Some helpful sources of information:

The first web site allows to display various spectra as well as provides a solar calculator you can use to verify your answers to homework assignments.

The second is an access to the Web of Science which allows to search research materials by author or topic. Useful for preparing your term paper. For UMD users, free download of articles.

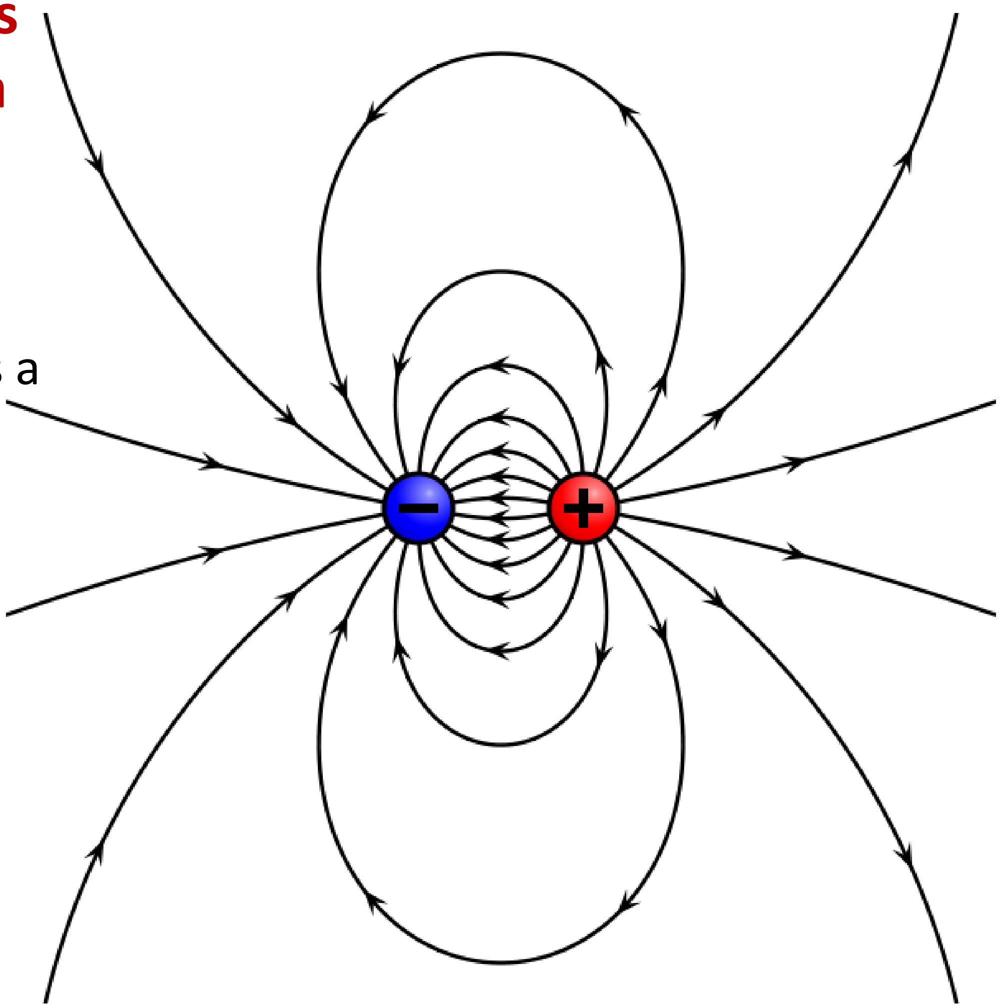
- http://www.spectralcalc.com/calc/spectralcalc.php
- http://apps.webofknowledge.com/UA_GeneralSearch_input.do?product=UA&search_mode=GeneralSearch&SID=1A9dMX2bGQ29DoDGxJc&preferencesSaved=

- Review of basic concepts identifies in last lecture as needing a refresher.
- Things to keep in mind if you use different textbooks on the topic of last lecture.

The presence of a dipole has implications for absorption/emission capabilities by a molecule.

What is a dipole?

An electric dipole is a separation of positive and negative charges. The simplest example of this is a pair of electric charges of equal magnitude but opposite sign, separated by some (usually small) distance.



If there is an excess of positive charge on one end of the molecule and an excess of negative charge on the other, the molecule has a dipole moment (i.e., a measurable tendency to rotate in an electric or magnetic field).The dipole moment (μ) is defined as the product of the magnitude of the charge, e, and the distance separating the charges.

