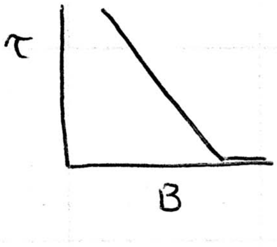
Radiative equilibrium requires a "temperature-slip" at the surface.

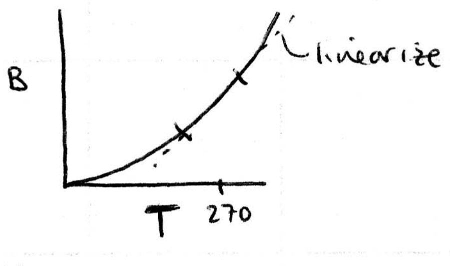
$$F_{\uparrow} = \pi B_g = \pi B(\tau^*) + \frac{\sigma T_e^4}{2}$$

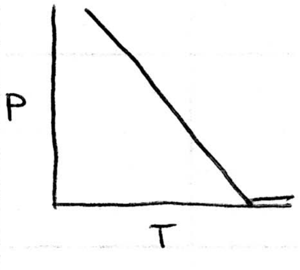
$$\downarrow \qquad\qquad \downarrow$$

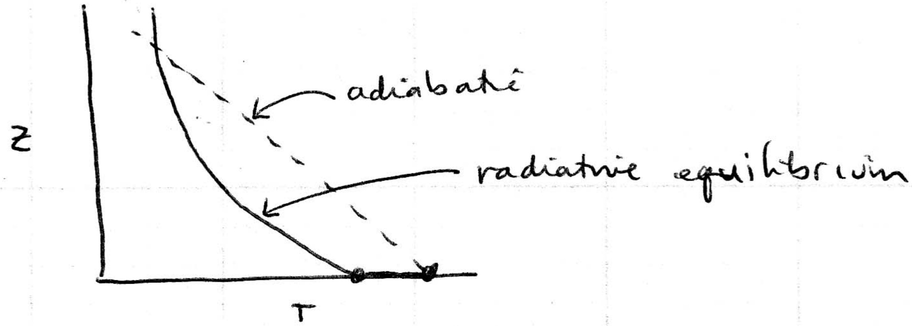
$$\underset{\text{ground temp.}}{\sigma T_g^4} = \underset{\text{air temp at ground}}{\sigma T_0^4} + \frac{\sigma T_e^4}{2}$$

Convert from $B(\tau)$ to $T(z)$. Use $\tau \propto p \propto e^{-z}$.



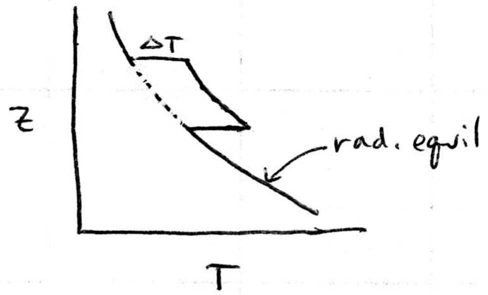


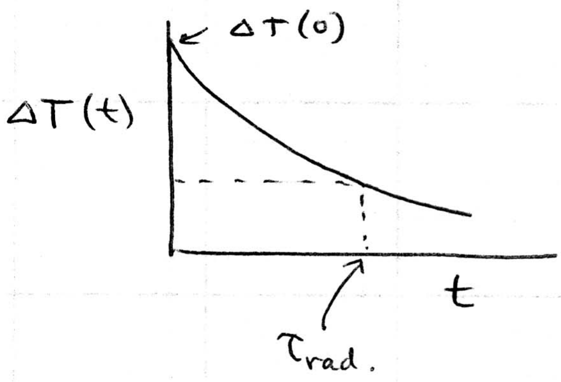




Time scale for establishment of radiative equilibrium.

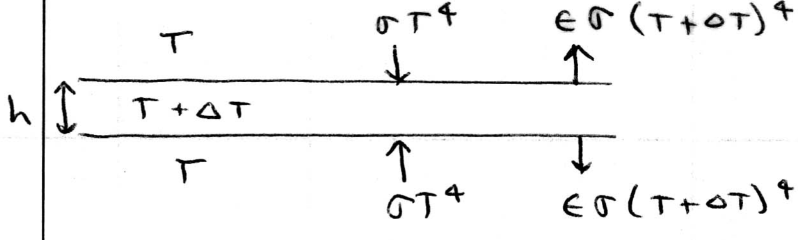
(Houghton p. 15).





Perturbation decays in time. Define the radiative relaxation time τ_{rad} as the time to reduce ΔT to $\frac{1}{e}$ of its initial value, by means of radiative processes.

Consider the radiation budget of a thick atmospheric layer, with temperature $T+\Delta T$ and emissivity ϵ, surrounded by opaque atmosphere of temperature T.



Heating rate = gains - losses.

$$\underbrace{\underset{\frac{J}{g\,deg}}{c_p}\ \underset{\frac{g}{m^3}}{\rho}\ \underset{m}{h}\ \underset{\frac{deg}{sec}}{\frac{d\Delta T}{dt}}}_{W\,m^{-2}} = \underbrace{2a}_{2\epsilon}\sigma T^4 - 2\epsilon\sigma(T+\Delta T)^4$$

Use Taylor-series approximation for $\Delta T \ll T$

$$f(x) \approx f(x_0) + (x-x_0)\left.\frac{df}{dx}\right|_{x=x_0} . \qquad f(x_0) = \sigma T^4 \qquad x - x_0 = \Delta T$$

$$\sigma(T+\Delta T)^4 \approx \sigma T^4 + \Delta T \frac{d}{dT}(\sigma T^4)$$

$$= \sigma T^4 + 4\sigma T^3 \Delta T$$

So

$$C_p \rho H \frac{d\Delta T}{dt} = 2\epsilon\sigma T^4 - 2\epsilon\left[\sigma T^4 + 4\sigma T^3 \Delta T\right]$$

$$= -(2\epsilon)(4\sigma T^3 \Delta T) .$$

$$\frac{d\Delta T}{\Delta T} = \frac{-8\epsilon\sigma T^3}{C_p \rho h} dt.$$ Integrate from $t=0$.

$$\ln \frac{\Delta T(t)}{\Delta T(0)} = \frac{-8\epsilon\sigma T^3}{C_p \rho h} t$$

$$\Delta T(t) = \Delta T(t=0)\, e^{-t/\tau_{rad}}$$

where $\tau_{rad} = \dfrac{C_p \rho h}{8\epsilon\sigma T^3}$, a radiative relaxation time.

For earth's atmosphere, take $C_p = 1000$ J kg^{-1} deg^{-1}, ρ at 500 mb, $h = 8$ km $= 1$ scale height, $T = 270$ K, $\epsilon = \frac{1}{2}$.

Then $\tau_{rad} \sim 12$ days, i.e. slow relative to convection.

Actually τ_{rad} is longer than this, about 50 days, according to figure on next page.

MANABE & STRICKLER 1964

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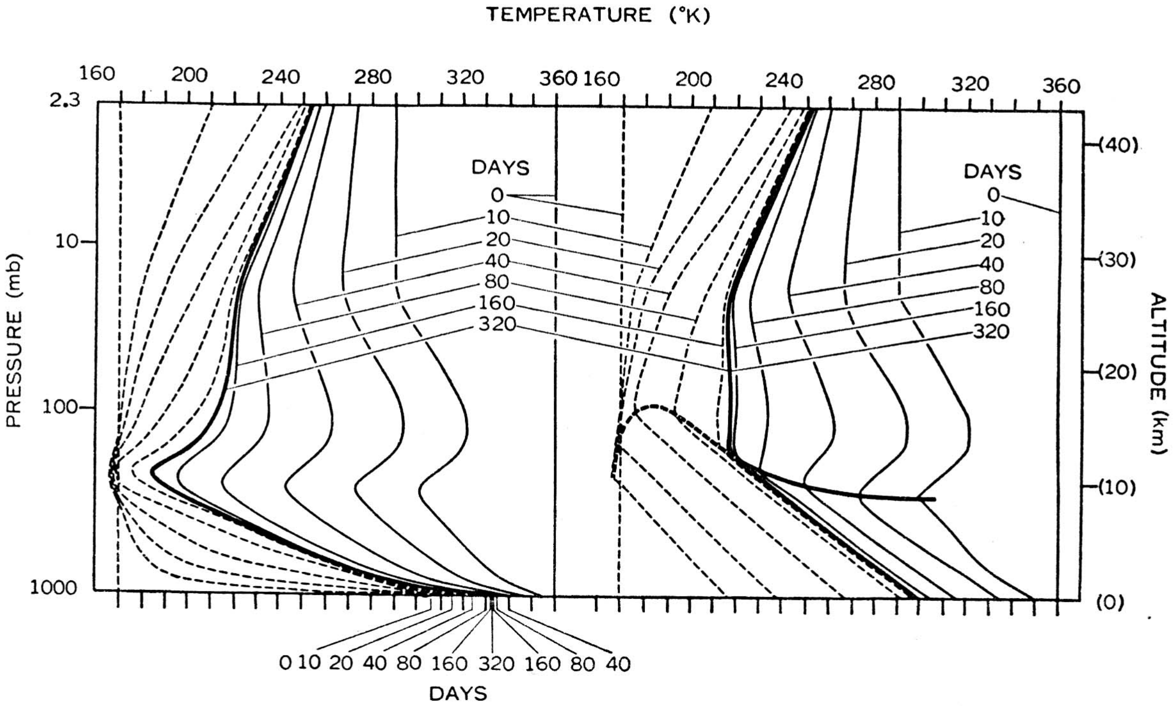

FIG. 1. The left and right hand sides of the figure, respectively, show the approach to states of pure radiative and thermal equilibrium. The solid and dashed lines show the approach from a warm and cold isothermal atmosphere.

from both initially warm and cold isothermal atmospheres. Refer to Section 4a for the amount of solar insolation and the distribution of gaseous absorbers which are adopted for these computations. Δt was 8 hr and the convergence criterion, δ, was 10^{-3} deg day^{-1}. It takes about one or two years to satisfy this criterion. At this time the relative magnitude of the difference between the net outgoing long wave radiation and the net incoming solar radiation is approximately 5×10^{-4} times either of these fluxes. The maximum difference in temperature between the two final states when approached from opposite directions is about 0.2 deg. These figures indicate that the final states may be regarded as steady states.[2]

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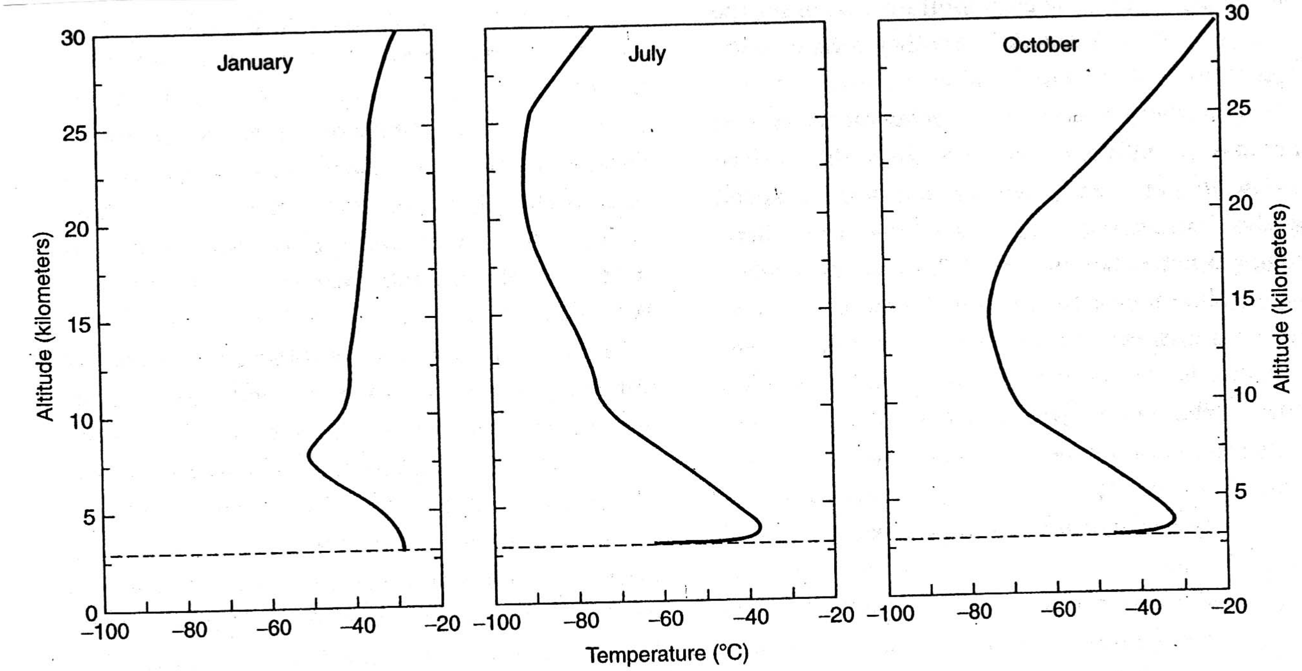
Warren & Town 2011

Encyclopedia of Climate and Weather



ANTARCTICA. Figure 3. *Monthly average atmospheric temperature, as a function of altitude above sea level, obtained from balloon-borne radiosondes launched at South Pole Station in 1992.* **The horizontal dashed line marks the surface elevation, 2835 meters. (Data and figure provided by Ash Mahesh and Von Walden, University of Washington.)**

A Look at the Surface-Based Temperature Inversion on the Antarctic Plateau

64b

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(Manuscript received 25 June 2004, in final form 2 November 2004)

Journal of Climate
2005

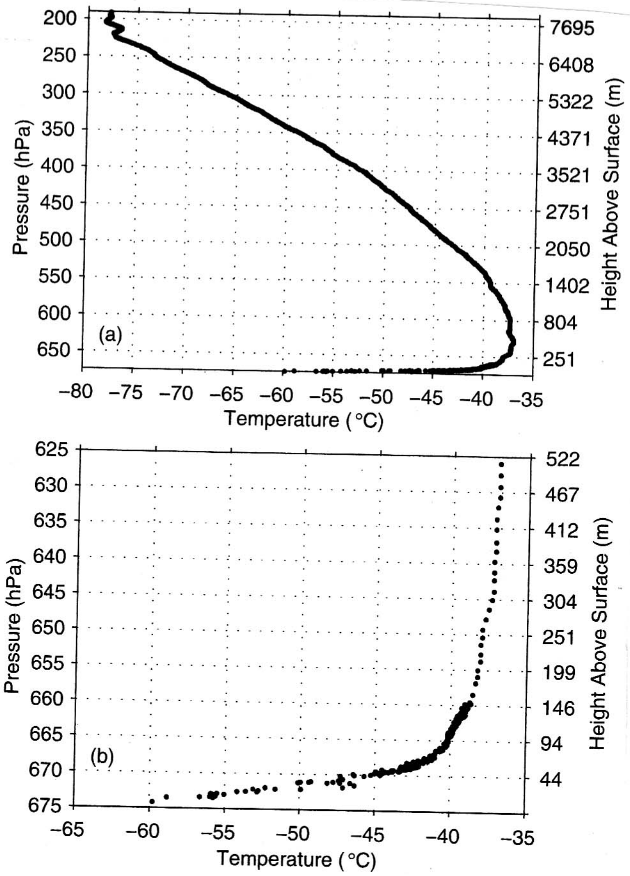

FIG. 3. Temperature profile measured at South Pole Station on 25 Sep 2001. Data above 660 hPa are from a routine radiosounding with an RS80; those below 660 hPa are from a tethered sounding with an RS80. (a) The full tropospheric sounding is shown, and (b) the lowest 500 m are enlarged. The surface pressure was 674 hPa.

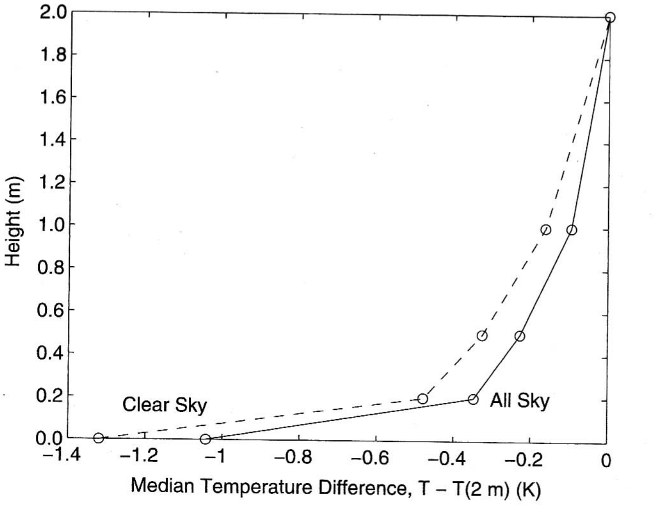

FIG. 13. Median temperature difference relative to 2 m. Data are from South Pole during the 2001 polar night. Separate profiles are shown for the overall median (All Sky, solid line) and the clear-sky median (dashed line).

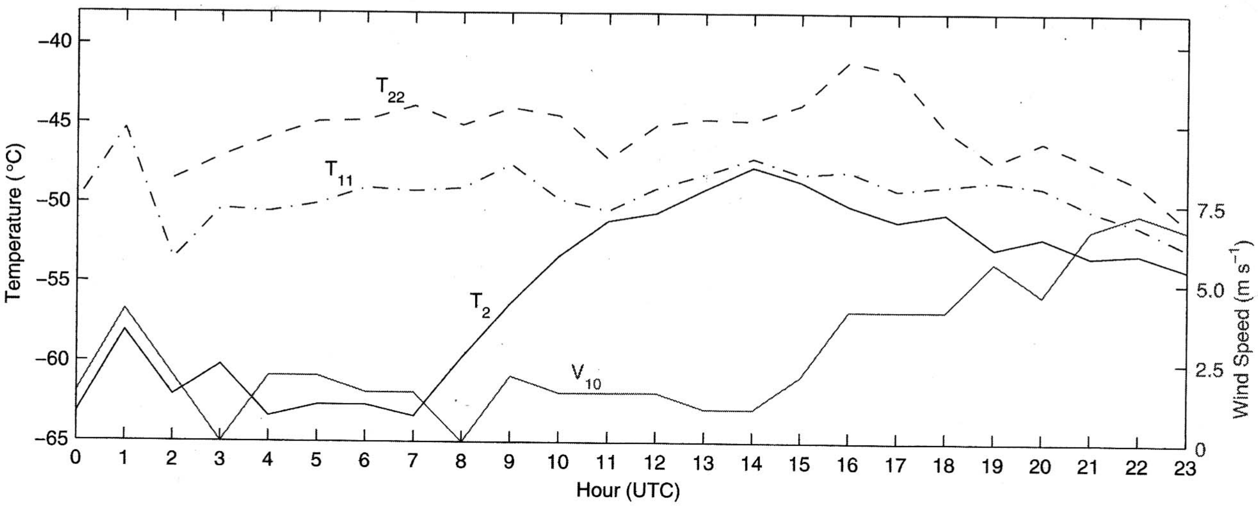

FIG. 18. Air temperatures at 2, 11, and 22 m, and 10-m wind speed (V_{10}) at South Pole on 8 Sep 1992.

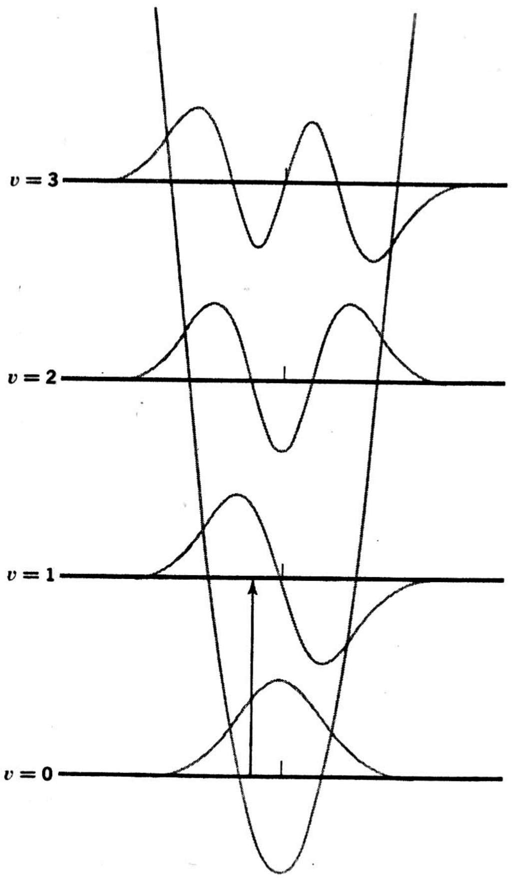

FIG. 2-5 The harmonic-oscillator wave functions and the fundamental vibrational transition.

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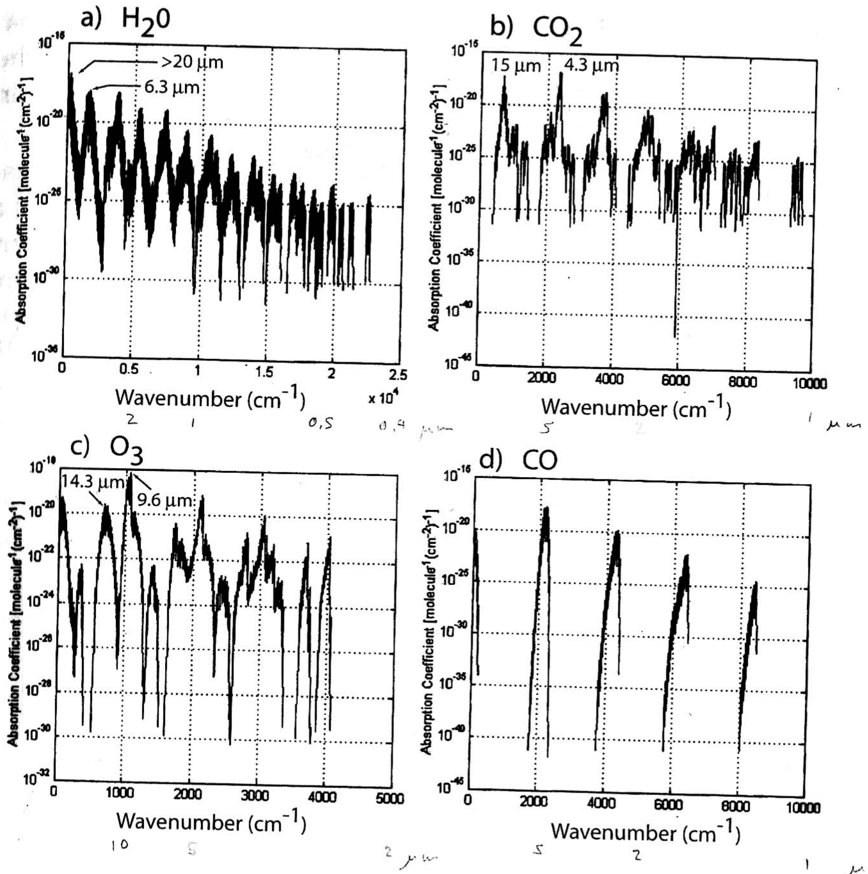

Fig. 9.10: Spectra of absorption cross-sections for several molecules encountered in the atmosphere. Absorption bands of particular significance for thermal radiative transfer in the atmosphere are labeled with the center wavelength. (a) Water vapor. (b) Carbon dioxide. (c) Ozone. (d) Carbon monoxide.

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FIG. 2-6 The vibrational energy levels calculated for HCl. Pattern (*a*) is based on the harmonic-oscillator approximation and the frequency of the fundamental transition. Pattern (*b*) is based on the anharmonic values of Table 2-2.

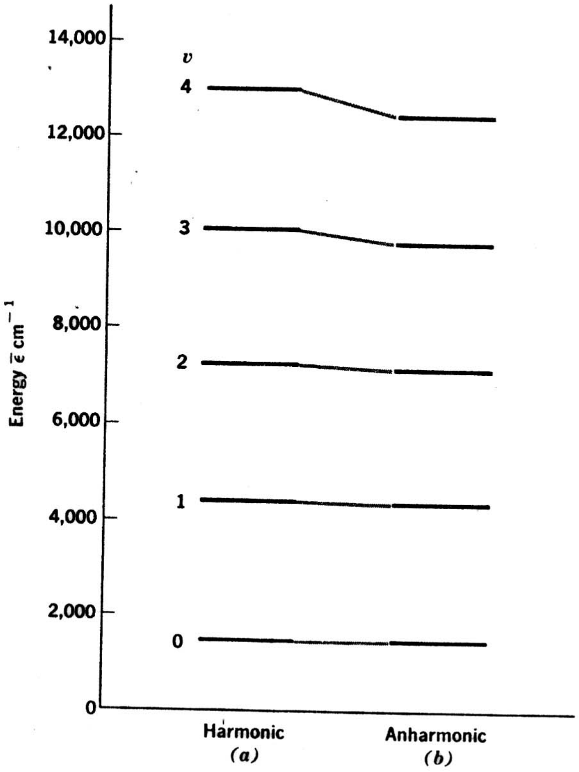


FIG. 3-5 Rotational energy levels and transitions for a rigid-rotor linear molecule. The symbol $\bar{B}$ is used to represent the quantity $h/8\pi^2Ic$.

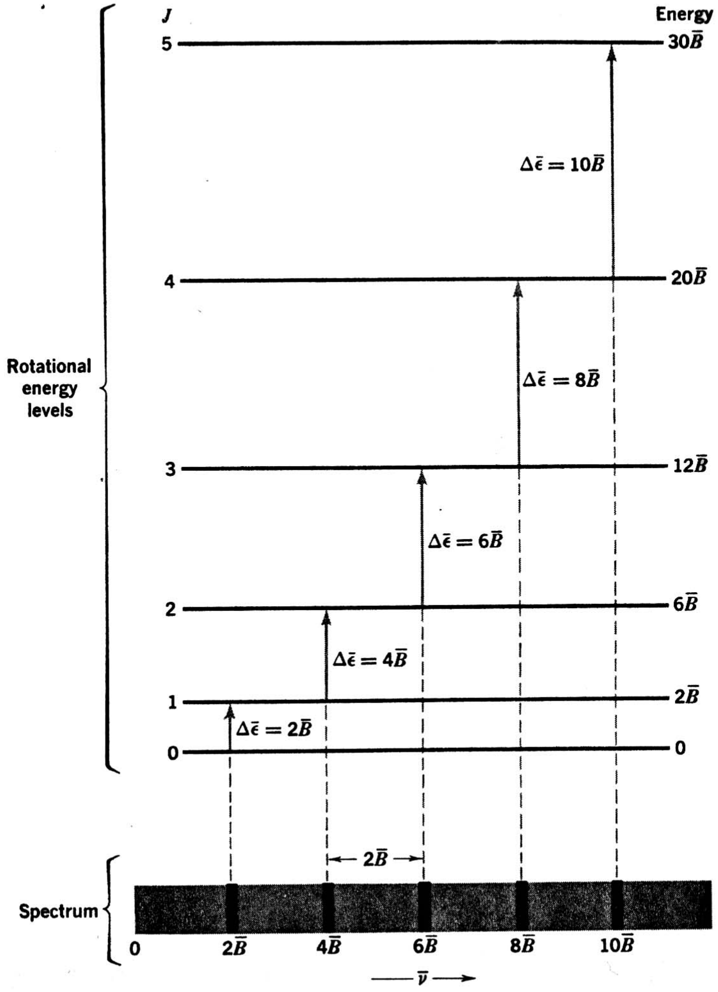
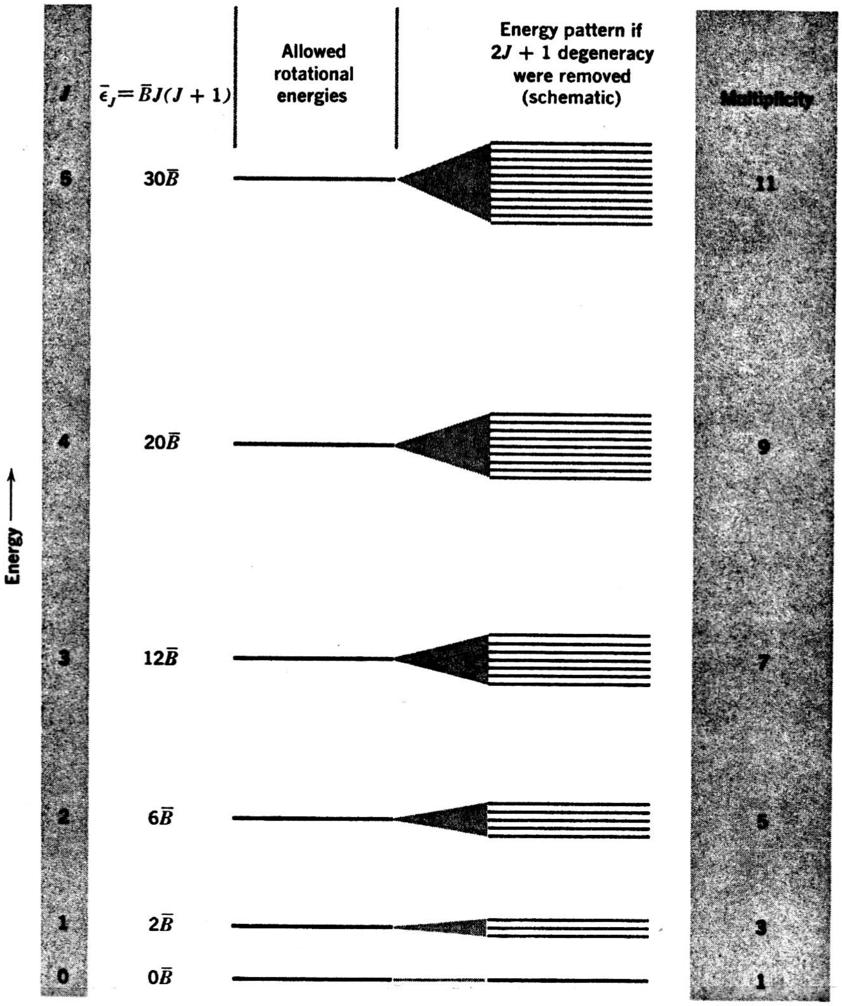


FIG. 3-3 The energy-level pattern for a rotating linear molecule. The degeneracy, or multiplicity, of each rotational level is indicated by the number of levels that would appear if an electric field were applied to the rotating molecule.



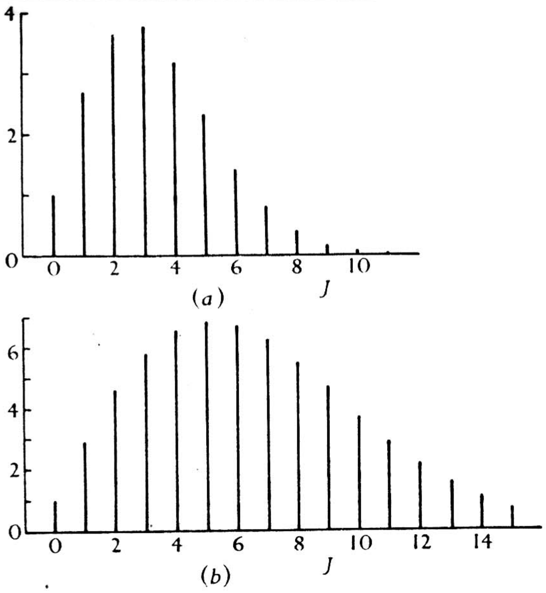


FIG. 2.6. Relative populations of rotational levels for HCl in the ground vibrational state. The ordinate scale is the function $(2J+1)\exp\{-BJ(J+1)hc/kT\}$, (a) for $T = 300°$ K, (b) for $T = 1000°$ K.

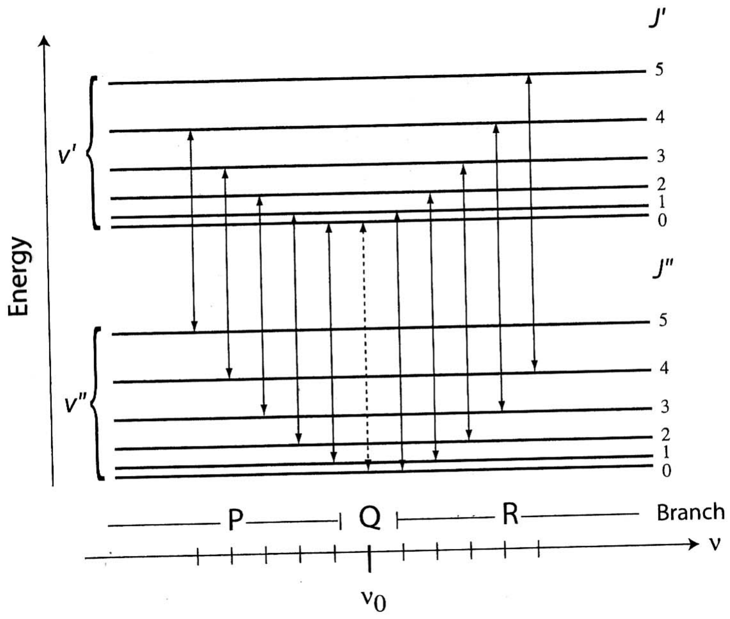


Fig. 9.3: Vibrational-rotational transitions for $\Delta v = \pm 1, \Delta J = [-1, 0, +1]$, showing the relative positions of the transitions in the spectrum. The P-branch corresponds to transitions involving $\Delta J = -1$, while the R-branch corresponds to $\Delta J = +1$. The Q-branch, when present, represents a superposition of all possible transitions involving $\Delta J = 0$ and occurs close to frequency $\nu_0 = \Delta E/h$, where ΔE is the energy associated with pure vibrational transitions.

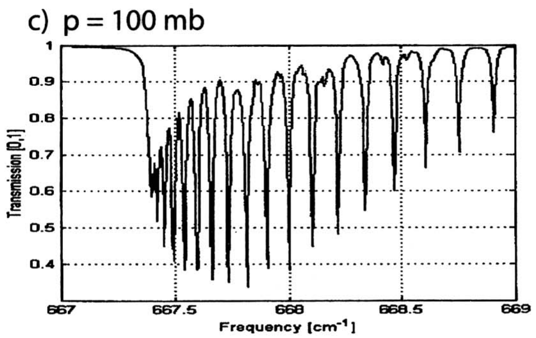


Fig. 9.13: (a) High resolution depiction of the transmission spectrum of a one-meter path through air with typical CO_2 concentration, at 1000 mb pressure. (b) Same as (a), but "zoomed in" on the central Q-branch. (c) Same as (b), but at reduced atmospheric pressure of 100 mb, revealing that what previously appeared as a single absorption line is actually a cluster of closely spaced but distinct lines.

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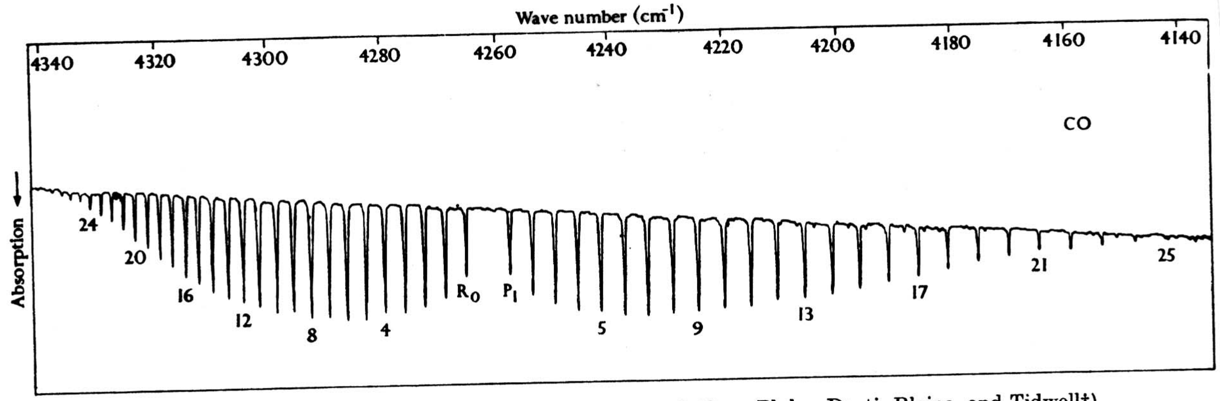

FIG. 2.3. (c) Recording of absorption in the 0–2 band of CO (from Plyler, Denti, Blaine, and Tidwell†).

† *J. Res. natn. Bur. Stand.* **A64**, 29 (1960).

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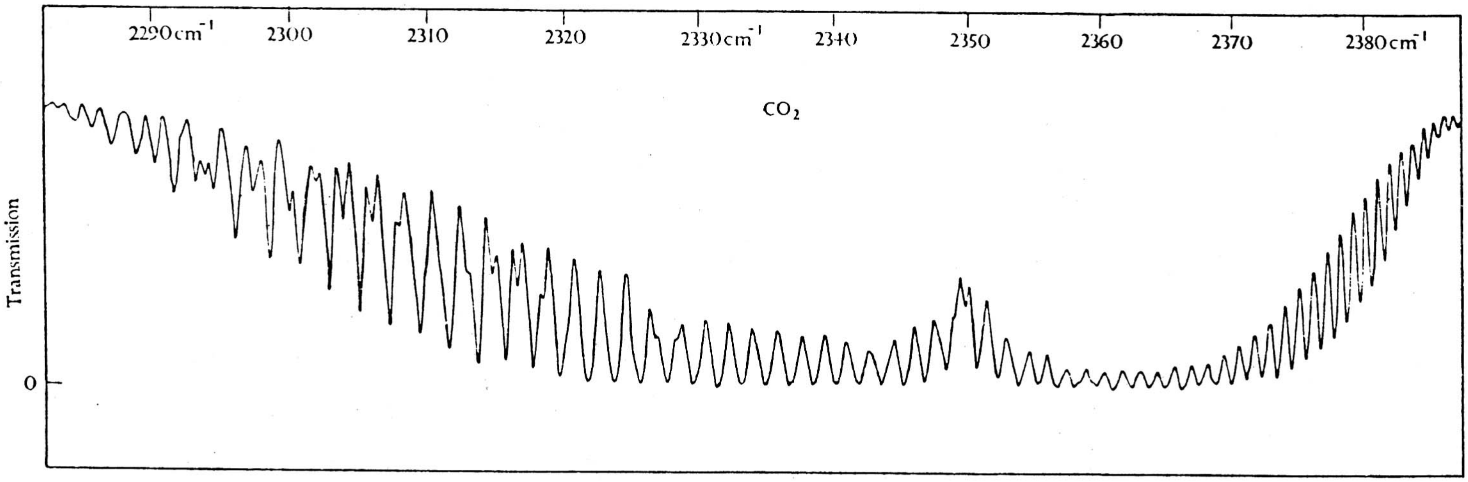

FIG. 2.13. Recording of absorption by CO_2. (*a*) the ν_3 band at 4·3 μ (from Plyler, Blaine, and Tidwell†).

† *J. Res. natn. Bur. Stand.* **55**, 183 (1955).

Q-branch absent ↗

Q-branch present ↘

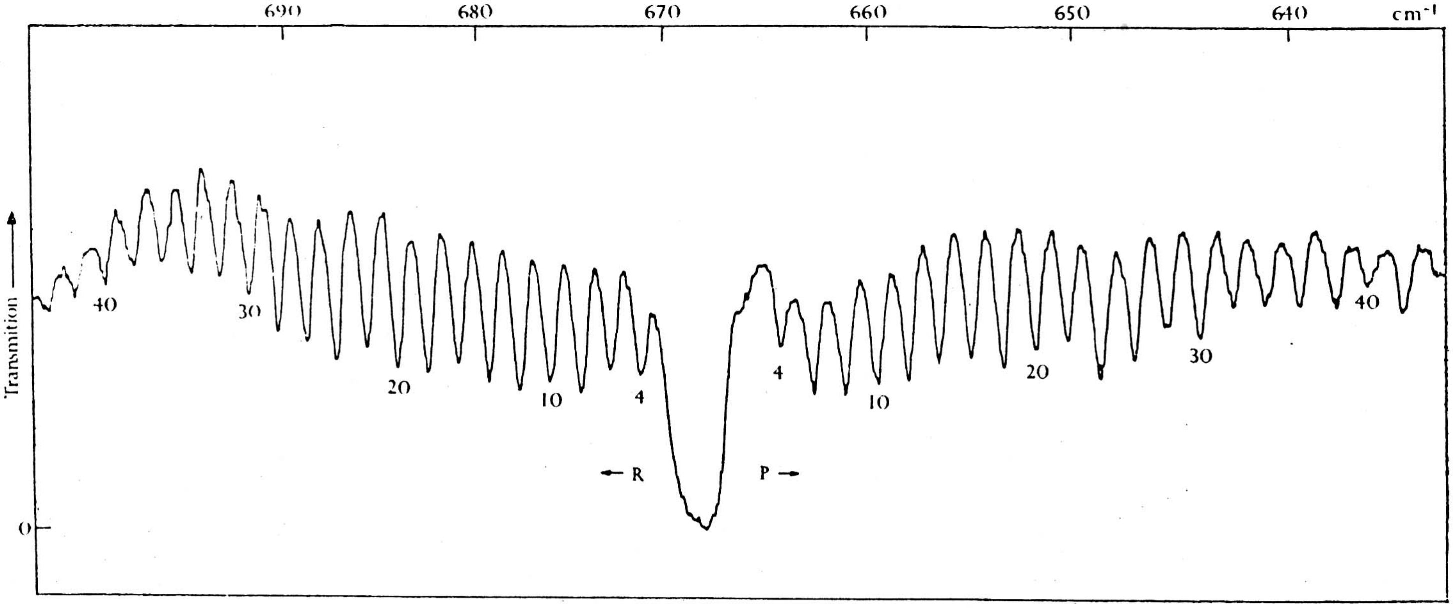

FIG. 2.13. (*b*) the ν_2 band at 15 μ (from Plyler, Donti, Blaine, and Tidwell†). The additional structure in the wings of the P-branches is due to the isotope $^{13}C^{16}O_2$.

† Ibid. **64** A, 29 (1960).

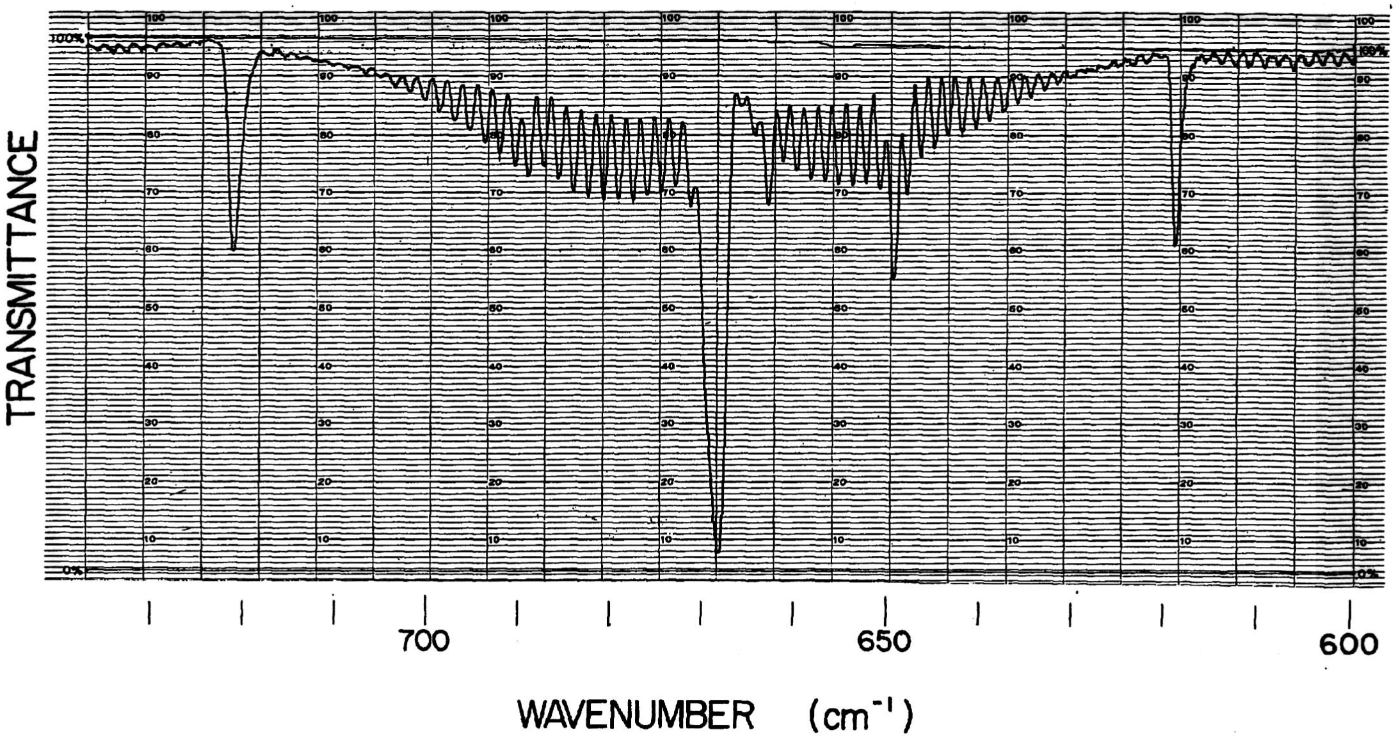

FIGURE 1.—A medium-high resolution spectrum of the 15-micron carbon dioxide band. This spectrum was obtained from a 10-cm. path of pure carbon dioxide at 63 mb. and 38° C. The strong *Q* branch at 667 cm.$^{-1}$ flanked by the *P*- and *R*-branch lines dominate the absorption. **The weaker *Q* branches at 618, 648, 662, 688, and 721 cm.$^{-1}$ appear in this figure.**

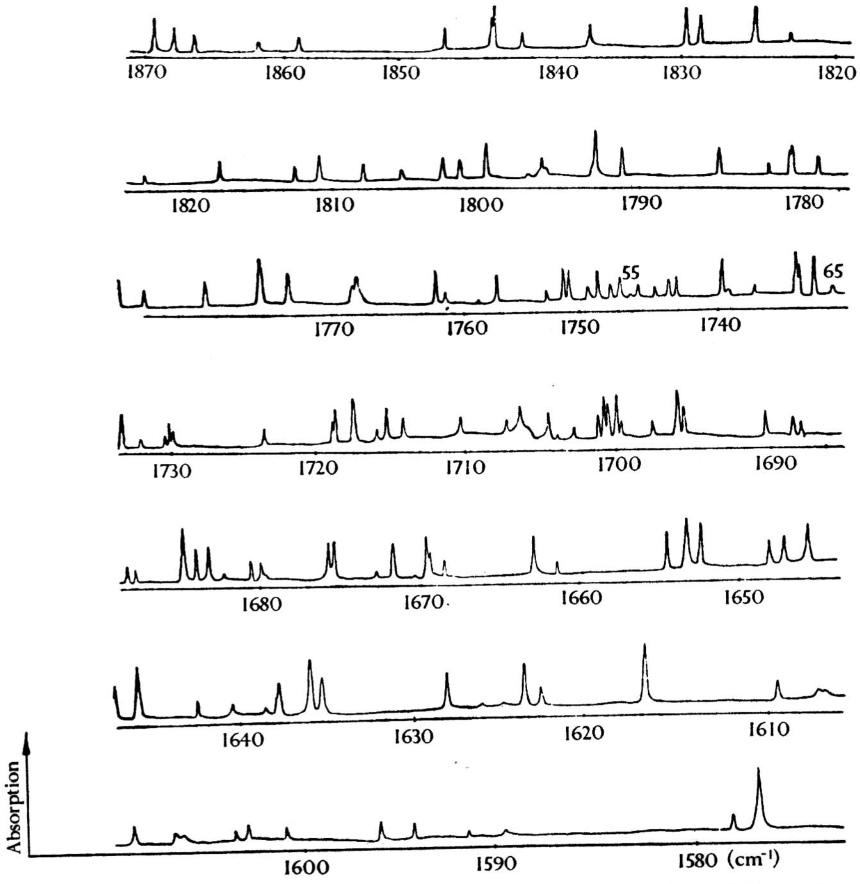

FIG. 2.14. Part of the ν_2 band of H_2O at $6\cdot3\,\mu$ in absorption (from Dalby and Nielsen†).