Units used in different spectral regions

Note: Different units used for different spectral regions:

Spectra	Energy expressed as a function of
Visible	Wavelength λ
Infrared	Wave number $n = 1/\lambda$
Microwave	Frequency $\nu=1/t$, in GHz (since Hz is small)

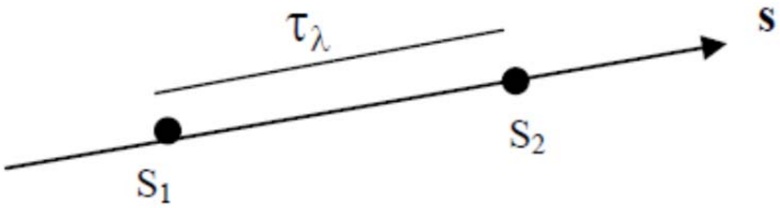
The **hertz** (symbol **Hz**) is a unit of frequency in the International System of Units (SI) and is defined as one cycle per second. It is named for Heinrich Rudolf Hertz, the first person to provide conclusive proof of the existence of electromagnetic waves.

Giga (G) denotes a factor of billion (10^9)

Keep in mind if using different textbooks:

Optical depth can be expressed in many ways:

$$\tau_\lambda(s_1;s_2) = \int_{s_1}^{s_2} \beta_{e,\lambda} ds = \int_{s_1}^{s_2} \rho k_{e,\lambda} ds = \int_{s_1}^{s_2} N\sigma_{e,\lambda} ds$$



What are the most accurate methods to model radiative transfer in the IR?

The method is known as a line-by line (LBL) approach. It accounts for all known gas absorption/emission lines in the wavenumber range of 0 to about 23,000 cm^{-1}.

The Fast Atmospheric Signature Code (FASTCODE) is the benchmark for testing simplified models both in the visible and IR part of the spectrum.

Need to keep in mind that atmospheric pressure affects absorption of gases (pressure broadening) which poses a difficult problem in computing the transfer of IR radiation in an atmosphere with changing pressure, temperature and concentration of gases.

High-resolution TRANsmission Spectroscopic database HITRAN of molecular absorption

http://cfa-www.harvard.edu/hitran//

A project started by the Air Force Cambridge Research Laboratories (AFCRL) in the late 60's to provide detailed information on IR properties of the atmosphere.

Version 13.0 of the database contains 2,713,968 spectral lines for 39 different molecules. Provided is also information on UV line by line absorption cross section parameters, and aerosol indices of refraction.

Supplementary information on the still unsolved issue of what is known as the “Water Vapor Continuum” can be found at:

http://www.met.reading.ac.uk/caviar/water_continuum.html

For convenience, it is reproduced at the end of this lecture labeled as “Supplements”.

AOSC400-2015
October 22, Lecture # 14

Absorption and Emission by Gas Molecules

- The Schwarzchild's equation revisited
- Heating of atmosphere in IR
- Remote Sensing applications - *start discussion*
- ❖ Supplements- more details on the Water Vapor Continuum issue.

*Sources of information used for this lecture are listed in updated Syllabus.

Allowing both extinction and emission of radiation over a path S leads to the Schwarzchild's equation:

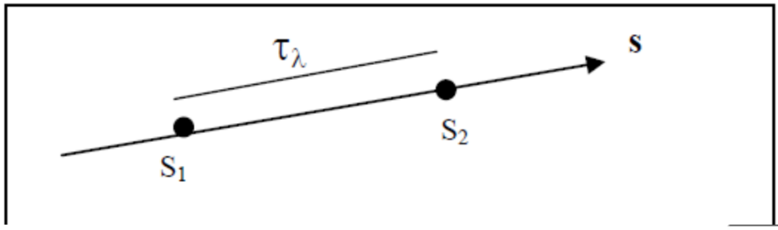
$$-\frac{dI_\lambda}{d\tau_\lambda} = -I_\lambda + J_\lambda$$

or as

$$\frac{dI_\lambda}{d\tau_\lambda} = I_\lambda - J_\lambda \qquad (1)$$

Where:

$$\tau_\lambda(s_2;s_1) = \int_{s_1}^{s_2} \beta_{e,\lambda}(s)ds$$



After several manipulations of this equation, we get:

$$I_\lambda(s_1) = I_\lambda(0)\exp(-\tau_\lambda(s_1;0)) + \int_0^{s_1} \exp(-\tau_\lambda(s_1;s))J_\lambda \beta_{e,\lambda} ds \qquad (2)$$

Guidelines will be provided in homework # 3 how to get to (2) from (1).