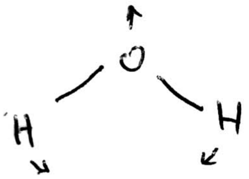

FIG. 10-1 Potential-energy functions, vibrational energy levels, and vibrational probability functions ψ^2 for two typical electronic states of a diatomic molecule.

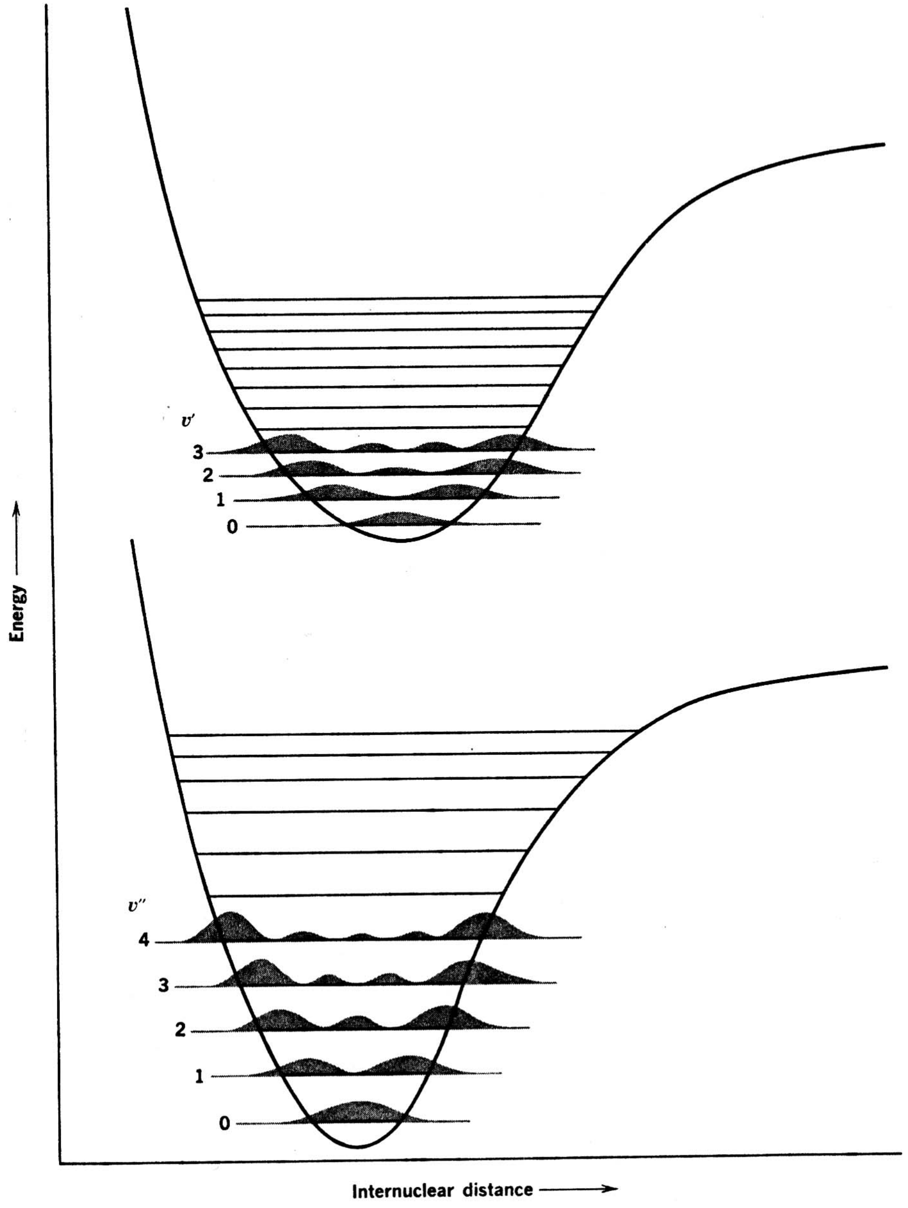

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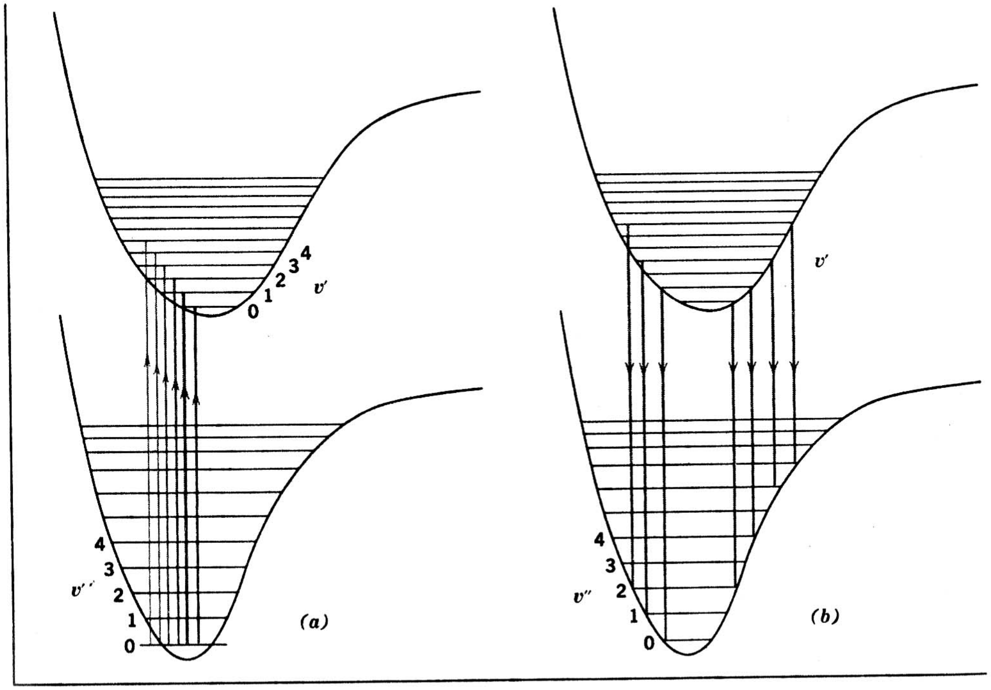
FIG. 10-2 (a) Some of the most probable transitions, for an absorption experiment at a relatively low temperature, for the potential-energy curves of Fig. 10-1. (b) Examples of the most probable emission transitions between vibrational levels of two electronic states. (Note, as Table 10-1 shows, that for a given value of v transitions to states with two different values of v are preferred.)



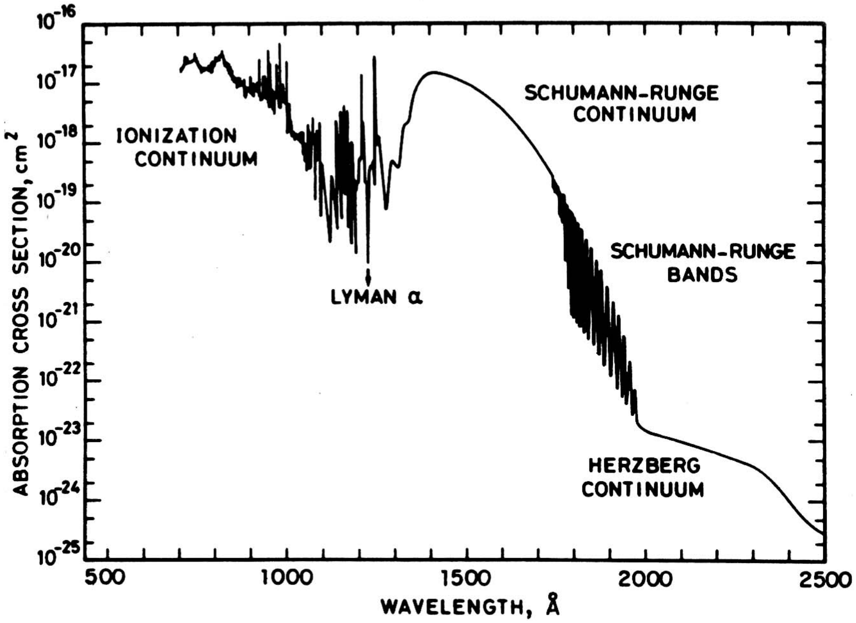


Fig. 5.4. Absorption cross section of $^{16}O^{16}O$ in the ultraviolet spectrum. After Brasseur and Solomon (1984).

oxygen

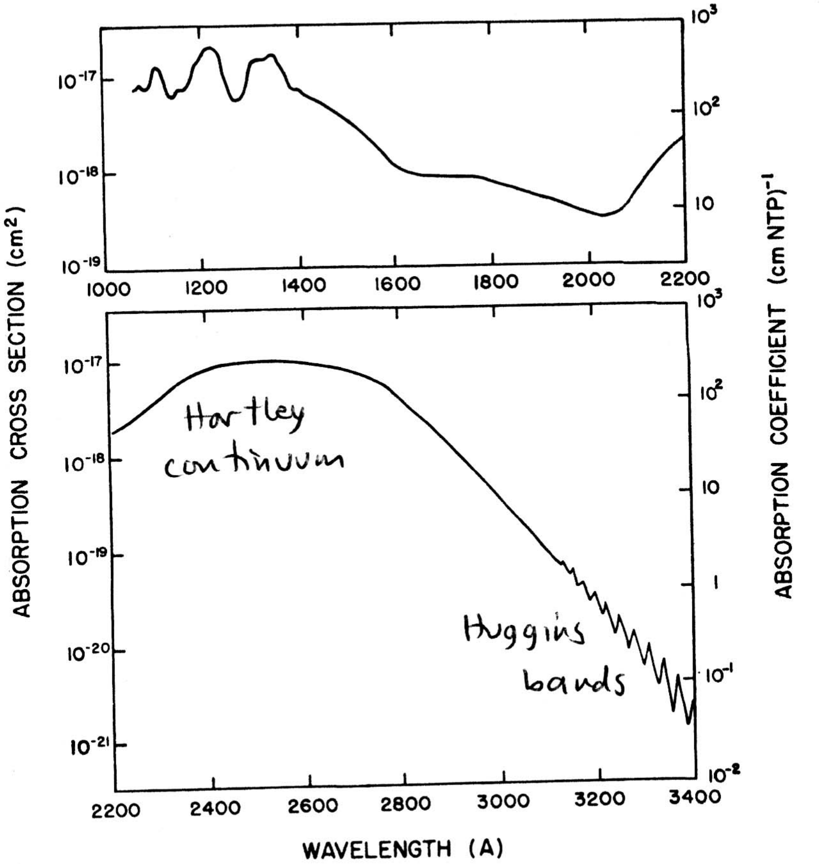


FIG. 4.18. Absorption spectrum of O_3. Near 2600 A some band structure has been smoothed out.

ozone

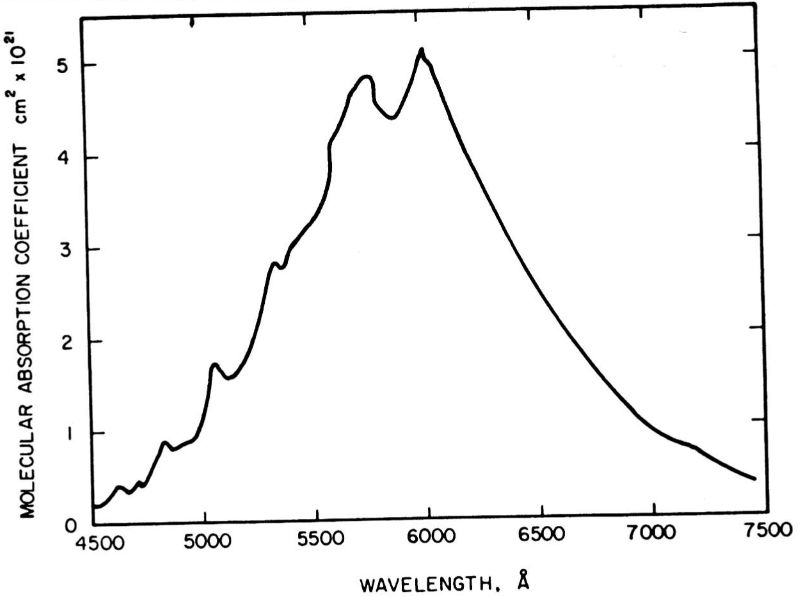


Fig. 5.13. The Chappuis bands of ozone at 291 K. After Vigroux (1953).

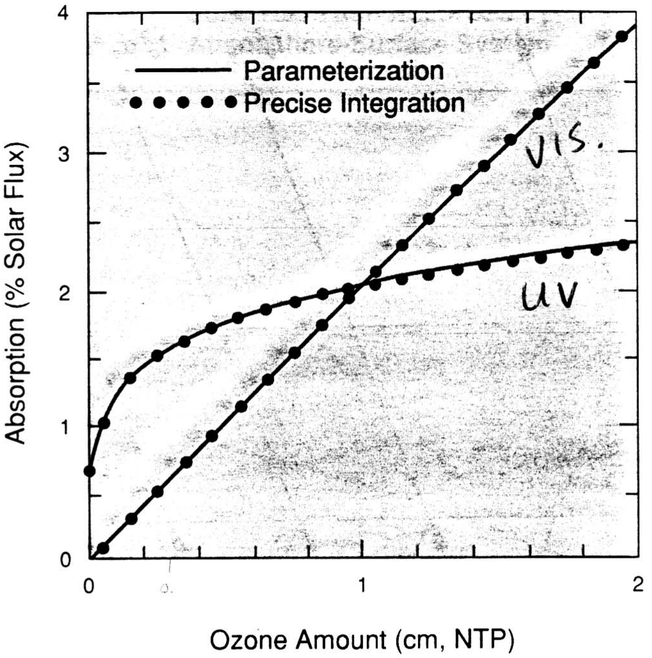


Fig. 10.9 Percent of total solar flux absorbed by ozone as a function of ozone amount. Solid lines are functional relations for two spectral regions (visible, ultraviolet), dots are line-by-line results. From Lacis and Hansen (1974).

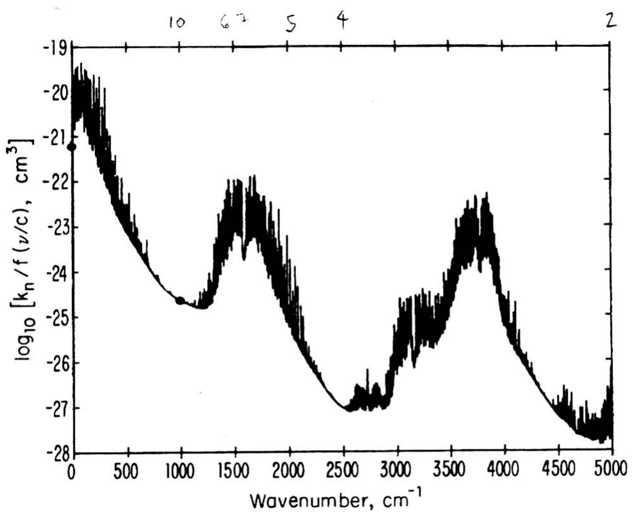


Fig. 5.7. Theoretical absorption coefficients for pure water vapor at 1 bar and 296 K. The vertical axis is the molecular absorption coefficient divided by a "radiation term,"

$$f(\nu/\mathbf{c}) = (\nu/\mathbf{c}) \tanh(\mathbf{h}\nu/2\mathbf{k}\theta),$$

which is approximately equal to $\nu/\mathbf{c}$ (the frequency in wave numbers) for $\nu/\mathbf{c} > 500\,cm^{-1}$. After Clough et al. (1980).

GOODY & YUNG

5.4.3. *Continuum absorption*

The window between the water vapor 6.3 μm band and the rotation band occurs close to the peak of the Planck function at atmospheric temperatures and the transmission of thermal radiation through this window is of crucial importance for some atmospheric problems. The window region contains weak high-*J* lines of both bands but these are superimposed on a stronger continuum that absorbs about 10% of the incident radiation for a vertical path through an atmosphere containing $1\,g\,cm^{-2}$ of water vapor.

There is a debate about the reason for this continuum; as for the collision-induced bands of oxygen (§ 5.3.4), the debate centers around the alternatives of dimers of finite lifetime or events taking place only during collisions. Both yield binary absorption coefficients, although results are sometimes given in terms of normal coefficients with linear pressure dependence, which amounts to the same thing. To attribute the continuum to events occurring during collisions is equivalent to saying that it is caused by the far wings of strong lines positioned close to band centers. This is the most popular explanation and there are reasonable line shapes that give a good account of the observed continuum absorption.

Figure 5.7 shows a calculation based upon a theoretical line shape. The envelope beneath the curve is the continuum; the fine structure by itself would normally be identified as rotation lines; but, in fact, both continuum and lines result from the same data on line positions and line shapes. The figure makes the point that continua occur at all frequencies. Window regions are those in which continuum absorption is stronger than line absorption (ca. 1000, 2400, and 4300 cm^{-1}), but only the 1000 cm^{-1} region is important for atmospheric calculations.

Laboratory measurements of binary absorption coefficients for the 1000 cm^{-1} window are shown in Fig. 5.8. These are for water–water collisions. The same investigators found the coefficients for water–nitrogen collisions to be so small that, despite the much larger concentation of nitrogen molecules, the contribution of water–nitrogen collisions is probably unimportant in the atmosphere. This view corresponds to that

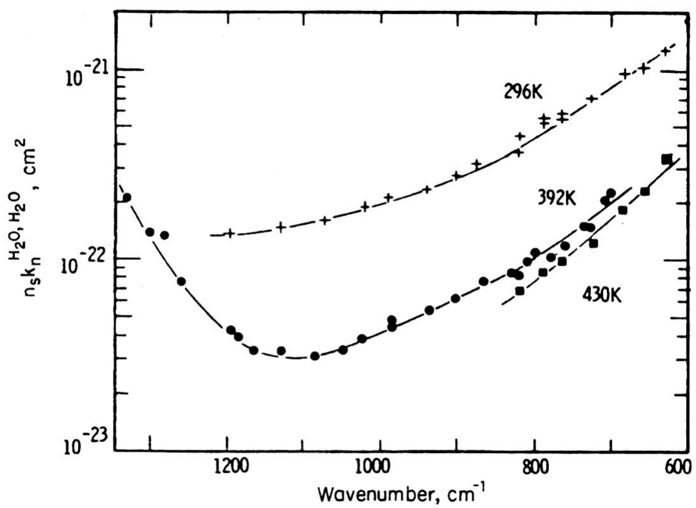


Fig. 5.8. Binary absorption coefficients for water–water collisions in the 1000 cm^{-1} window. n_s is Loschmidt's number. After Burch and Gryvnak (1980).

of some field investigators, based on studies of the correlation between atmospheric absorption and water vapor pressure. The term *e-type absorption* (from the meteorological symbol for water vapor pressure) is often used to describe the self-broadening nature of this phenomenon.

The increase of absorption with decreasing temperature shown in Fig. 5.8 has been cited as a reason to favor dimer theories of the continuum, but this temperature variation is also consistent with far wing line shapes, given appropriate interaction potentials.

Figure 5.9 shows binary absorption coefficients in the 2600 cm^{-1}

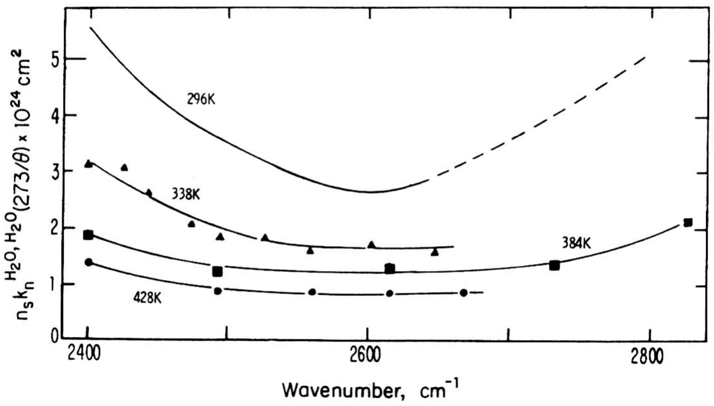


Fig. 5.9. Binary absorption coefficients for water–water collisions in the 2500 cm^{-1} window. n_s is Loschmidt's number. The data for 296 K are extrapolated. After Burch and Gryvnak (1980).

region of the spectrum. This region is not as free from rotation lines as is the 1000 cm^{-1} window and the investigators have used numerical methods to correct for the absorption by nearby lines, so that only continuum absorption is represented.

The self-broadening coefficients shown in Fig. 5.9 are unimportant for atmospheric calculations. However, water–nitrogen collisions are more important than for the 1000 cm^{-1} window, and it may be desirable to take account of them under some circumstances. The ratio of nitrogen–water to water–water coefficients is about 0.08, which is offset by the large ratio of nitrogen to water molecular densities.

Theoretical basis of selection rules and line strengths

(Barrow, Intro. to Molec. Spectroscopy, Chap. 4).

Use time-dependent Schrödinger equation.

$$\frac{-h^2}{8\pi^2 m}\frac{\partial^2 \Psi(x,t)}{\partial x^2} + U(x)\,\Psi(x,t) = \frac{-h}{2\pi i}\frac{\partial \Psi(x,t)}{\partial t}. \qquad (1)$$

convention: use capital Ψ for time dep: $\Psi(x,t)$; $\psi(x)$.

abbreviation: $H \equiv \frac{-h^2}{8\pi m^2}\frac{\partial^2}{\partial x^2} + U$; the energy operator

so $H\Psi = \frac{-h}{2\pi i}\frac{\partial \Psi}{\partial t}$.

Try separation of variables $\Psi = \psi(x)\,\phi(t)$.

Then we can separate ψ on l.h.s. and ϕ on r.h.s.

$$\underbrace{\frac{1}{\psi}\left[\frac{-h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial x^2}\right] + U}_{\text{independent of } \phi} = \underbrace{\frac{-h}{2\pi i}\frac{1}{\phi}\frac{d\phi}{dt}}_{\text{independent of } \psi} \qquad (2)$$

So each side must equal a constant. We identify this constant as the total energy ϵ, from the time-independent equation $H\psi = \epsilon\psi$.

The solution to (2) is $\phi_n = e^{-\left(\frac{2\pi i}{h}\right)\epsilon_n t}$

$$\therefore \Psi = \psi_n\, e^{-\left(\frac{2\pi i}{h}\right)\epsilon_n t}.$$

In general, Ψ may be a sum of states, eg for 2 states

$$\Psi = a_n \psi_n e^{-(\frac{2\pi i}{h})\epsilon_n t} + a_\ell \psi_\ell e^{-(\frac{2\pi i}{h})e_\ell t} \qquad (3)$$

IF Ψ consists of a single state n, then the observable probability function $\Psi^*\Psi$ is time-independent, i.e. a stationary state: Using (3),

$$\Psi^*\Psi = \psi^*\psi \underbrace{e^{+}e^{-}} = \psi^*\psi$$

these cancel if $n = \ell$, destroying time dependence.

Absorption and emission are changes from one stationary state to another. During the transition, $\Psi^*\Psi$ is time-dependent and tells the time-evolution of the system.

Consider just two states; how do we go from one to the other

$—— \psi_m, \epsilon_m$ $\qquad \Psi_\ell = \psi_\ell e^{-(2\pi i/h) e_\ell t}$

$—— \psi_\ell, \epsilon_\ell.$ $\qquad \Psi_m = \psi_m e^{-(2\pi i/h) e_m t}.$

During the transition, Ψ will be a superposition of these two orthogonal ψ's: $\Psi = a_\ell \Psi_\ell + a_m \Psi_m$

where $0 < a_\ell < 1$

$0 < a_m < 1$

Start initially at in state ℓ, i.e. $a_\ell = 1$.
Then absorb radiation to go to state m.

Call unperturbed energy operator H_0. (Then we will add an EM wave which changes U.)

so $H_0 \Psi = \frac{-h}{2\pi i}\frac{\partial \Psi}{\partial t}$ has solutions Ψ_l, Ψ_m. (4)

At $t=0$ we are in state l. Then along comes the EM wave, so now $U = U_0 + U'$, and Ψ_l will no longer satisfy (4).

The solution is now not Ψ_l but rather

$$\Psi(t) = a_l(t)\,\Psi_l + a_m(t)\,\Psi_m . \qquad (5)$$

The coefficients a_l, a_m describe the evolution of the system.

Put (5) into the differential equation (1):

$$(H_0 + H')\left(a_l \Psi_l + a_m \Psi_m\right) = \frac{-h}{2\pi i}\frac{\partial}{\partial t}\left(a_l \Psi_l + a_m \Psi_m\right) \qquad (6)$$

Then multiply (6) by Ψ^* and integrate over all space $\int dx$.

The result is $(H' = U')$

$$\frac{da_m}{dt} = \frac{-2\pi i}{h}\, a_l\, e^{-\left(\frac{2\pi i}{h}\right)(E_l - E_m)t}\int_{-\infty}^{\infty} \psi_m^* H' \psi_l \, dx \qquad (7).$$

$a_l = 1$ initially.

↑ Initial rate of increase of population of level m.

Now what is this H' ?

The oscillating electric field of the EM wave can disturb the potential U and allow the molecule to escape its initial stationary state.

The electric field in the x direction, E_x, oscillates with frequency ν: $E_x = E_x^\circ \cos 2\pi\nu t$.

The dipole moment in the x-direction is μ_x.

So the potential energy change is ΔU

$$\Delta U = E_x \mu_x = H'$$

Then the integral in (7) becomes

$$\int \psi_m^* H' \psi_\ell \, dx = E_x \underbrace{\int \psi_m^* \mu_x \psi_\ell \, dx}$$

abbreviate this $|\mu_{x\ell m}|$, the transition moment

$$= E_x |\mu_{x\ell m}| = E_x^\circ \cos 2\pi \nu t \, |\mu_{x\ell m}| \qquad (8)$$

Now substitute (8) into (7) and integrate from $t' = 0$ to $t' = t$ to get $a_m(t)$. The result (Barrow p. 67) is

$$a_m(t) = |\mu_{x\ell m}| \frac{E_x^\circ}{2} \underset{\uparrow}{a_\ell} \underbrace{\left[\frac{1 - e^{(2\pi i/h)(E_m - E_\ell - h\nu)t}}{E_m - E_\ell - h\nu} \right]} \qquad (9)$$

[$a_\ell = 1$ initially] these brackets contain a complex quantity.

[a_m is complex, but the observable quantity is $a_m^* a_m$]

Note
1) a_m increases as E° increases
2) a_m increases as $|\mu_{x\ell m}|$ increases
3) denominator $\to 0$ as $(E_m - E_\ell) \to h\nu$, faster than numerator $\to 0$, so a_m is maximum at $(E_m - E_\ell) \approx h\nu$.

Now integrate over all τ, and compute the observable quantity $a_m^* a_m$, which gives the probability of finding the system in state m.

$$a_m^*(t)\, a_m(t) = \frac{2\pi^2}{h^2} |\mu_{x\ell m}|^2 (E_x^0)^2\, t\, \underbrace{a_\ell^* a_\ell}_{=1 \text{ initially at } t=0 .} \qquad (10)$$

Note

1) $a_m^* a_m$ increases with L, the radiance, because $L \propto (E_x^0)^2$.

2) $a_m^* a_m$ increases with the square of the transition moment $|\mu_{x\ell m}|$

3) $a_m^* a_m$ increases with time. initially linear in time.

IF we have isotropic radiation then $\mu_{x\ell m} = \mu_{y\ell m} = \mu_{z\ell m}$ for randomly oriented molecules,

and $|\mu_{\ell m}|^2 = |\mu_{x\ell m}|^2 + |\mu_{y\ell m}|^2 + |\mu_{z\ell m}|^2$,

so to go to 3 dimensions we replace $|\mu_{x\ell m}|$ by $|\mu_{\ell m}|$ and L by $\bar{L} = \frac{1}{4\pi}\int L\, d\omega$, the average radiance.

Differentiating (10), we then obtain

$$\frac{d}{dt}(a_m^* a_m) = \frac{2\pi^2}{h^2} |\mu_{\ell m}|^2\, \bar{L}\, a_\ell^* a_\ell . \qquad (11)$$

Notice that (11) looks like our definition of the Einstein coefficient for induced absorption $\underline{\underline{B_{\ell m}}}$:

$$\frac{d}{dt}(a_m^* a_m) = B_{\ell m} \; a_\ell^* a_\ell$$

where (in our earlier notation) we identify $n_m = a_m^* a_m$ and $n_\ell = a_\ell^* a_\ell$

This means that $\boxed{B_{\ell m} = \frac{2\pi^2}{h^2} |\mu_{\ell m}|^2}$.

We can thus relate $|\mu_{\ell m}|$ to the Einstein coeff. $B_{\ell m}$.

It can also be related to the absorption coefficient k_a in Beer's law $dL = L_o e^{-k_a \rho \, ds}$.

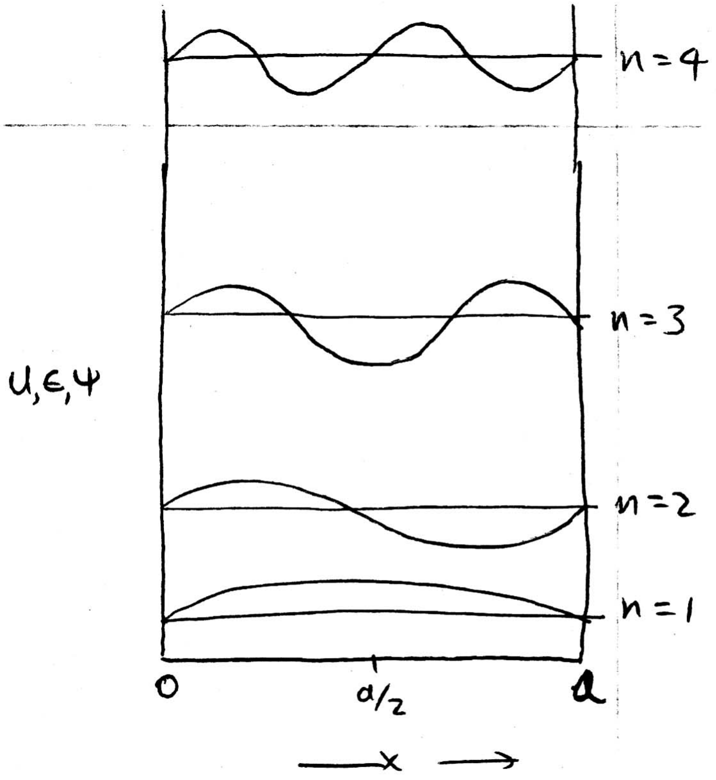
we find that $k_a \propto |\mu_{\ell m}|^2$. (Barrow p.70)

<u>Example of selection rule</u>.

$|\mu_{\ell m}| = 0$ means $\frac{d}{dt}(a_m^* a_m) = 0$, so this means the transition from ℓ to m is <u>forbidden</u>.

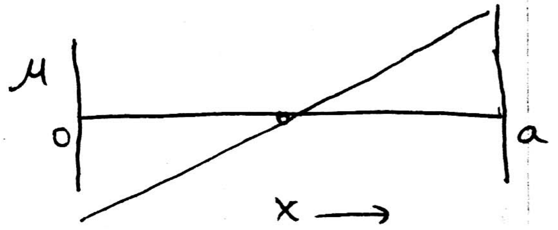
What conditions might make $|\mu_{\ell m}| = 0$?

As an example we do the particle-in-a-box problem.



Put the ⊕ nucleus at the center, $x = a/2$; allow the electron to stray from the center. The dipole moment will then be $\mu = e(x - a/2)$, where e is the electronic charge. So μ as a function of x is as plotted here →

Note that μ is an ODD function of x



Now $\int \psi_\ell \mu \psi_m \neq 0$ only if ψ_ℓ, ψ_m are (even, odd) functions or if ψ_ℓ, ψ_m are (odd, even).

So we find that 1→2, 1→4, 2→3, 3→4 are *allowed*, as drawn in the figure. Transitions 1→3 and 2→4 are *forbidden*.

WATER-VAPOR CONTINUUM ABSORPTON.

(D. TOBIN Ph.D. THESIS, UNIV. MARYLAND, 1996)

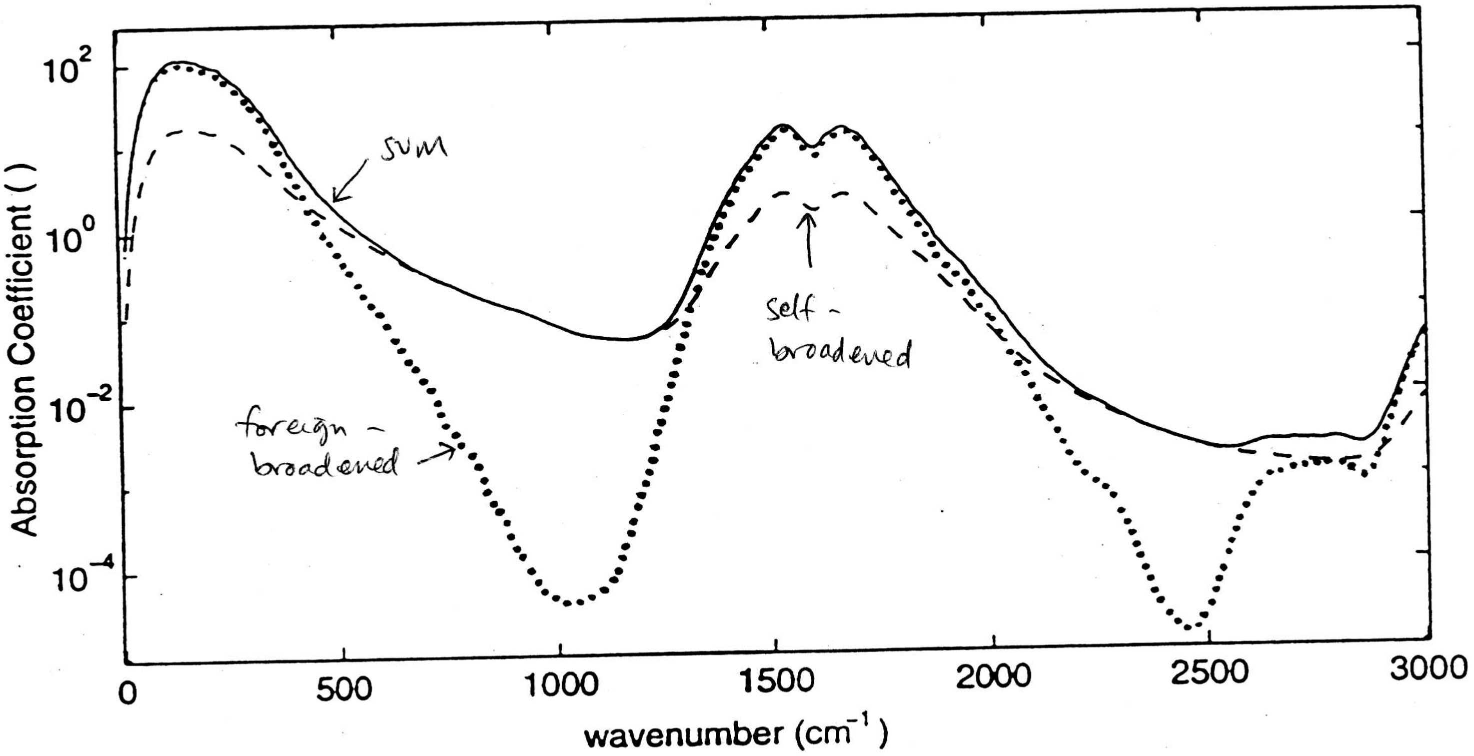
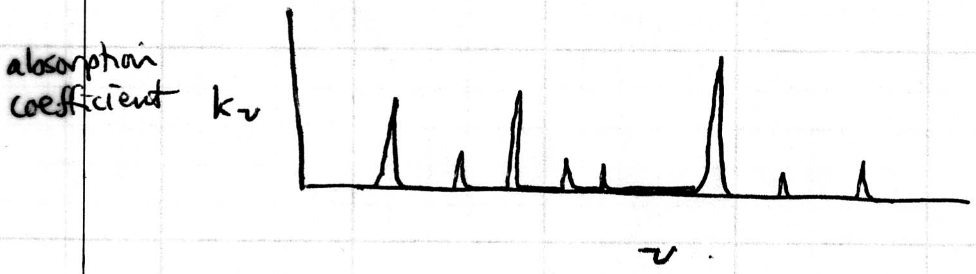


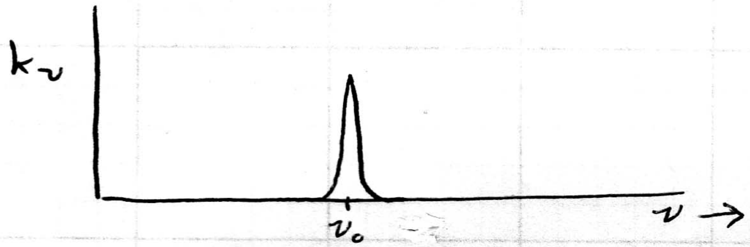
Figure 4.13: Total (solid curve), self-broadened (dashed curve), and foreign-broadened (dotted curve) continuum absorption coefficients calculated with CKDv2.1 for 16 torr H_2O, 760 torr N_2, 310K, and unit path length.

Definition of line strength, line profile



The lines overlap in their wings, so that several lines may contribute to the measured k_ν.

Consider a single line; ignore all neighboring lines.



Define line strength $S \equiv \int_0^\infty k_\nu \, d\nu$

[In practice the limits of integration need not extend far from the line center.]

Define normalized line profile $\phi(\nu) \equiv \dfrac{k_\nu}{S}$.

So $\int_0^\infty \phi(\nu)\, d\nu = \frac{1}{S}\int k_\nu \, d\nu = 1$

And $k_\nu = S\phi(\nu)$. The absorption coefficient at a particular frequency is the product of the line strength and the line profile. This is a useful representation because the dependences of S and ϕ on temperature are different, and ϕ depends on pressure whereas S does not.

KINETIC THEORY OF GASES

I Relate pressure to mean molecular speed.

Pressure is the rate of transfer of momentum, per unit area.

For a gas in a container: molecules hit the walls and transfer their momentum to the walls. How many molecules will hit the wall in time dt?

A. Define *number-density* $= \frac{\text{number}}{\text{volume}}$

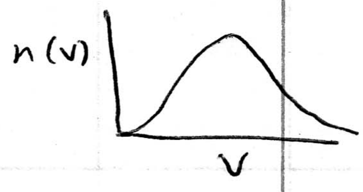
$$n = \frac{N}{V} \qquad \frac{\text{molecules}}{m^3}$$

Group molecules by direction- and velocity-classes

B. *Number-distribution function* $n(v)$: $\frac{\text{molecules}}{(m3)(\text{velocity interval})}$

$n(v)\,dv$ is the number-density of molecules with speeds between v, $v+dv$.

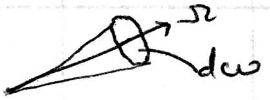
we want to derive (in part II) this distribution



so $n = \int_0^\infty n(v)\,dv$

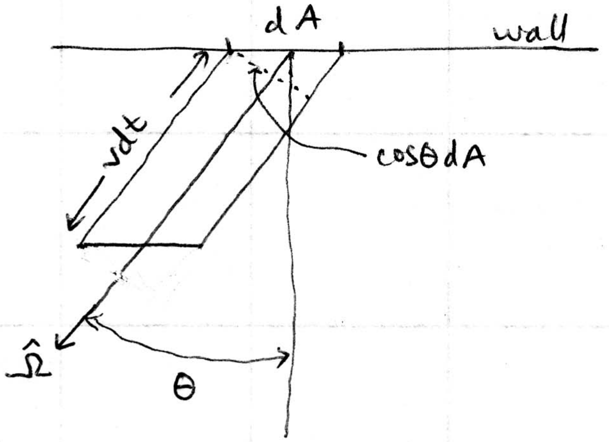
C. If the *directions* of the velocities are random then the number-density of molecules with speeds between v and $v+dv$ *and* with velocity in direction within solid angle element $d\omega$ about $\hat{\Omega}$

is $n(v)\,dv\,\frac{d\omega}{4\pi}$



D. Now ask: which molecules of this speed and direction will hit the wall element dA within time dt?

construct a cylinder in direction $\hat{\Omega}$ of length $v dt$.



Its cross-section will have area $\cos\theta\, dA$

The molecules of this velocity category (speed and direction) will hit area dA within time dt if they are enclosed in the cylinder. [Other molecules inside and outside this cylinder will also hit the wall; we later sum over all velocity and angle classes.]

Number of molecules of this class, contained in cylinder:

$$dN(\hat{\Omega}, v) = (\text{number-density}) \cdot (\text{volume})$$

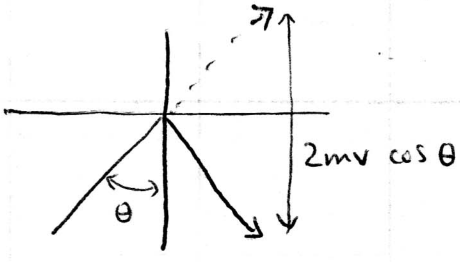
$$= n(v)\, dv \frac{d\omega}{4\pi} \cdot \cos\theta\, dA\, v dt$$

E. Flux of molecules (of this class) hitting the wall: $\left(\frac{\text{molecules}}{m^2 \cdot sec}\right)$

$$d\phi_n(\hat{\Omega}, v) = \frac{dN(\Omega, v)}{dA\, dt} = \frac{v n(v)}{4\pi} dv \cos\theta\, d\omega$$

(number-flux)

F. These molecules transfer momentum to the wall when they hit it. Assuming an elastic collision, the change in momentum per molecule is $2mv\cos\theta$ $\left(\frac{g}{\text{molecule}} \cdot \frac{m}{sec}\right)$



So the flux of momentum from molecules in this class is

$$d\Phi_p = \left[2mv\cos\theta\right] d\Phi_n \qquad \left(\frac{gm}{m^2 sec^2}\ ;\ \text{units of pressure}\right)$$

$$= \frac{n(v)}{4\pi} 2mv^2\, dv \cos^2\theta \underbrace{d\omega}_{\to \sin\theta\, d\theta\, d\phi}$$

G. <u>Pressure</u> is the total flux of momentum, adding up all classes of molecules.

$$P = \int \Phi_p = \frac{2m}{4\pi} \int n(v)\, v^2 dv \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \underbrace{\int_0^{\pi/2} \cos^2\theta \sin\theta\, d\theta}_{1/3}$$

$$= \frac{m}{3} \int v^2 n(v)\, dv$$

$$= \frac{m}{3} \overline{v^2}\, n$$ where $\overline{v^2}$ is <u>mean-squared velocity</u>.

i.e. $$\overline{v^2} \equiv \frac{\int v^2 n(v)\, dv}{\int n(v)\, dv} = \frac{\int v^2 n(v)\, dv}{n}$$

so $$PV = \frac{Nm\overline{v^2}}{3}$$

comparing with ideal gas law, $$PV = \overset{\text{number of molecules}}{N} \underset{\text{Boltzmann's constant}}{k} T,$$

we identify $$kT = \frac{m\overline{v^2}}{3}.$$

The <u>average kinetic energy</u> per molecule is $\frac{1}{2} m\overline{v^2} = \frac{3}{2} kT$

but $v^2 = v_x^2 + v_y^2 + v_z^2$ so $\frac{1}{2} m\overline{v_x^2} = \frac{1}{2} kT$

The root-mean-square speed is

$$V_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} .$$

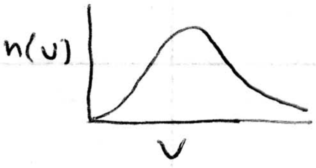
So heavier molecules travel slower than light molecules at the same temperature.

e.g. O_2 at $T = 283K$ has $V_{rms} = 460 \frac{m}{sec}$.

KINETIC THEORY OF GASES

Reference: Sears & Salinger 1975
Chapter 11

II Distribution of molecular velocities



Ⓐ We get the distribution of velocities by relating velocity to energy, $\epsilon_i = \frac{mv_i^2}{2}$, and using the distribution of molecules among energy states from <u>statistical mechanics</u>.

The assumption of statistical mechanics is that "all possible states are occupied with equal probability, subject to the constraint of total (or average) energy."

There may be several states which have the same energy. If so, the energy level is "degenerate." The number of states in an energy level is called the degeneracy (g).

For example: ϵ_3 — — — — — $g_3 = 5$
ϵ_2 — — — $g_2 = 3$
ϵ_1 — $g_1 = 1$
ϵ_0 — $g_0 = 1$

The assumption of statistical mechanics leads to the <u>Maxwell-Boltzmann distribution function</u>:

$$\frac{n_1}{n_0} = \frac{g_1}{g_0} e^{-(\epsilon_1-\epsilon_0)/kT}$$

or

$$n_i = n_0 \frac{g_i}{g_0} e^{-\epsilon_i/kT} e^{\epsilon_0/kT} \qquad (1)$$

where n_i is the number of molecules in energy level i.

Note that n_i is proportional to g_i.

Eq. (1) gives n_i in terms of n_0. It is more useful to write n_i in terms of N, the total number of molecules in the system:

$$N = \sum_i n_i$$

$$= \frac{n_0}{g_0} e^{\epsilon_0/kT} \underbrace{\sum_i g_i e^{-\epsilon_i/kT}}_{\downarrow}$$

This summation is given the symbol Z and called the partition function

so $$\frac{n_0}{g_0} = \frac{N}{Z} e^{-\epsilon_0/kT} \quad \text{and} \quad \frac{n_0}{g_0} e^{\epsilon_0/kT} = \frac{N}{Z} \qquad (2)$$

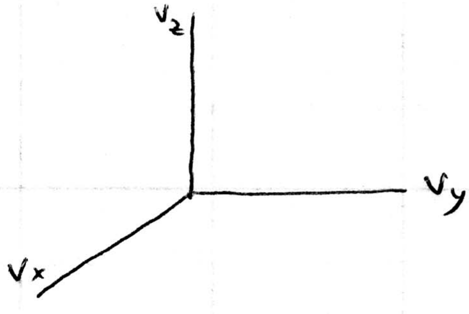
substituting (2) into (1), the Maxwell-Boltzmann distribution becomes

$$\boxed{n_i = g_i \frac{N}{Z} e^{-\epsilon_i/kT}} \quad \text{where } \epsilon_i = \frac{mv_i^2}{2}. \qquad (3)$$

Ⓑ what we now need, inorder to plot n vs v (or ϵ_i) is the degeneracy g_i, or $g(\epsilon)$, or $g(v)$.

The degeneracy is obtained by assuming that all values of a velocity component (v_x, v_y, or v_z) are equally probable (subject to the constraint of average total energy of the system).

In other words, a contour-map of g, plotted on three-dimensional velocity space, would be blank: the density of allowed states is constant throughout this space.



[contours are density of g]

We now find the number of states per speed-interval.

The speed v is related to the velocity components by

$$v^2 = v_x^2 + v_y^2 + v_z^2 .$$

The total number of states (G) out to speed v, is

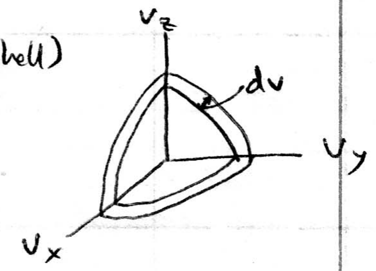
$$G \propto \frac{4}{3}\pi v^3 .$$

The density of states (per unit speed interval), is

$$\frac{dG}{dv} \propto 4\pi v^2 .$$

[The density of states in velocity space is constant, and this causes the density of states as a function of speed to be proportional to v^2, not a constant.]

The degeneracy of a velocity interval dv (spherical shell)



is $g = dG \propto 4\pi v^2 dv$,

or $g = c_1 v^2 \Delta v$ where c_1 is a constant

ⓒ Then the distribution function (3) becomes

$$\frac{n_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{\sum_i g_i e^{-\epsilon_i/kT}} = \frac{c_1 v_i^2 e^{-mv_i^2/2kT}\,\Delta v}{\sum_i c_1 v_i^2 e^{-mv_i^2/2kT}\,\Delta v}$$

$\frac{n_i}{N}$ is the fraction of molecules in energy state i.