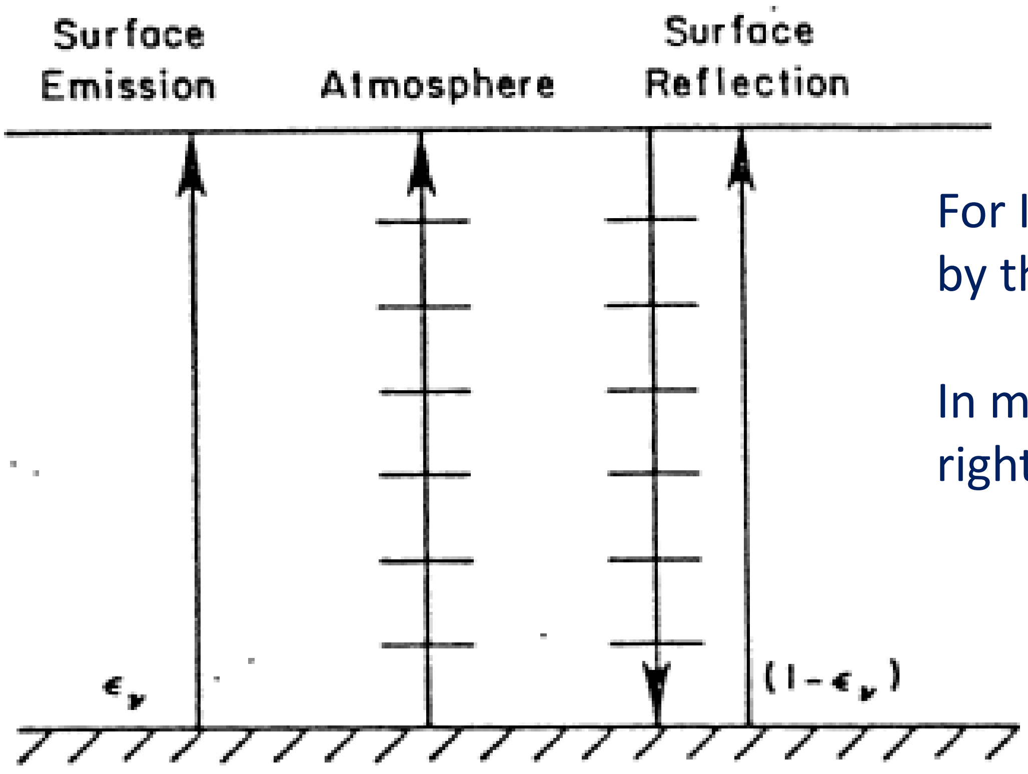
Simple interpretation of eq. (2):

Imagine that you apply the equation to a case that represents emission from the surface to the Top of the Atmosphere (TOA).

The emitted radiation $I_\lambda (s_1)$ at the TOA equals the emission from the surface attenuated over the entire path from the surface to the top of the atmosphere (first term) plus the emission from each layer attenuated by the atmosphere only above that layer.

Schematically, shown in following slide:

Contribution of each term to the emitted energy at the top or the atmosphere



For IR radiation, only the cases represented by the first 3 arrows are relevant.

In microwave, the fourth arrow on the right is important (to be discussed later.

In the textbook, the source function J_λ which gives the intensity of the emitted radiation is replaced by the blackbody emission function $B_\lambda(T)$, yielding :

$$dI_\lambda(\text{emission}) = B_\lambda(T)\varepsilon_\lambda$$

We obtain the Schwarzchild's equation as given in textbook:

$$dI_\lambda = -(I_\lambda - B_\lambda(T))k_\lambda \rho r ds \qquad (4.41)$$

or:

$$I_\lambda(s_1) = I_{\lambda 0}e^{-\tau_\lambda(s_1,\,0)} + \int_0^{s_1} k_\lambda \rho r B_\lambda[T(s)]e^{-\tau_\lambda(s_1,\,s)}ds \qquad (4.42)$$

Which is the same as eq. (2) on slide 17

$$\boxed{I_\lambda(s_1) = I_\lambda(0)\exp(-\tau_\lambda(s_1;0)) + \int_0^{s_1} \exp(-\tau_\lambda(s_1;s))J_\lambda \beta_{e,\lambda} ds}$$

The plane parallel approximation

Many atmospheric radiative transfer calculations can be simplified by using the *plane-parallel approximation* in which temperature and the densities of the various atmospheric constituents are assumed to be functions of height (or pressure) only.

Applying boundary conditions to eq. (2) at the TOA and at the surface and integrating I_λ over all wavelength and azimuthaly (in all directions) will yield the total flux at the two boundaries $F\uparrow$ and $F\downarrow$

(the detailed derivation will be skipped).