Now group all molecules in a velocity interval dv:

n_i becomes $n(v)$, where $\int_0^\infty n(v)\,dv = N$

$\sum_i$ becomes $\int_0^\infty dv$

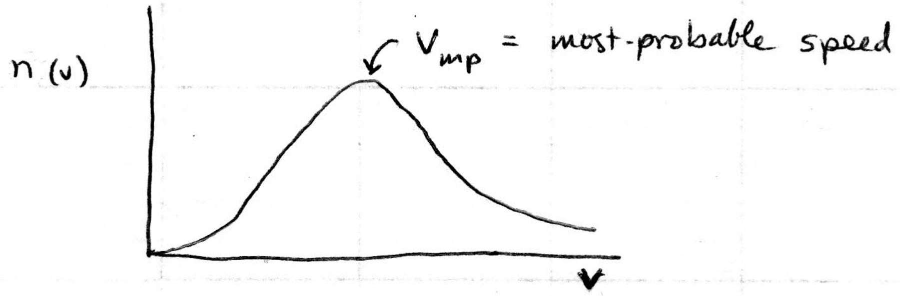
↑

[units of $n(v)$: molecules $\cdot$ m^{-3} $\cdot$ $(m\,sec^{-1})^{-1}$]

So
$$\frac{n(v)}{N} = \frac{v^2 e^{-mv^2/2kT}}{\int_0^\infty v^2 e^{-mv^2/2kT}\, dv}$$

The denominator has the value $\frac{\sqrt{\pi}}{4}\left(\frac{2kT}{m}\right)^{3/2}$, so

$$\boxed{\frac{n(v)}{N} = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2kT}\right)} \qquad (4)$$



This distribution displayed in velocity space looks like this:

54 THE STRUCTURE OF GASES

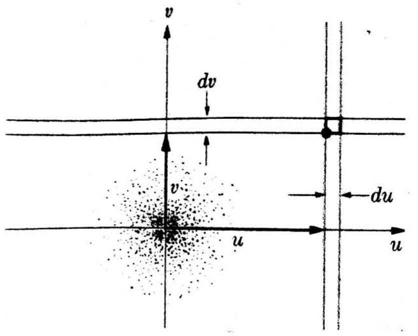


FIG. 4-6. Two-dimensional velocity space.

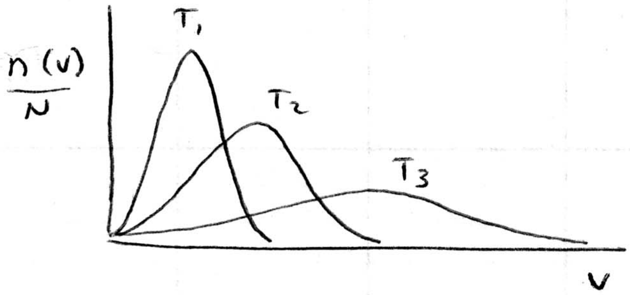
Ⓓ The <u>most probable speed</u> V_{mp} is obtained by setting the derivative of (4) to zero:

$$\frac{d}{dv}\left(\frac{n(v)}{N}\right) = 0 \quad \Rightarrow \quad V_{mp} = \sqrt{\frac{2kT}{m}}$$

so V_{mp} increases with temperature.

Then (4) can be written more compactly as

$$\frac{n(v)}{N} = \frac{4}{\sqrt{\pi}\, V_{mp}^3} \; V^2 \exp\left(\frac{-V^2}{V_{mp}^2}\right)$$



$T_3 > T_2 > T_1$

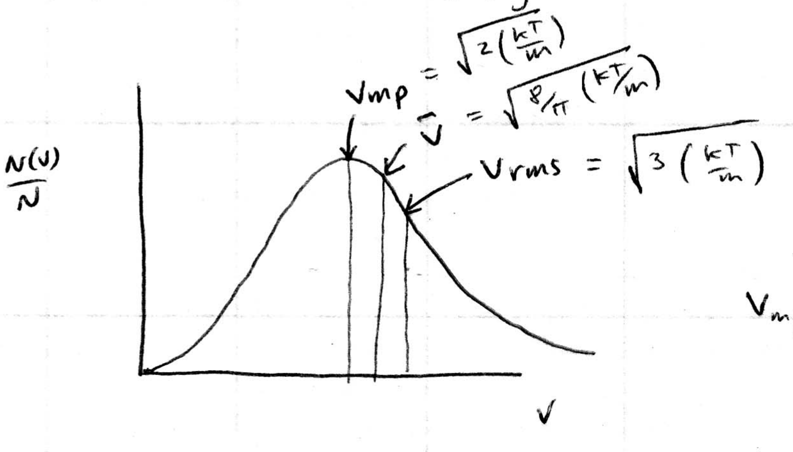
The <u>mean speed</u> $\bar{V}$ is obtained by summing over speeds, each speed weighted by the number of molecules at that speed.

$$\bar{V} = \frac{1}{N}\int_0^\infty v\, n(v)\, dv = \sqrt{\frac{8}{\pi}\frac{kT}{m}}$$

The <u>root-mean-square speed</u> V_{rms} :

$$V_{rms} = \sqrt{\overline{V^2}} = \sqrt{\frac{1}{N}\int_0^\infty v^2\, n(v)\, dv} = \sqrt{\frac{3kT}{m}} .$$

This is the same result we obtained before by comparing pressure as obtained from molecular collisions with that obtained from the ideal gas law.



$V_{mp} : \bar{V} : V_{rms} = 1, 1.13, 1.22$

Ⓕ Maxwell-Boltzmann velocity distribution for one component of velocity.

We saw that the M-B speed distribution had a maximum at $v_{mp} > 0$. This is due to the increase of $g(v)$ with v. But that was a consequence of $g(v_x)$ being constant:

Speed	velocity component
$G(v) \propto \frac{4}{3}\pi v^3$	$G(v_x) \propto v_x$
$\frac{dG}{dv} \propto v^2$	$\frac{dG}{dv_x} \propto v_x^0$ i.e. constant

The distribution function is obtained from (3), but with g_i constant:

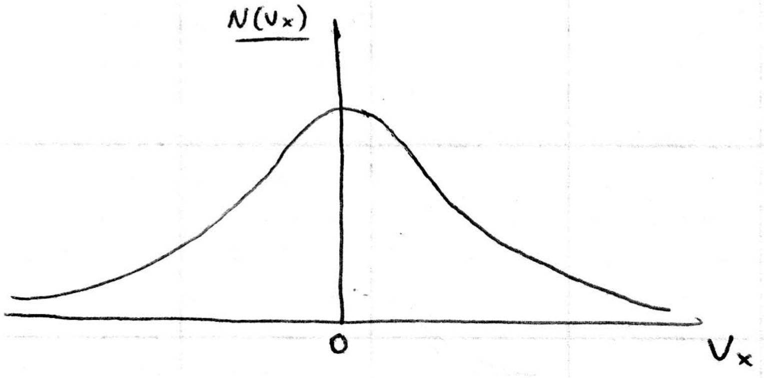
$$\frac{n_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{\sum_i g_i e^{-\epsilon_i/kT}} = \frac{e^{-mv_x^2/2kT}}{\left.\int_{\boxed{-\infty}}^{\infty} e^{-mv_x^2/2kT}\,dv_x \right] \rightarrow \sqrt{2\pi \frac{kT}{m}}}$$

note!

$$= \sqrt{\frac{m}{\pi kT \cdot 2}}\exp\left[\frac{-mv_x^2}{2kT}\right]$$

$$\boxed{\frac{n(v_x)}{N} = \frac{1}{\sqrt{\pi}\, v_{mp}} \exp\left[\frac{-v_x^2}{v_{mp}^2}\right]}$$

in terms of v_{mp}



The most probable v_x is zero, as is also seen from the figure on page 4.

LINE SHAPES.

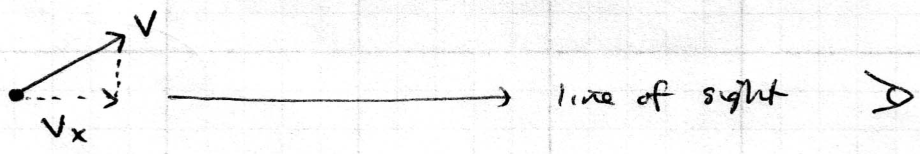
References:

Goody { sec 3.6 first edition
{ sec 3.3 second edition

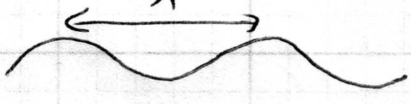
Houghton & Smith sec. 2.7.

DOPPLER-BROADENING

For a transition at frequency ν_0, the absorbed or emitted frequency ν will be different from ν_0 due to thermal motion in the direction the light is traveling.

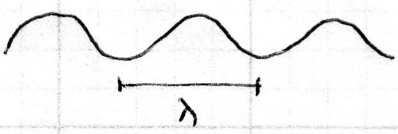


Emitter at rest emits



$\lambda = c/\nu_0$

Emitter in motion toward observer while emitting:

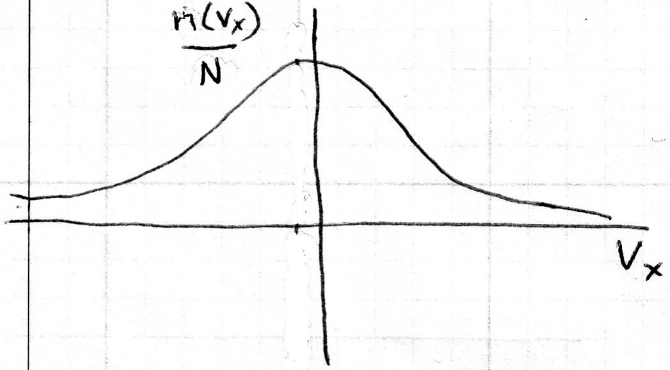


$$\lambda = \frac{c - V_x}{\nu_0}$$

Apparent frequency:

$$\nu = \frac{c}{\lambda} = c\,\frac{\nu_0}{c - V_x}\,\frac{(c+V_x)}{(c+V_x)} = \frac{c^2\nu_0\left(1 + \frac{V_x}{c}\right)}{c^2 - V_x^2} \underset{\overset{\uparrow}{c^2 \gg V_x^2}}{\approx} \nu_0\left(1 + \frac{V_x}{c}\right)$$

So the distribution of frequencies ν will be determined by the distribution of molecular velocities in the direction of view.



$$\int n(V_x)\,dV_x = N.$$

units of N: molecules / m^3

units of $n(V_x)$:

$[\text{molecules } m^{-3} (m \text{ sec}^{-1})^{-1}]$

recall

$$\frac{n(V_x)}{N} = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(\frac{-mV_x^2}{2kT}\right)$$

Use abbreviation $x \equiv \frac{m}{2kT}$ and drop subscript $_x$

$$\frac{n(v)}{N} = \left(\frac{x}{\pi}\right)^{1/2} \exp\left(-xv^2\right)$$

$$\underbrace{\frac{1}{N}\, n(v)\, dv}_{} = \left(\frac{x}{\pi}\right)^{1/2} \exp\left(-xv^2\right) dv.$$

↑ This is the fraction of molecules in velocity range dv.

Now convert it to the fraction emitting in frequency range $d\nu$:

$$\nu = \nu_0\left(1 + \frac{v}{c}\right), \text{ so } v = \frac{c}{\nu_0}(\nu - \nu_0) \text{ and } dv = \frac{c}{\nu_0}\, d\nu.$$

$$\underbrace{\frac{1}{N}\, n(\nu)\, d\nu}_{\text{Fraction of molecules emitting in frequency range } d\nu} = \underbrace{\frac{c}{\nu_0}\left(\frac{x}{\pi}\right)^{1/2} \exp\left[-x\frac{c^2}{\nu_0^2}(\nu-\nu_0)^2\right]}_{\text{Probability density } \phi(\nu) \text{ (line profile)}} d\nu$$

$\phi(\nu)$ is normalized :

$$\frac{1}{N}\underbrace{\int_{-\infty}^{\infty} n(\nu)\,d\nu}_{N} = \int_{-\infty \to 0}^{\infty} \phi(\nu)\,d\nu = 1 .$$

Now relate this to $k(\nu)$:

$$\int_0^{\infty} k(\nu)\,d\nu = S \qquad \text{line strength}$$

↑ integral over one line only

$$\int_0^{\infty} \phi(\nu)\,d\nu = 1 \qquad \text{so} \quad k(\nu) = S\,\phi(\nu)$$

so

$$\boxed{k(\nu) = S\,\frac{c}{\nu_0}\left(\frac{x}{\pi}\right)^{1/2} \underbrace{\exp\left[\frac{-xc^2}{\nu_0^2}(\nu-\nu_0)^2\right]}_{\text{This factor} \to 1 \text{ at } \nu = \nu_0}}$$

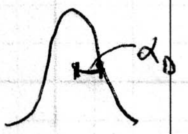
DOPPLER LINE SHAPE

particular values of $k(\nu)$:

a) At line center $\nu = \nu_0$.

$$k(\nu_0) = \frac{Sc}{\nu_0}\left(\frac{x}{\pi}\right)^{1/2}$$

b) At half-maximum $k(\nu) = \frac{1}{2}k(\nu_0)$.



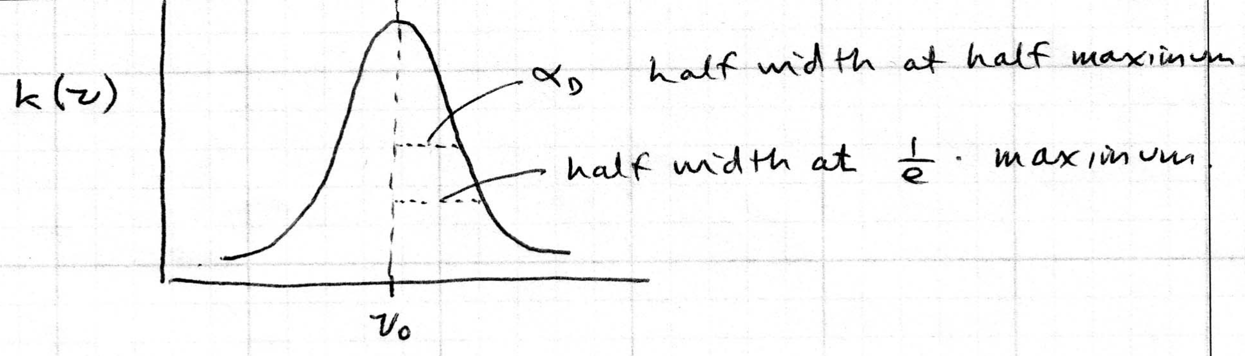
Define α_D (the "Doppler line width") as the half width at half-maximum.

$$\text{so}\quad k(\nu_0+\alpha_D) = \frac{1}{2}k(\nu_0)$$

$$\text{or}\quad \exp\left[\frac{-xc^2}{\nu_0^2}(\nu_0+\alpha_D-\nu_0)^2\right] = \frac{1}{2}$$

$$\text{solution :}\quad \alpha_D = \frac{\nu_0}{c}\sqrt{\frac{\ln 2}{x}} \underset{\uparrow\ \text{substitute for } x}{=} \boxed{\frac{\nu_0}{c}\left(\frac{2kT}{m}\ln 2\right)^{1/2}}$$

DOPPLER HALF-WIDTH



$$\alpha_D = \frac{\nu_0}{c}\left(\frac{2kT}{m}\ln 2\right)^{1/2}$$

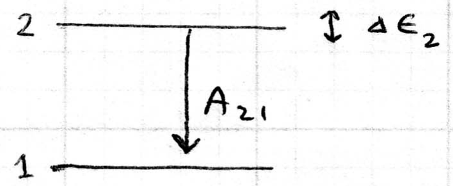
Some define α_D not at half maximum but instead at $\frac{1}{e}\cdot$ maximum, in which case the $\sqrt{\ln 2}$ is missing, where $\sqrt{\ln 2} = 0.83$.

example.

O_2 electronic transition at $\lambda = 0.76\ \mu m$ $\qquad \alpha_D \approx 10^{-2}\ cm^{-1}$

H_2O rotation $\qquad \alpha_D \approx 3.5 \times 10^{-4}\ cm^{-1}$
$\lambda \approx 80\ \mu m$

NATURAL BROADENING



Spontaneous emission for a vibrational transition (or rotational) $A_{21} \approx 10\ \text{sec}^{-1}$.

So natural life time τ_2 of the upper state is $\tau_2 = A_{21}^{-1} = 0.1$ sec. $= \tau_{Natural} \equiv \tau_N$

[The natural lifetime of the ground state is very large, $\tau_1 \to \infty$]

Heisenberg uncertainty principle.

$$\tau_2 \, \Delta E_2 \sim \frac{h}{2\pi}$$

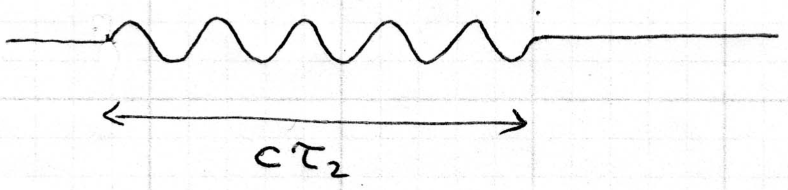
$$\Delta E_2 = h\Delta\nu = \frac{h}{2\pi\tau_2} \quad ; \quad \Delta\nu\ (\text{Hz}) = \boxed{\frac{1}{2\pi\tau_2} \equiv \alpha_N}$$

NATURAL LINE WIDTH.

If $\tau_2 \approx 0.1$ sec then $\alpha_N \approx 1.6$ Hz or $5\times10^{-11}\ \text{cm}^{-1}$

i.e. $\underline{\underline{\alpha_N \ll \alpha_D}}$

So far we have obtained only the width. To get the shape, we say that the molecule in state 2 is radiating an electromagnetic wave of frequency ν_0 but it is truncated because of the finite life time of state 2.



A spectral analysis of this wavetrain shows a spread of frequencies about ν_0.

Usually the wavetrain is interrupted by collisions long before τ_2. At STP $\tau_c \sim 10^{-9}\tau_N$.

Dependence of τ_2 on ν, S : Goody & Yung P. 34

$$\tau_2 = \frac{1}{A_{21}} \qquad \alpha_N = \frac{1}{2\pi\tau_2} = \frac{A_{21}}{2\pi}$$

Planck function $B = \dfrac{2h\nu^3}{c^2\left(e^{h\nu/kT}-1\right)}$ $\text{W}\ \text{m}^{-2}\text{sr}^{-1}\text{Hz}^{-1}$

$\text{W} \to \text{J sec}^{-1}$

or $B = \dfrac{2\nu^2}{c^2\left(e^{h\nu/kT}-1\right)}$ $\dfrac{\text{photons}}{\text{sec}}\ \text{m}^{-2}\text{sr}^{-1}\text{Hz}^{-1}$

Units of A_{21}: sec^{-1}

Units of B_{12}: sec^{-1} intensity^{-1}

$A_{21} = \dfrac{2h\nu^3}{c^2} B_{12}$ if intensity is in $\text{W m}^{-2}\text{sr}^{-1}\text{Hz}^{-1}$

or $A_{21} = \dfrac{2\nu^2}{c^2} B_{12}$ if intensity in $\dfrac{\text{photons}}{\text{sec}}\ \text{m}^{-2}\text{sr}^{-1}\text{Hz}^{-1}$

From notes on two-level-atom:

$k_\nu \propto h\nu B_{12}$ if intensity in $\text{W m}^{-2}\text{sr}^{-1}\text{Hz}^{-1}$

so $k_\nu \propto B_{12}$ if intensity in $\dfrac{\text{photons}}{\text{sec}}\ \text{m}^{-2}\text{sr}^{-1}\text{Hz}^{-1}$

But line strength $S \propto k_\nu \propto B_{12}$

So $A_{21} \propto \dfrac{2\nu^2}{c^2} S_{12}$

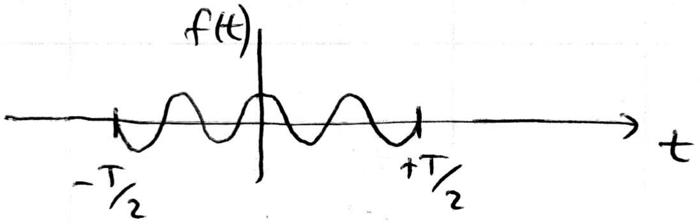
so $\boxed{\alpha_N \propto \nu^2 S}$

Natural broadening becomes important at higher frequency (UV, X-ray).

LORENTZ - BROADENING

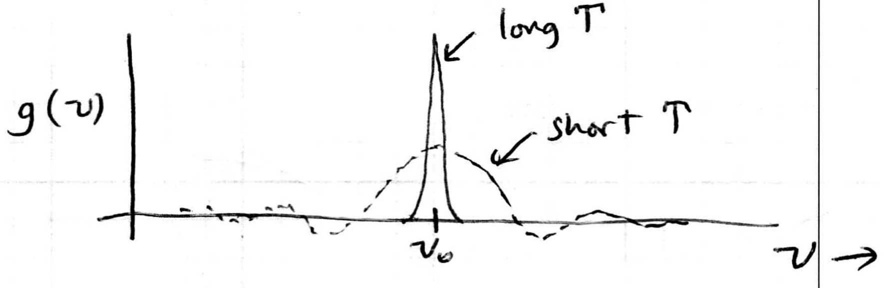
(collision broadening; pressure broadening)

The shape of a pressure-broadened line is explained by assuming that a molecule emits a wave-train $f(t)$ of EM radiation only for the time interval T between collisions. Because the wave is truncated it has a spectrum of frequencies $g(\nu)$



$$f(t) = \overset{\substack{\uparrow \\ \text{(amplitude of EM wave)}}}{A} \cos 2\pi\nu_0 t \;; \qquad -\frac{T}{2} < t < T/2 .$$

Amplitude Spectrum:



The amplitude spectrum is obtained by Fourier analysis;

$$g(\nu, T) = \frac{A}{\sqrt{2\pi}} \int_{-T/2}^{T/2} f(t) \cos 2\pi\nu t \, dt$$

$$= \frac{A}{\sqrt{2\pi}} \int_{-T/2}^{T/2} \cos 2\pi\nu_0 t \cos 2\pi\nu t \, dt$$

To integrate, use the trigonometric identity

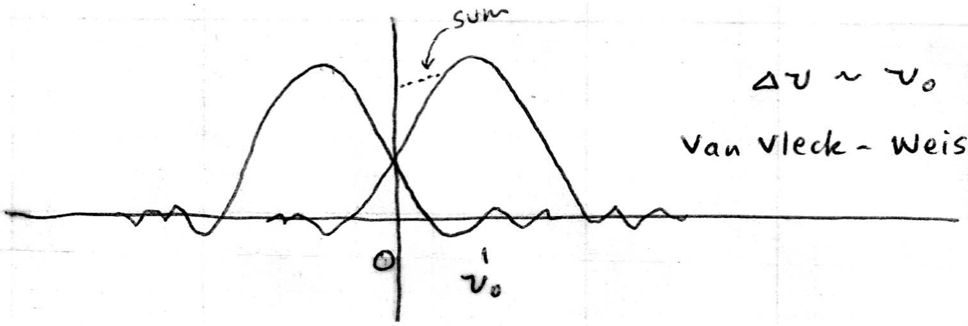
$$\cos a \cos b = \frac{1}{2}\cos(a-b) + \frac{1}{2}\cos(a+b) .$$

Then
$$g(\nu, T) = \frac{A}{(2\pi)^{3/2}} \left\{ \frac{\sin \pi(\nu_0+\nu)T}{\nu_0+\nu} + \frac{\sin \pi(\nu_0-\nu)T}{\nu_0-\nu} \right\}$$

In the infrared, $\bar{\nu} \sim 1000$ cm^{-1}, and line width $\Delta\bar{\nu} \sim 0.1$ cm^{-1}

so $\underset{\sim 2000}{|\nu_0+\nu|} >> \underset{\sim 0.1}{|\nu_0-\nu|}$ so the first term can be neglected.

The first term is important if $\bar{\nu}_0 \lesssim 1$ cm^{-1} (microwave).

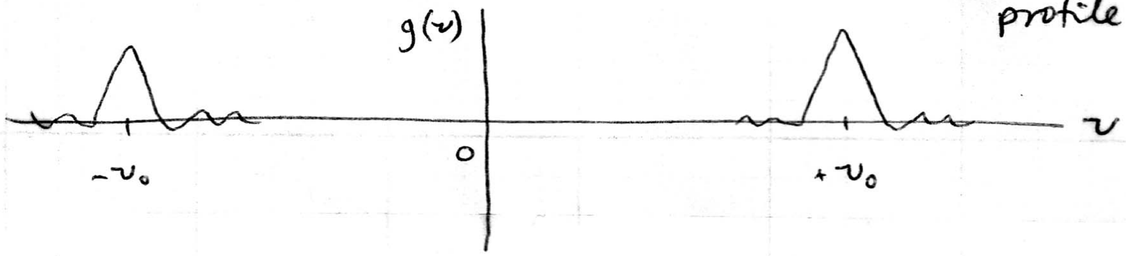


$\Delta\nu \sim \nu_0$

Van Vleck - Weisskopf profile.

$\Delta\nu \ll \nu_0$

Lorentz profile



The LORENTZ profile results from neglecting the first term:

$$g(\nu, T) = \frac{A}{(2\pi)^{3/2}} \frac{\sin[\pi(\nu_0-\nu)T]}{\nu_0-\nu}$$

But this is just for one inter-collision time T. We must integrate over all T to get the line profile.

Distribution of collision times

Let $P(T)$ be the probability distribution of times until collision. Then $P(T)\,dT$ is the probability that a new collision occurs between T and $T+dT$ (where $T=0$ is the present time).

Consider an assembly of N molecules at $T=0$ and watch them collide. Let $N(T)$ be the number of uncollided molecules at time T. N changes by the amount dN at in time dT; dN is negative and is proportional to N and dT:

$$dN = -\alpha N\, dT \qquad (1)$$

Integrating (1), $N(T) = N_0 e^{-\alpha T}$.

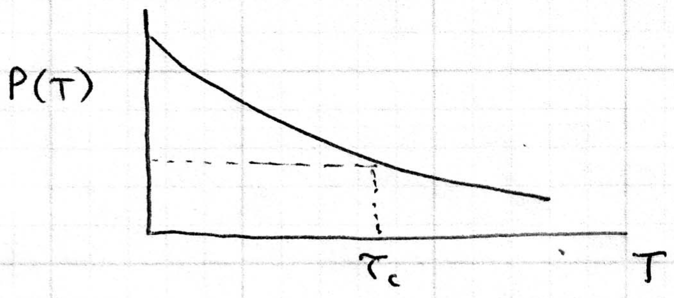
The number whose first collision occurs between T and $T+dT$ will be proportional to the number that remain uncollided at time T, so $P(T) \propto e^{-\alpha T}$.

Normalize $\int_0^\infty P(T)\,dT = 1$, so $P(T) = \alpha e^{-\alpha T}$,

or $\boxed{P(T) = \frac{1}{\tau_c} e^{-T/\tau_c}}$ where $\tau_c \equiv \frac{1}{\alpha}$.

τ_c is the mean time between collisions.

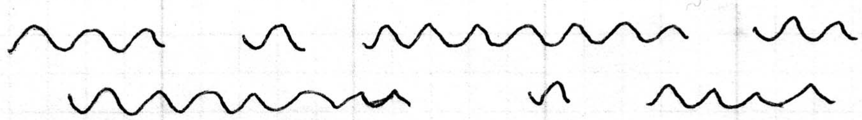
(Exercise: show that $\overline{T} \equiv \dfrac{\int T\,P(T)\,dT}{\int P(T)\,dT} = \tau_c$.)



$$P(T) = \frac{1}{\tau_c} e^{-T/\tau_c}$$

P(T) has units sec^{-1}

So we have a distribution of lengths of the truncated wave-train:



The intensity of radiation is the sum of the squares of the amplitudes of the wavetrains. So to get the emission or absorption coefficient $k(\nu)$ we need the power spectrum which is the square of the amplitude spectrum:

$$k(\nu) \propto \langle g(\nu,T)^2 \rangle = \frac{\int_0^\infty [g(\nu,T)]^2 \, P(T)\, dT}{\int_0^\infty P(T)\, dT} .$$

[Denominator = 1.]

$$\langle g^2 \rangle = \frac{A^2}{(2\pi)^3} \int_0^\infty \frac{\sin^2[\pi(\nu_0-\nu)T]}{(\nu_0-\nu)^2} \frac{1}{\tau_c} e^{-T/\tau_c}\, dT .$$

$$= \frac{A^2}{(2\pi)^3 \tau_c (\nu_0-\nu)^2} \underbrace{\int_0^\infty \sin^2[\pi(\nu_0-\nu)T]\, e^{-T/\tau_c}\, dT}$$

This integral is of the form $\int e^{ax} \sin^2 bx \, dx$

and has the value $\dfrac{2\tau_c \pi^2 (\nu_0-\nu)^2}{\frac{1}{\tau_c^2} + 4\pi^2(\nu_0-\nu)^2}$

so

$$\langle g^2 \rangle = \frac{A^2}{(2\pi)^3} \; \frac{2\pi^2}{\frac{1}{\tau_c^2} + 4\pi^2(\nu_0-\nu)^2} \cdot \frac{\left(\frac{1}{4\pi^2}\right)\left(\frac{2\pi\tau_c}{2\pi\tau_c}\right)}{\left(\frac{1}{4\pi^2}\right)}$$

$$= \frac{A^2\pi\tau_c}{(2\pi)^3} \; \frac{\frac{1}{2\pi\tau_c}}{\left(\frac{1}{2\pi\tau_c}\right)^2 + (\nu_0-\nu)^2} .$$

Let $\alpha_L \equiv \frac{1}{2\pi\tau_c}$ [α_L will turn out to be the half-width.]

$$= \underbrace{\frac{A^2\pi\tau_c\alpha_L}{(2\pi)^3}}_{\text{collection of constants independent of } \nu.} \; \frac{1}{\alpha_L^2 + (\nu_0-\nu)^2}$$

$$\left.\begin{matrix}\text{collection of} \\ \text{constants} \\ \text{independent of } \nu.\end{matrix}\right\} = \frac{A^2}{16\pi^3} \equiv A'$$

$k(\nu) \propto \langle g(\nu,T)^2 \rangle$, so $k(\nu) = A' \dfrac{1}{\alpha_L^2 + (\nu_0-\nu)^2}$.

Find A' by the requirement $\int_0^\infty k(\nu)\,d\nu = S$ the line-strength.

$$S = \int_0^\infty k(\nu)\,d\nu = A'\int_0^\infty \frac{1}{\alpha_L^2 + (\nu-\nu_0)^2}\,d\nu$$

$$= A'\int_{-\nu_0}^{\infty} \frac{1}{\alpha_L^2 + (\Delta\nu)^2}\,d(\Delta\nu) \approx A'\int_{-\infty}^{\infty} \frac{1}{\alpha_L^2 + (\Delta\nu)^2}\,d(\Delta\nu) = \frac{A'\pi}{\alpha_L}$$

so $A' = \dfrac{S\alpha_L}{\pi}$ and

$$\boxed{k(\nu) = \frac{S\alpha_L/\pi}{(\nu-\nu_0)^2 + \alpha_L^2}}$$

LORENTZ LINE SHAPE

$$\boxed{k(\nu) = \frac{S}{\pi} \frac{\alpha_L}{(\nu-\nu_0)^2 + \alpha_L^2}}$$

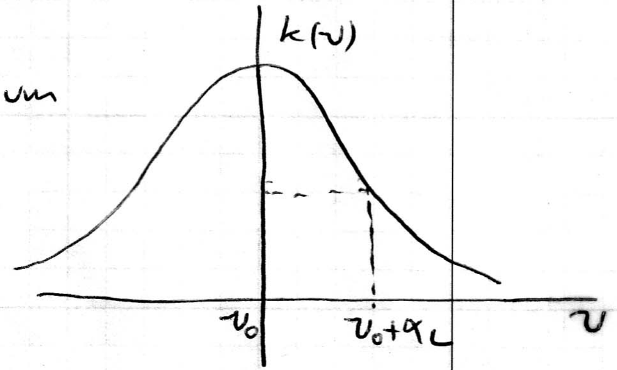
where $S =$ line strength

and $\alpha_L \equiv \frac{1}{2\pi\tau_c}$. [$\alpha_L$ will be the half-width of the line.]

where τ_c is the mean time between collisions.

Note

① At $\nu=\nu_0$, $k = \frac{S}{\pi\alpha_L}$. This is the maximum



② At half-maximum:

$$\frac{S}{\pi} \frac{\alpha_L}{(\nu-\nu_0)^2 + \alpha_L^2} = \frac{1}{2} \frac{S}{\pi\alpha_L}$$

which gives

$$\nu = \nu_0 \pm \alpha_L$$

so α_L is the half-width at half-maximum.

③ In the wings of the line ($\Delta\nu \gg \alpha_L$)

$$k(\nu) \approx \frac{S}{\pi} \frac{\alpha_L}{(\nu-\nu_0)^2}$$

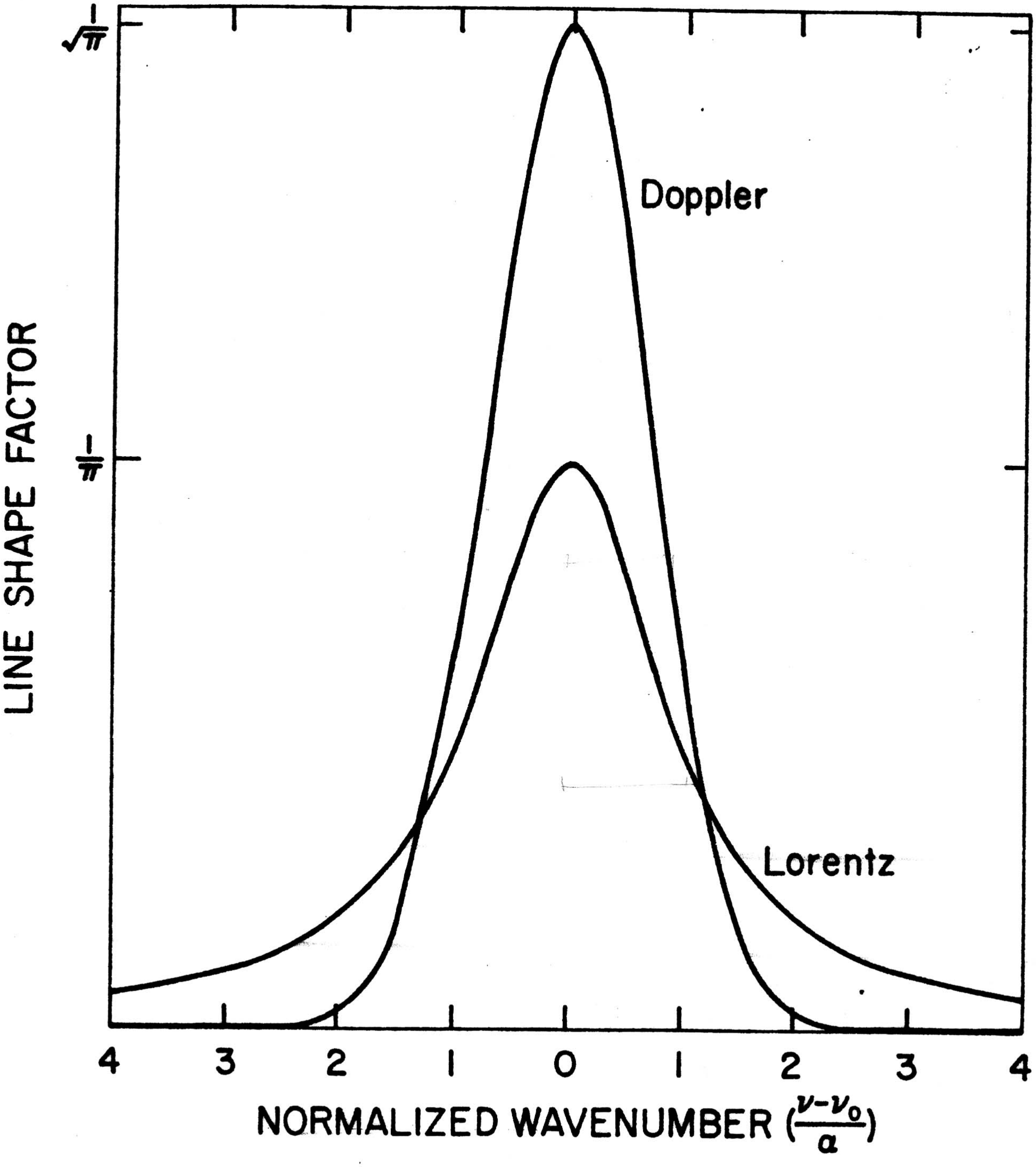
Contrasting Lorentz and Doppler <u>wings</u>:

LORENTZ $k(\nu) \sim (\Delta\nu)^{-2}$

DOPPLER $k(\nu) \sim e^{-a(\Delta\nu)^2}$

so Doppler wings drop off more rapidly.

Rodgers 1976



X

Fig. 1 Doppler and Lorentz line shapes.

ESTIMATION OF COLLISION TIME τ_c.

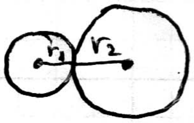
τ_c will depend on pressure and temperature.

For example, the broadening of a water vapor line is due to collisions of H_2O with

O_2, N_2, CO_2, ... ("foreign broadening")

and with H_2O ("self-broadening")

Consider two molecules of radii r_1 & r_2; $r_{12} \equiv r_1 + r_2$

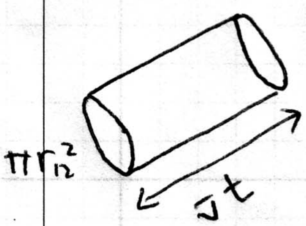


A collision will occur if the nuclei come closer than r_{12}.

e.g. for H_2O and N_2, the sum of their van der Waals radii is $r_{12} \approx 3.2\,\text{Å} = 0.32\,\text{nm}$.

So the effective cross-section for collision is πr_{12}^2.

Let $\bar{v}$ be the mean speed of gas molecules. A molecule moving at speed $\bar{v}$ sweeps out a cylinder in time t



Cylinder volume $= \bar{v} t \pi r_{12}^2$.

Number of collisions in time t is the number of molecules in this volume:

$N = n \bar{v} t \pi r_{12}^2$ where n is number-density.

Number of collisions per unit time $\frac{N}{t} = n\bar{v}\pi r_{12}^2$.

Mean time τ_c between collisions $t = \tau_c$ for $N = 1$:

$$\tau_c = \frac{1}{n\bar{v}\pi r_{12}^2}$$

So $\alpha_L = \frac{1}{2\pi\tau_c} = \frac{1}{2} n\bar{v} r_{12}^2$

$\bar{v} \sim \sqrt{T}$ from Maxwell-Boltzmann velocity distribution

$n \sim \frac{P}{T}$ from ideal gas law:

$P = nkT$; $n = P/kT$

so $\alpha_L \sim \frac{P}{T^{1/2}}$

$\bar{v} = \sqrt{\frac{8}{\pi}\frac{kT}{\mu}}$ $\longrightarrow$ For relative velocity use reduced mass μ instead of **M**; $\mu < M$

$$\text{so } \alpha_L = \frac{1}{2}\frac{P}{kT}\sqrt{\frac{8}{\pi}\frac{kT}{\mu}}\, r_{12}^2 = \boxed{\frac{2r_{12}^2}{(2\pi k\mu)^{1/2}}\quad\frac{P}{T^{1/2}}}$$

so α_L varies depending on which gas is colliding

It also varies between bands because collisions are not elastic.

e.g. H_2O colliding with N_2 or O_2 : $r_{12} \approx 0.32$ nm

$\mu = \frac{18 \cdot 28.8}{18 + 28.8} = 11.1$ Daltons ; $\alpha_L = 9.9 \times 10^8$ sec^{-1}

or $\frac{\alpha_L}{c} = 0.033$ cm^{-1}

but actually $\alpha_L \sim 0.1$ cm^{-1} for H_2O-rotation band, Therefore we measure α_{L0} (STP) as a reference instead of calculating it, and get the T, p dependence from the Lorentz equation:

$$\alpha_{L0} = \frac{2 r_{12}^2}{(2\pi k_\mu)^{1/2}} \frac{p_0}{T_0^{1/2}} \quad , \text{ or } \quad \alpha_{L0} \propto \frac{p_0}{T_0^{1/2}}$$

$$\alpha_L \propto \frac{p}{T^{1/2}}$$

so $$\boxed{\frac{\alpha_L(T,p)}{\alpha_{L0}} = \frac{p}{p_0}\left(\frac{T_0}{T}\right)^{1/2}}$$.

In the atmosphere $\frac{\Delta T}{T_0} \ll \frac{\Delta p}{p_0}$.

Collision broadening and natural broadening have the same shape ("Lorentz" shape).

Combining them:

$$\alpha_{\text{collision}} = \frac{1}{2\pi\tau_c} \qquad \alpha_{\text{natural}} = \frac{1}{2\pi\tau_n}$$

$$\alpha_L = \frac{1}{2\pi\tau_c} + \frac{1}{2\pi\tau_n} = \frac{1}{2\pi}\left(\frac{1}{\tau_c} + \frac{1}{\tau_n}\right)$$

$$\approx \frac{1}{2\pi\tau_c} \quad \text{because} \quad \tau_c \ll \tau_n .$$

COMPARE α_N, α_D, α_L

	τ_N (sec)	$\alpha_N\,(\mathrm{cm}^{-1}) = \frac{1}{2\pi\tau_N c}$	α_D (STP)	α_L (STP)
electronic	$10^{-8} - 10^{-6}$	$10^{-5}\ \mathrm{cm}^{-1}$	$\sim 3.3 \times 10^{-2}\ \mathrm{cm}^{-1}$ (O_2)	$0.1\ \mathrm{cm}^{-1}$
vibrational	$10^{-2} - 10^{-1}$	$10^{-11}\ \mathrm{cm}^{-1}$	$\sim 1 \times 10^{-3}$ (H_2O 6.3 μm)	$0.1\ \mathrm{cm}^{-1}$
rotational	$1 - 10^{2}$	$10^{-13}\ \mathrm{cm}^{-1}$	$\sim 3.5 \times 10^{-4}$ (H_2O rotation)	$0.1\ \mathrm{cm}^{-1}$
		$\sim \nu^2 S$	$\sim \nu\sqrt{T}$	$\sim \frac{P}{\sqrt{T}}$

CONVOLUTION of LORENTZ and DOPPLER broadening gives "VOIGT" line-shape

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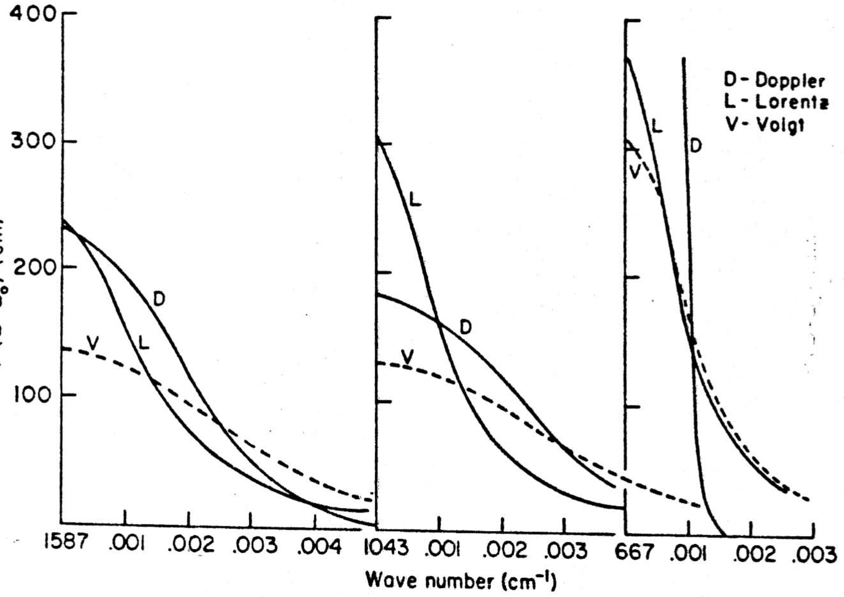


scale?

FIG. 2. Lorentz, Voigt and Doppler profiles corresponding to a pressure and temperature at 30 km for infrared lines centered at 1587 cm⁻¹ (water vapor), 1043 cm⁻¹ (ozone) and 667 cm⁻¹ (carbon dioxide).

Absorption by non-overlapping Lorentz lines.

Lorentz line :

$$k_\nu = S \frac{\alpha_L / \pi}{(\nu - \nu_0)^2 + \alpha_L^2}$$

$$\text{abs coef} = \begin{pmatrix}\text{line}\\ \text{strength}\end{pmatrix} \cdot \begin{pmatrix}\text{line}\\ \text{profile}\end{pmatrix}$$

$$k_\nu = S \cdot \phi(\nu)$$

$$\int_0^\infty k_\nu \, d\nu = S$$

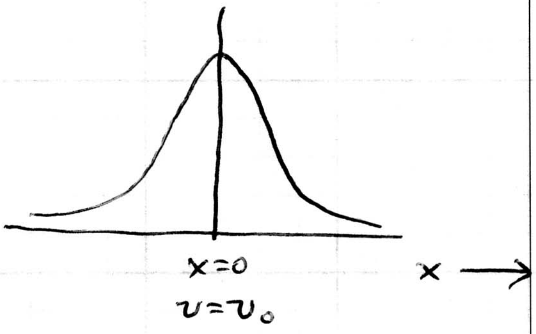
$$\int_0^\infty \phi(\nu) \, d\nu = 1$$

units.	
k	$m^2 g^{-1}$
ν	cm^{-1}
S	$(m^2 g^{-1})(cm^{-1})$

.. Coordinate system centered on line :

$$x \equiv \nu - \nu_0$$

$$\phi(x) = \frac{\alpha_L / \pi}{x^2 + \alpha_L^2}$$



Normalized profile :

$$\int_{-\nu_0}^{\infty} \phi(x)\, dx \approx \int_{-\infty}^{\infty} \phi(x)\, dx = 1$$

$\uparrow$ note !

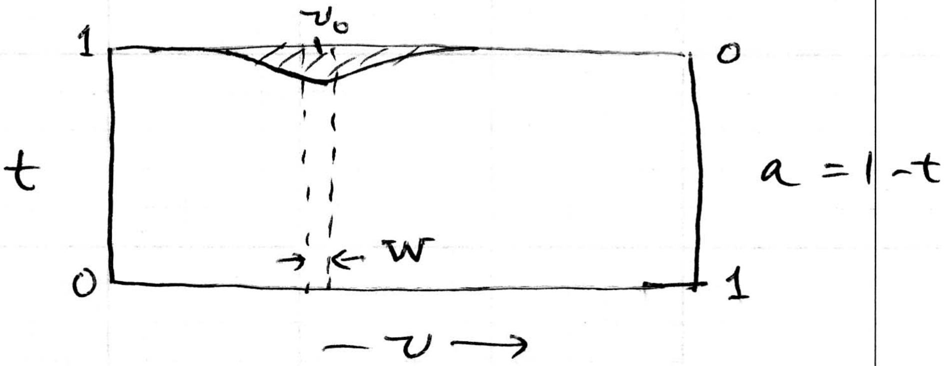
Monochromatic transmission $t = e^{-k_\nu m}$

where $m \left(\frac{kg}{m^2}\right) = \text{density} \left(\frac{kg}{m^3}\right) \cdot \text{path length (m)}$

$m = \int \rho(\vec{s})\, ds$ along a path

absorptance $a = 1 - t = 1 - e^{-k_\nu m}$.

A single line:

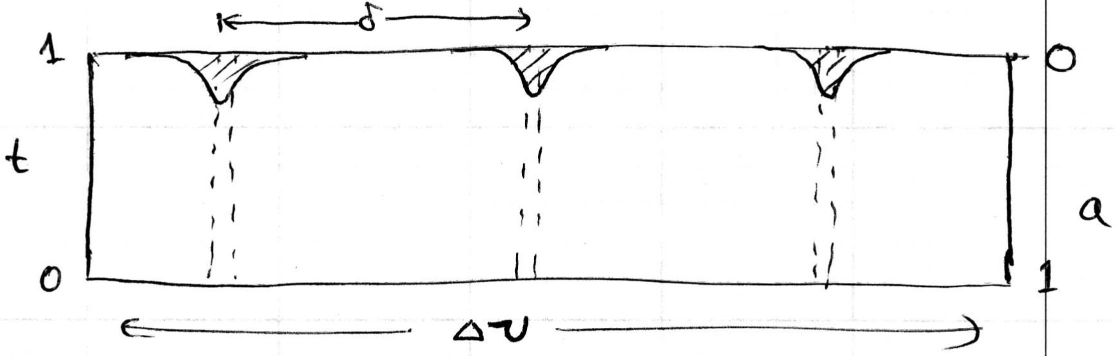


Define Equivalent Width $\overline{W}$ (units cm^{-1})

$$\overline{W} = \int_0^\infty a_\nu \, d\nu = \int_0^\infty (1 - t_\nu)\, d\nu = \int_0^\infty (1 - e^{-k_\nu m})\, d\nu.$$

(single line)

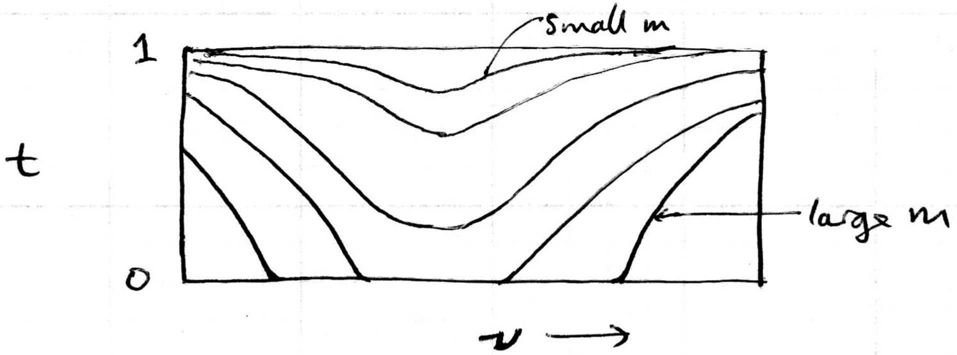
Average absorptance of nonoverlapping lines of equal strength.

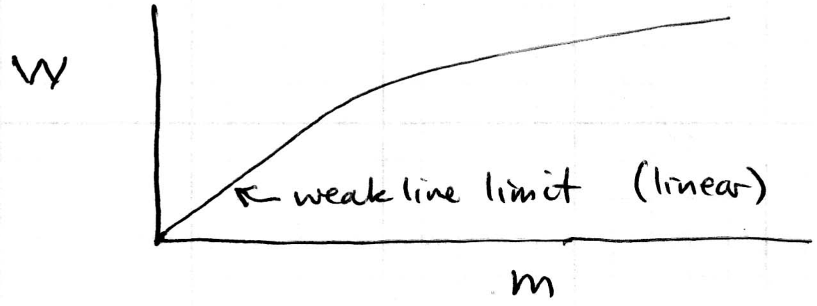


Average absorptance $A = \frac{1}{\Delta\nu} \int_{\Delta\nu} a \, d\nu$

Here $A = \frac{W \ (cm^{-1})}{\delta \ (cm^{-1})}$ If lines are of equal strength

How do transmittance and equivalent width vary with m?





① Weak-line approximation: $k_\nu m \ll 1$

so $e^{-k_\nu m} \approx 1 - k_\nu m$

$$W = \int_0^\infty d\nu\,[1-(1-k_\nu m)] = \int_0^\infty k_\nu m\, d\nu = m\int_0^\infty k_\nu d\nu = \underline{\underline{S\cdot m}}$$

$$\boxed{W = S\cdot m}$$ "linear regime" "weak-line regime"

② General case.

$$W = \int_0^\infty d\nu \left[1-\exp\left(-\frac{Sm}{\pi}\,\frac{\alpha_L}{(\nu-\nu_0)^2+\alpha_L^2}\right)\right] \qquad (1)$$

Ladenburg & Reiche solved this integral. The solution is Bessel functions. We'll look at it later; first derive the strong-line limit.

③ <u>Strong-line limit</u>. Consider the exponential under the integral in (1) :

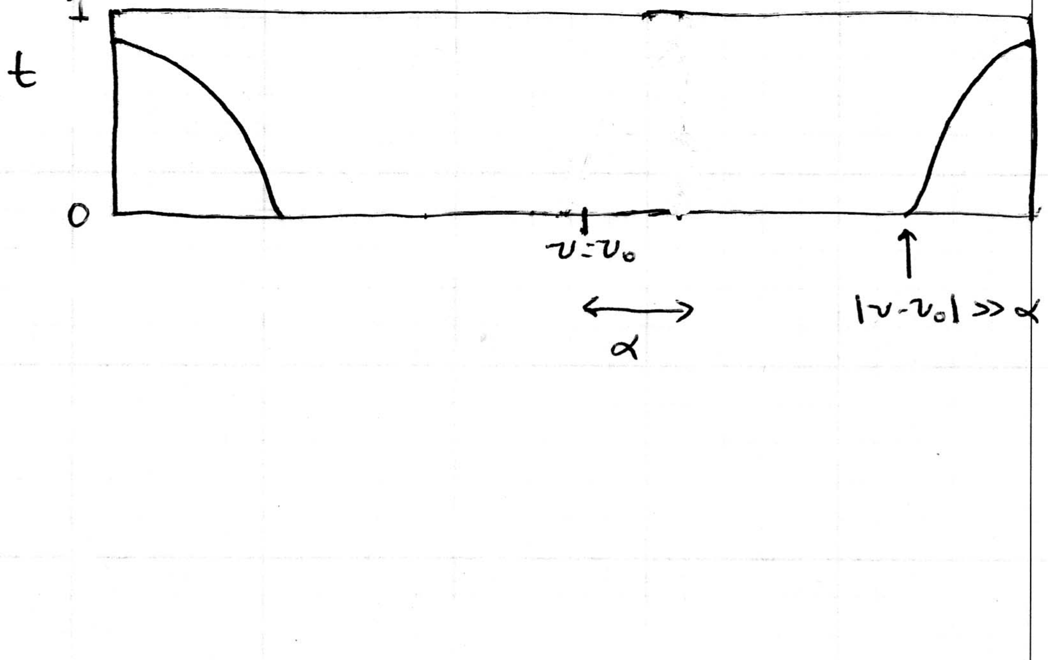
$$\exp\left(\frac{-Sm}{\pi}\,\frac{\alpha_L}{(\nu-\nu_0)^2+\alpha_L^2}\right),$$ and consider two cases

a) Far from line center.

Then $(\nu-\nu_0)^2 \gg \alpha_L^2$, and we can neglect α_L^2.

b) <u>NOT</u> far from line center.

For a strong line, this exponential is zero for several line-widths away from the center, because Sm is large. If α_L^2 is neglected in computing this exponential it will still be near zero; i.e. little error is caused by neglecting α_L^2 in the denominator.



Strong-line limit.

Ignoring α_L^2 in (1):

$$W \approx \int_0^\infty d\nu \left[1 - \exp\left(\frac{-Sm}{\pi} \frac{\alpha_L}{(\nu-\nu_0)^2}\right)\right]$$

substitute $a \equiv \sqrt{\frac{Sm\alpha_L}{\pi}}$

$x \equiv \nu - \nu_0$; $dx = d\nu$; limits on x: $-\nu_0$ to $+\infty$

$$W = \int_{-\nu_0}^{\infty} dx \left[1 - \exp\left(\frac{-a^2}{x^2}\right)\right] \approx \int_{-\infty}^{\infty}$$

(no contribution from $\nu < 0$)

substitute $\xi \equiv a/x$

$$dx = -a\xi^{-2} d\xi$$

$$W = a \underbrace{\int_{-\infty}^{\infty} \frac{d\xi}{\xi^2}\left[1 - e^{-\xi^2}\right]}_{2\sqrt{\pi}}$$

$$\doteq 2a\sqrt{\pi} = 2\sqrt{Sm\alpha_L}$$

$$\boxed{W = 2\sqrt{Sm\alpha_L}}$$ "square-root regime" "strong regime"

"Curve of growth"

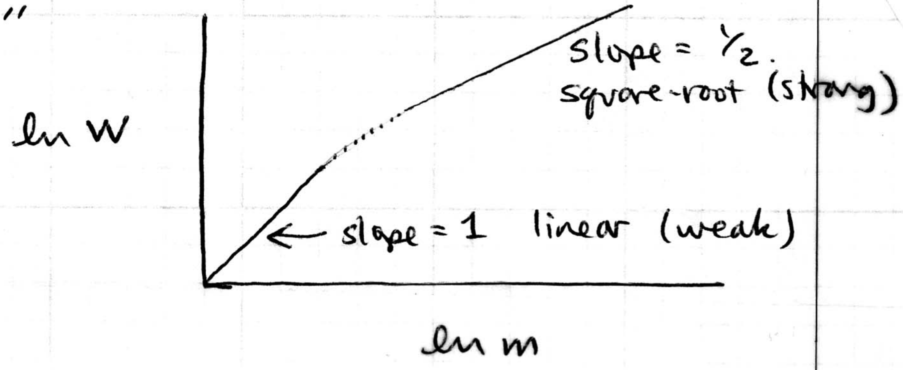


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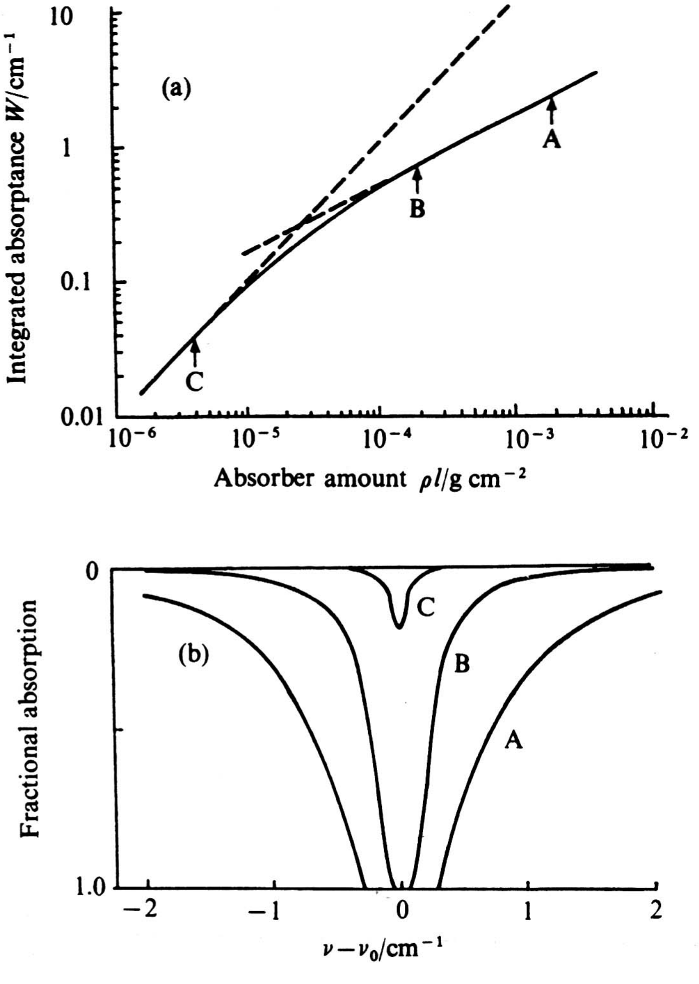
Fig. 4.2. (a) Curve of growth of a typical spectral line with $s = 10^4\ \mathrm{cm}^{-1}\ (\mathrm{g\ cm}^{-2})^{-1}$ and $\gamma_0 = 0.06\ \mathrm{cm}^{-1}$ showing the linear and square root regions of growth.

(b) Actual shapes of the spectral line for different values of ρl corresponding to the values shown by the arrows in (a).



Between the linear and square-root regimes,

In the transition region the Ladenburg-Reiche formula is needed.

Equivalent width of a single Lorentz line:

$$W = \int_0^\infty a_\nu \, d\nu = \int_{-\infty}^{\infty} \left\{ 1 - \exp\left[\frac{-S\alpha_L m}{\pi} \cdot \frac{1}{(\nu-\nu_0)^2 + \alpha_L^2} \right] \right\} d(\nu - \nu_0)$$

solution (given also by Liou):

$$W = \alpha_L \, x \, e^{-x} \, 2\pi \left[I_0(x) + I_1(x) \right]$$ (Ladenburg & Reiche, 1913)

where $x \equiv \dfrac{Sm}{2\pi\alpha}$

and I_0 & I_1 are modified Bessel functions.

The L-R formula has limits:

$x \ll 1$ $\quad W = Sm$

$x \gg 1$ $\quad W = 2\sqrt{S\alpha_L m}$

So the criterion for the weak line limit is actually

$\dfrac{Sm}{2\pi\alpha} \ll 1$. (A broad line can remain in the linear regime out to larger m)

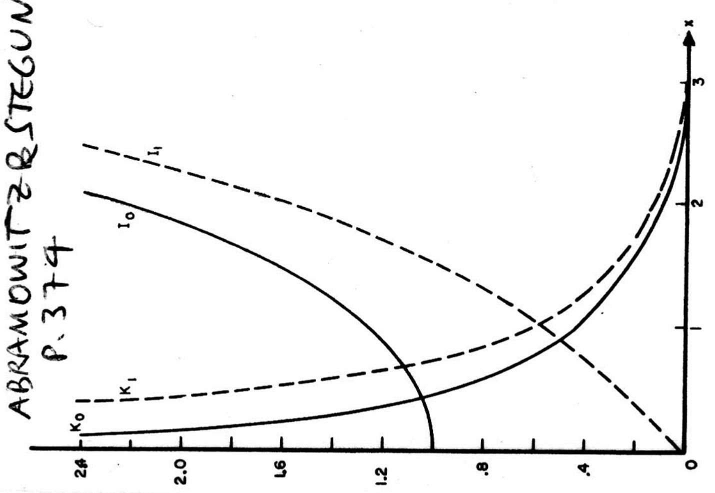


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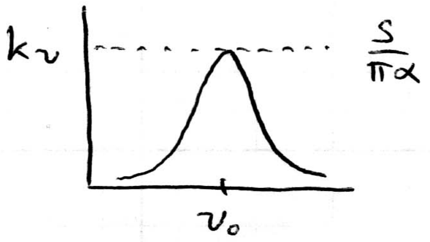
FIGURE 9.7. $I_0(x)$, $K_0(x)$, $I_1(x)$ and $K_1(x)$.

Recall the absorption coefficient at line center



so the optical depth at line center $= km = \frac{Sm}{\pi\alpha}$

so the weak line criterion is $\tau(\nu_0) \ll 2$

Summary

	equivalent width	average absorptance for nonoverlapping lines of equal strength and average spacing δ
Strong Lorentz line	$W = 2\sqrt{S\alpha_L m}$	$\bar{A} = \frac{2\sqrt{S\alpha_L m}}{\delta}$
weak line of any shape	$W = Sm$	$\bar{A} = \frac{Sm}{\delta}$
Strong Doppler line	$W = 2\alpha_D\sqrt{\ln\left(\frac{Sm}{\alpha_D\sqrt{\pi}}\right)}$	$\bar{A} = \frac{2}{\delta}\alpha_D\sqrt{\ln\left(\frac{Sm}{\alpha_D\sqrt{\pi}}\right)}$

GOODY & YUNG.

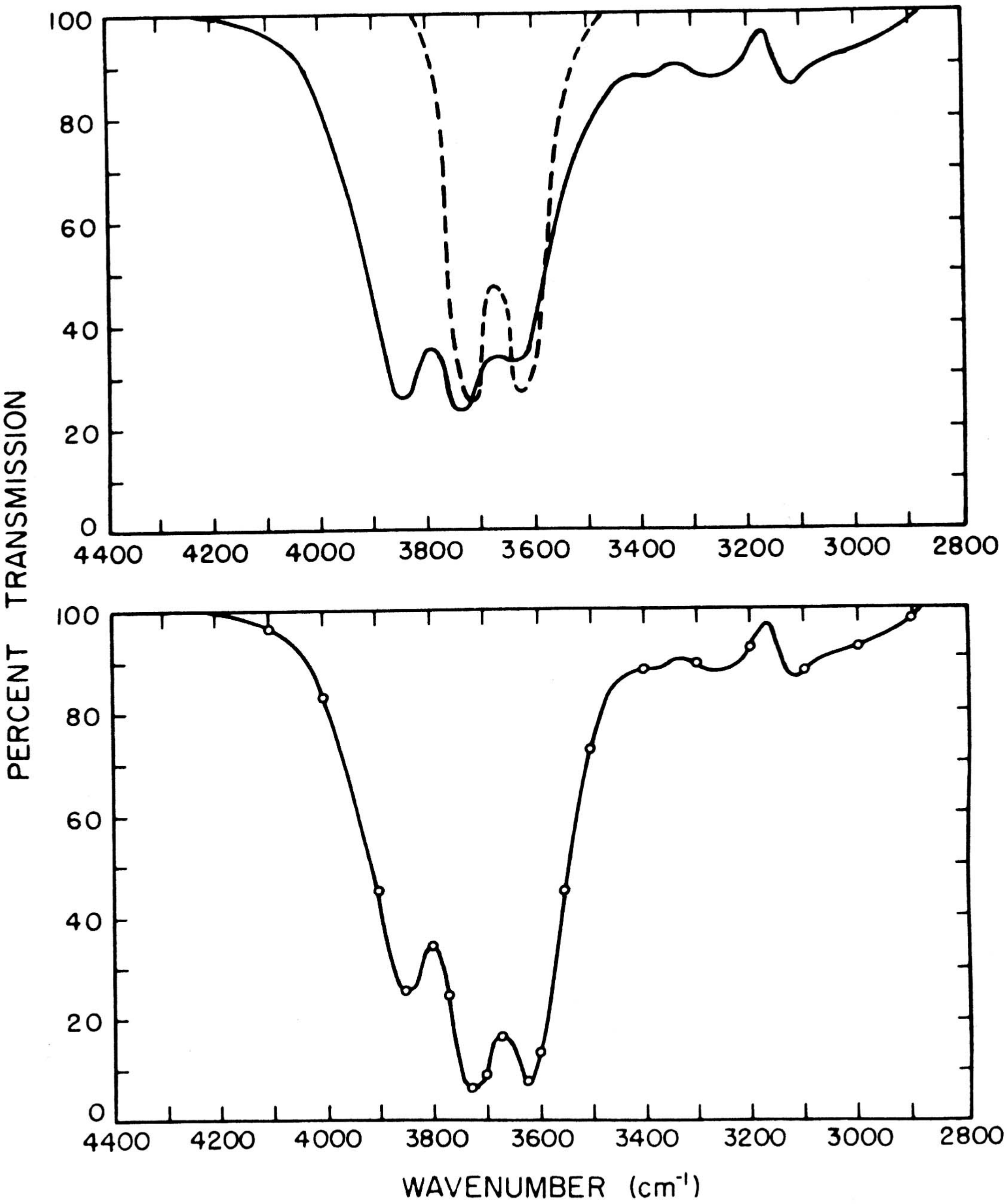


FIG. 4.1. The multiplication property of band transmission. The upper spectra are for CO_2 (broken line) and H_2O (solid line) individually. The lower spectrum is for the mixture; the solid line is observed and the points are obtained by multiplying together the two transmissions in the upper panel. The absorption path is 88 m, the H_2O partial pressure is 5 mm Hg, the CO_2 partial pressure is 4 mm Hg, and the total pressure is made up to 140 mm Hg with nitrogen. After Burch et al. (1956).

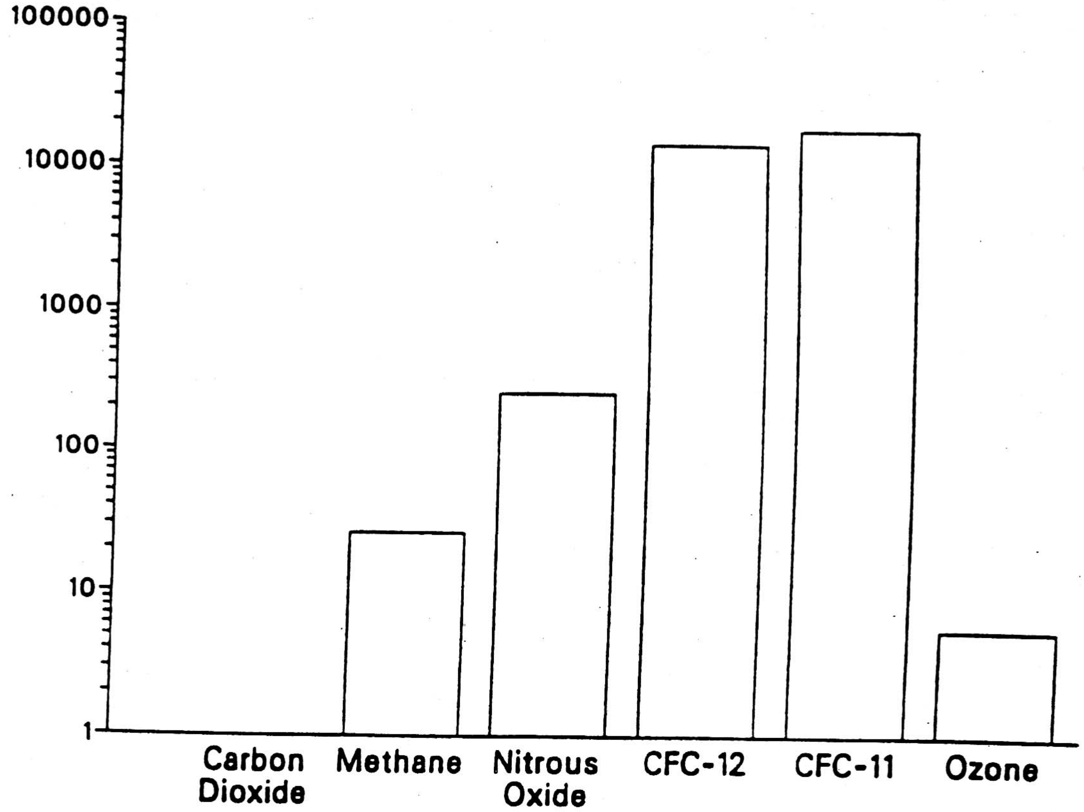
experimental evidence that bears this out. We shall, therefore, accept the multiplication property for two different arrays as a fundamental property of band transmission

IPCC 2007

120a

Table TS.2. *Lifetimes, radiative efficiencies and direct (except for CH_4) global warming potentials (GWP) relative to CO_2. {Table 2.14}*

Industrial Designation or Common Name (years)	Chemical Formula	Lifetime (years)	Radiative Efficiency (W m^{-2} ppb^{-1})	Global Warming Potential for Given Time Horizon			
				SAR‡ (100-yr)	20-yr	100-yr	500-yr
Carbon dioxide	CO_2	See below[a]	[b]$1.4\text{x}10^{-5}$	1	1	1	1
Methane[c]	CH_4	12[c]	$3.7\text{x}10^{-4}$	21	72	25	7.6
Nitrous oxide	N_2O	114	$3.03\text{x}10^{-3}$	310	289	298	153
Substances controlled by the Montreal Protocol							
CFC-11	CCl_3F	45	0.25	3,800	6,730	4,750	1,620
CFC-12	CCl_2F_2	100	0.32	8,100	11,000	10,900	5,200
CFC-13	$CClF_3$	640	0.25		10,800	14,400	16,400
CFC-113	CCl_2FCClF_2	85	0.3	4,800	6,540	6,130	2,700
CFC-114	$CClF_2CClF_2$	300	0.31		8,040	10,000	8,730
CFC-115	$CClF_2CF_3$	1,700	0.18		5,310	7,370	9,990
Halon-1301	$CBrF_3$	65	0.32	5,400	8,480	7,140	2,760
Halon-1211	$CBrClF_2$	16	0.3		4,750	1,890	575
Halon-2402	$CBrF_2CBrF_2$	20	0.33		3,680	1,640	503
Carbon tetrachloride	CCl_4	26	0.13	1,400	2,700	1,400	435
Methyl bromide	CH_3Br	0.7	0.01		17	5	1
Methyl chloroform	CH_3CCl_3	5	0.06		506	146	45
HCFC-22	$CHClF_2$	12	0.2	1,500	5,160	1,810	549
HCFC-123	$CHCl_2CF_3$	1.3	0.14	90	273	77	24
HCFC-124	$CHClFCF_3$	5.8	0.22	470	2,070	609	185
HCFC-141b	CH_3CCl_2F	9.3	0.14		2,250	725	220
HCFC-142b	CH_3CClF_2	17.9	0.2	1,800	5,490	2,310	705
HCFC-225ca	$CHCl_2CF_2CF_3$	1.9	0.2		429	122	37
HCFC-225cb	$CHClFCF_2CClF_2$	5.8	0.32		2,030	595	181
Hydrofluorocarbons							
HFC-23	CHF_3	270	0.19	11,700	12,000	14,800	12,200
HFC-32	CH_2F_2	4.9	0.11	650	2,330	675	205
HFC-125	CHF_2CF_3	29	0.23	2,800	6,350	3,500	1,100
HFC-134a	CH_2FCF_3	14	0.16	1,300	3,830	1,430	435
HFC-143a	CH_3CF_3	52	0.13	3,800	5,890	4,470	1,590
HFC-152a	CH_3CHF_2	1.4	0.09	140	437	124	38
HFC-227ea	CF_3CHFCF_3	34.2	0.26	2,900	5,310	3,220	1,040
HFC-236fa	$CF_3CH_2CF_3$	240	0.28	6,300	8,100	9,810	7,660
HFC-245fa	$CHF_2CH_2CF_3$	7.6	0.28		3,380	1030	314
HFC-365mfc	$CH_3CF_2CH_2CF_3$	8.6	0.21		2,520	794	241
HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$	15.9	0.4	1,300	4,140	1,640	500
Perfluorinated compounds							
Sulphur hexafluoride	SF_6	3,200	0.52	23,900	16,300	22,800	32,600
Nitrogen trifluoride	NF_3	740	0.21		12,300	17,200	20,700
PFC-14	CF_4	50,000	0.10	6,500	5,210	7,390	11,200
PFC-116	C_2F_6	10,000	0.26	9,200	8,630	12,200	18,200



Global-warming effect of greenhouse gases relative to CO_2

GOODY 1964

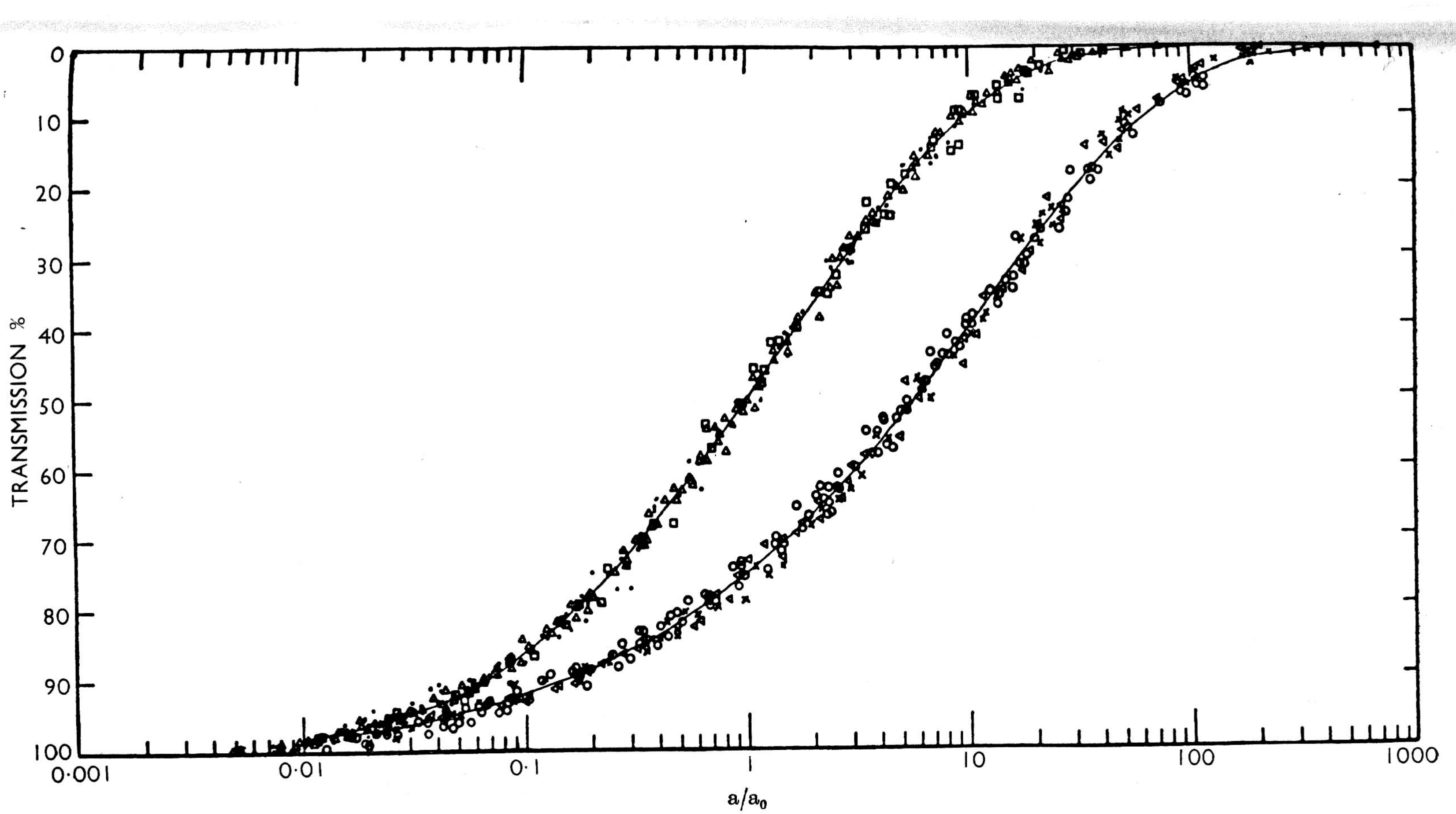


FIG. 4.14. Comparison between the random model (full line) and observation (points) for sections of the 6·3 μ, 2·7 μ, 1·87 μ, 1·38 μ, and 1·1 μ bands of water vapour.

The left-hand curve is for a pressure of 740 mm Hg and the right-hand curve is for 125 mm Hg of dilutant nitrogen. a_0 is the amount of matter giving a transmission of $\frac{1}{2}$ at a pressure of 740 mm Hg. After Howard, Burch, and Williams (1956).

	Symbols	
Band	740 *mm Hg*	125 *mm Hg*
6·3 μ	□	×
2·6 μ, 3·2 μ	△	▽
1·87 μ, 1·38 μ, 1·1 μ	●	○

WISCOMBE

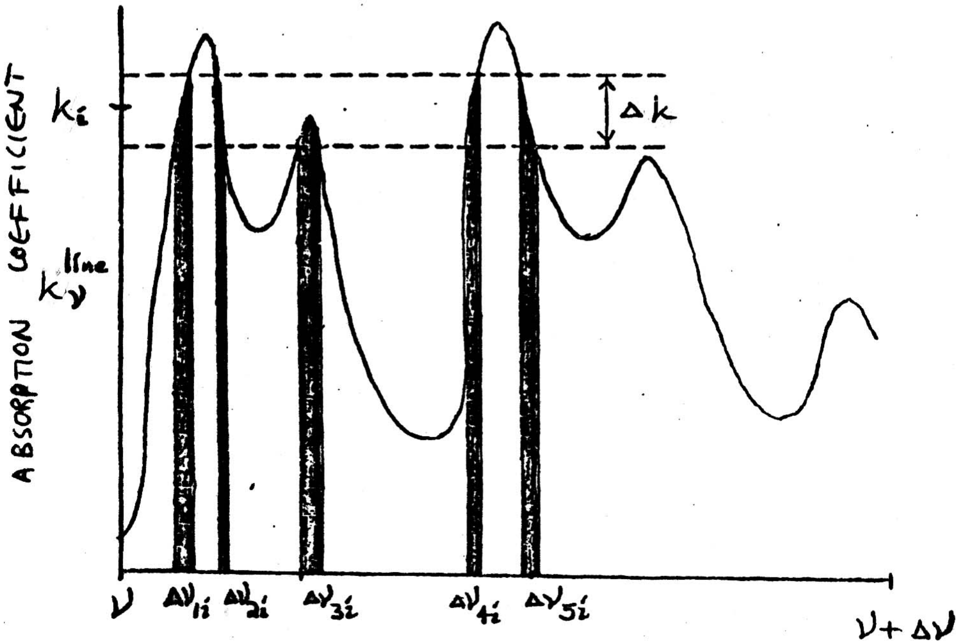


Figure 5. Schematic representation of line absorption coefficient in spectral interval ($\nu,\nu + \Delta\nu$), showing how ESFT method works.

WISCOMBE

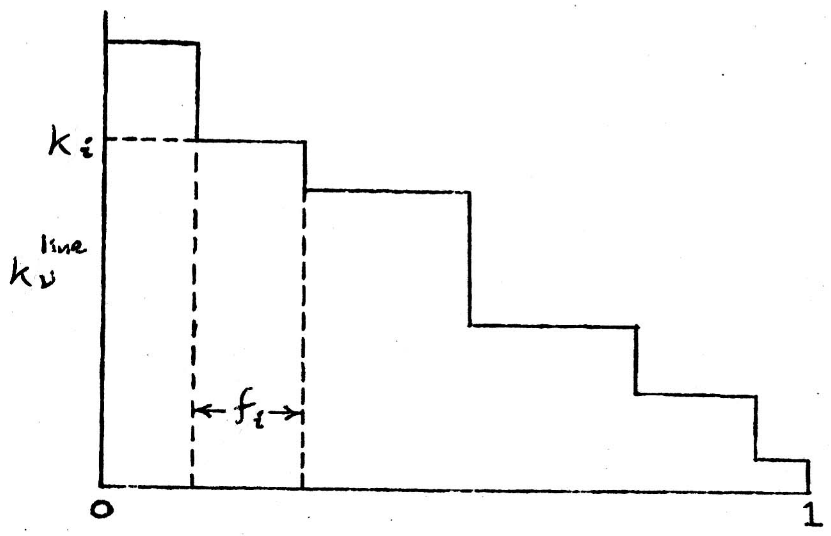


Figure 6. Rearrangement of line absorption coefficient of Figure 5 into histogram form. This is only approximate, but the accuracy of the representation increases if the number of steps is increased.

L10u

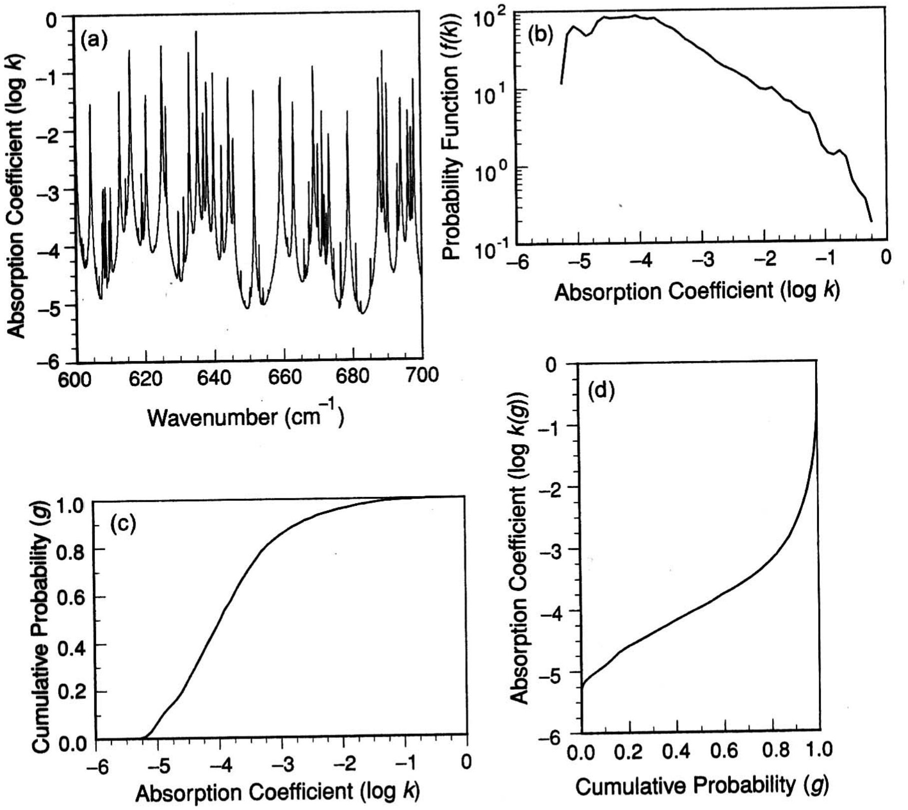


Figure 4.5 (a) Absorption coefficient k_ν in units of (cm atm)$^{-1}$ as a function of wavenumber with a resolution of 0.01 cm^{-1} in the H_2O rotational band with $p = 600$ mb and $T = 260$ K. (b) The probability function $f(k)$ of the absorption coefficient. (c) The cumulative probability function for $f(k)$ shown in (b), plotted as a function of k. (d) Same as (c), except that values of the absorption coefficient are expressed as a function of g.

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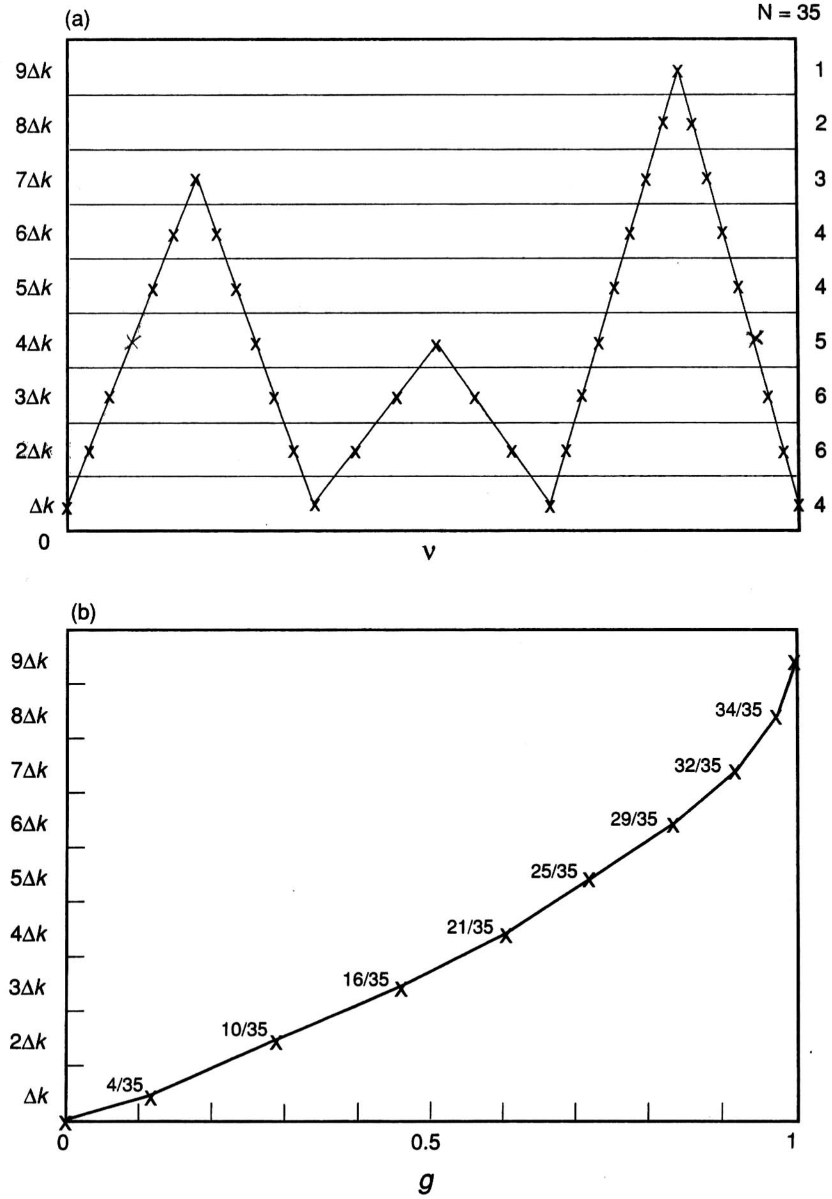

Figure 4.7 Illustration of the mapping of the absorption coefficient from the ν-domain to the g-domain. (a) Absorption coefficients of three lines in the ν-domain and division of the k-space into 10 equal intervals. The numbers are the data points in each interval with a total number of 35. (b) By definition, $g(j\Delta k) = n(0, j\Delta k)/N$, $j = 0, 1, \ldots, 9$. Thus, the data points in the ν-domain are transformed to the g-domain, where g is a monotonic increasing function.

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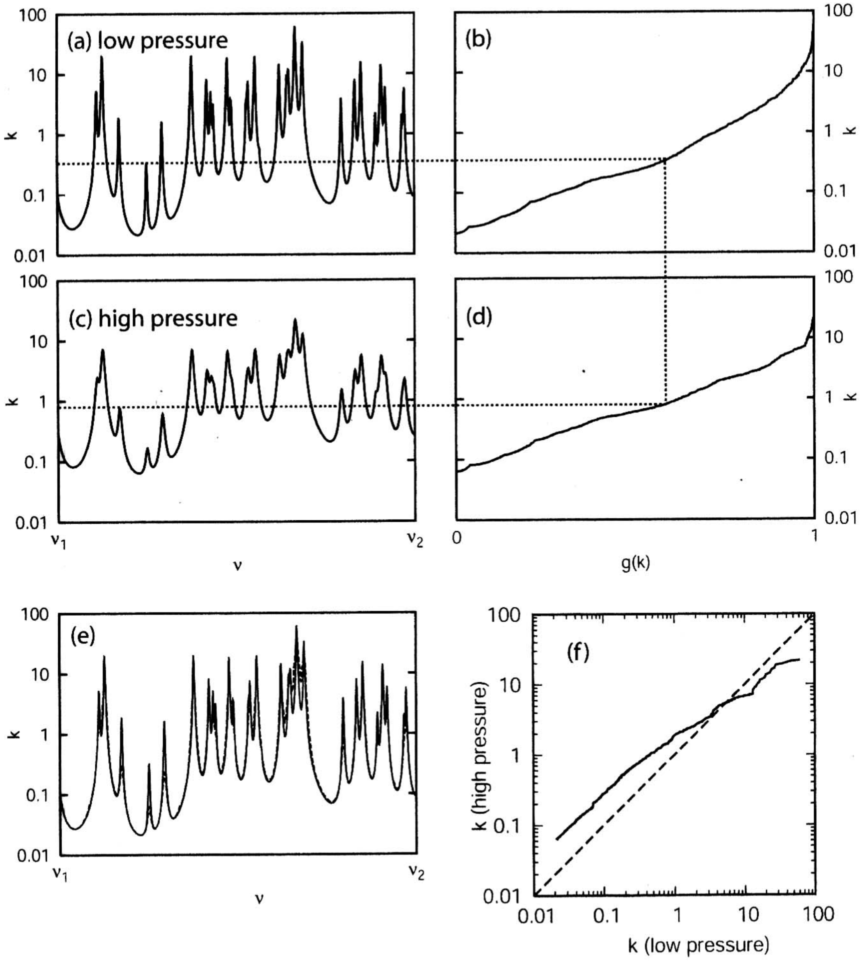

Fig. 10.5: Illustration of the k-distribution method and its extension, the correlated-k method. (a) A hypothetical spectrum of absorption coefficient k at relatively low pressure. (b) By sampling the spectrum at fine intervals and then sorting the results so that k increases monotonically, we define the function $0 \leq g(k) \leq 1$ (horizontal axis). Panels (c) and (d) are the same as (a) and (b) except with stronger pressure broadening. (e) Comparison of the actual spectrum for low pressure [from panel (a)] (solid curve) with one estimated from the spectrum at higher pressure [panel (c)] (dotted curve), using the mapping in panel (f). (f) The mapping between k values at the two pressure levels, based on equal values of g.

LIOU

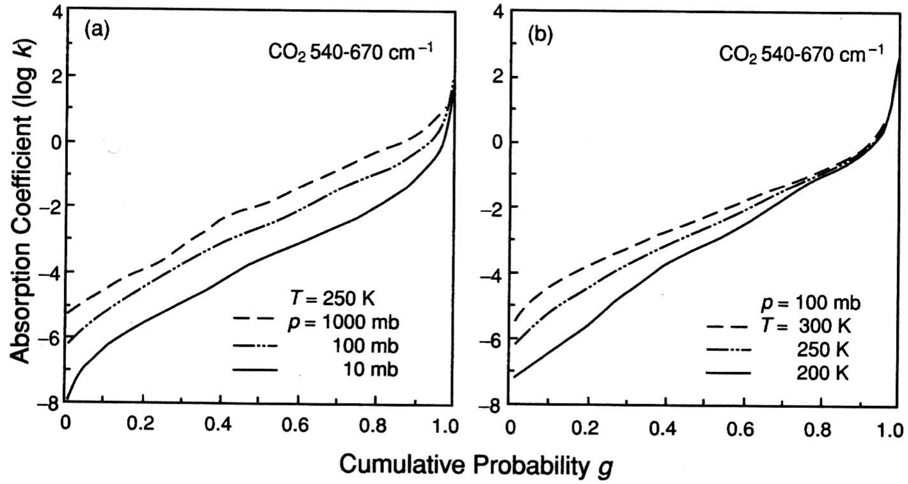

Figure 4.8 The absorption coefficient in (cm atm)$^{-1}$ as a function of the cumulative probability g for the CO_2 540–670 cm^{-1} spectral region (a) for a temperature of 250 K with three pressures and (b) for a pressure of 100 mb with three temperatures.

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GOODY & YUNG

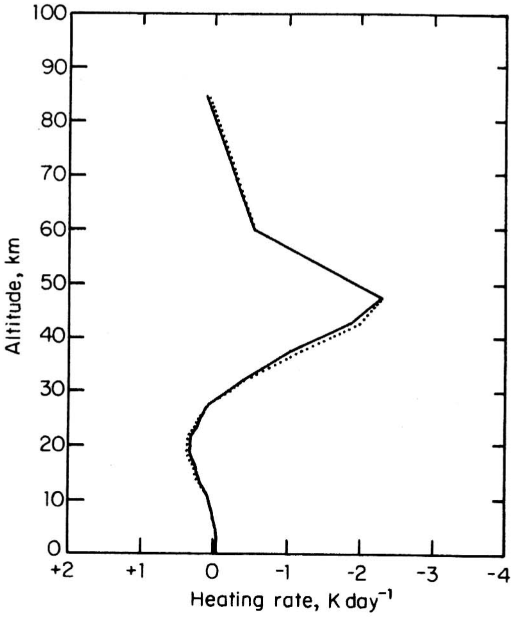

FIG. 6.7. Heating rates for ozone (975–1175 cm^{-1}). The solid line is the result of a line-by-line calculation. The dotted line uses the c-*k* method. After Lacis and Oinas (1986).

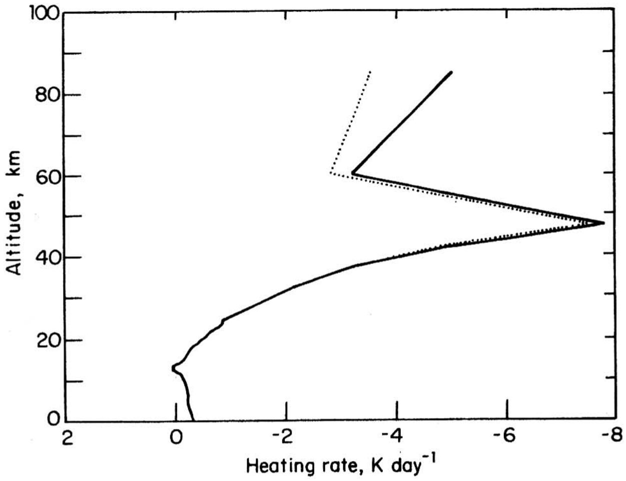

FIG. 6.8. Heating rates for carbon dioxide (500–1000 cm^{-1}). The solid line is the result of a line-by-line calculation. The dotted line uses the c-*k* method. Only one data point is used above 60 km. After Lacis and Oinas (1986).