So the total net flux at a given height is given by:

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

Denoting the net flux $F(z + \Delta z)$ at the level $z + \Delta z$, the net flux divergence for the layer Δz is:

$$\Delta F = F\ (z + \Delta z) - F(z)$$

Heating Rates *(namely, radiative flux divergence)*

$$\rho c_p \frac{dT}{dt} = -\frac{dF(z)}{dz} \qquad (4.52)$$

where $F = F\uparrow - F\downarrow$

is the net flux and ρ is the total density of air.

The radiative heating or cooling rate is defined as the rate of temperature change of the layer dz due to radiative energy gain or loss, given as:

$$\boxed{\left(\frac{dT}{dt}\right) = -\frac{1}{c_p \rho}\frac{dF_{net}}{dz} = \frac{g}{c_p}\frac{dF_{net}}{dp}} \qquad (3)$$

c_p is the specific heat at constant pressure
(c_p = 1004.67 J/kg/K and ρ is the air density in a given layer.

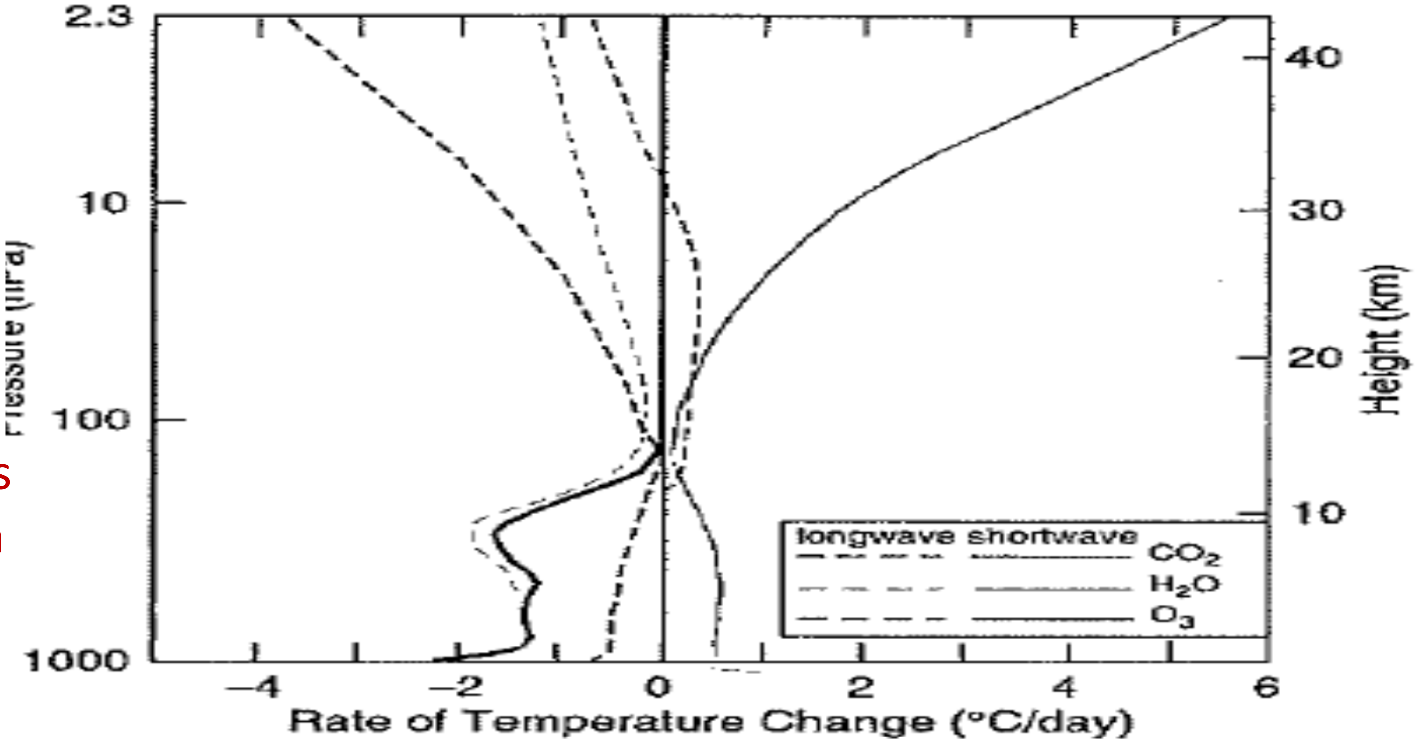
To evaluate the heating rate in equation (3), one needs:

1. Profile of IR upwelling and downwelling fluxes

To compute the IR downward and upward fluxes, one needs:

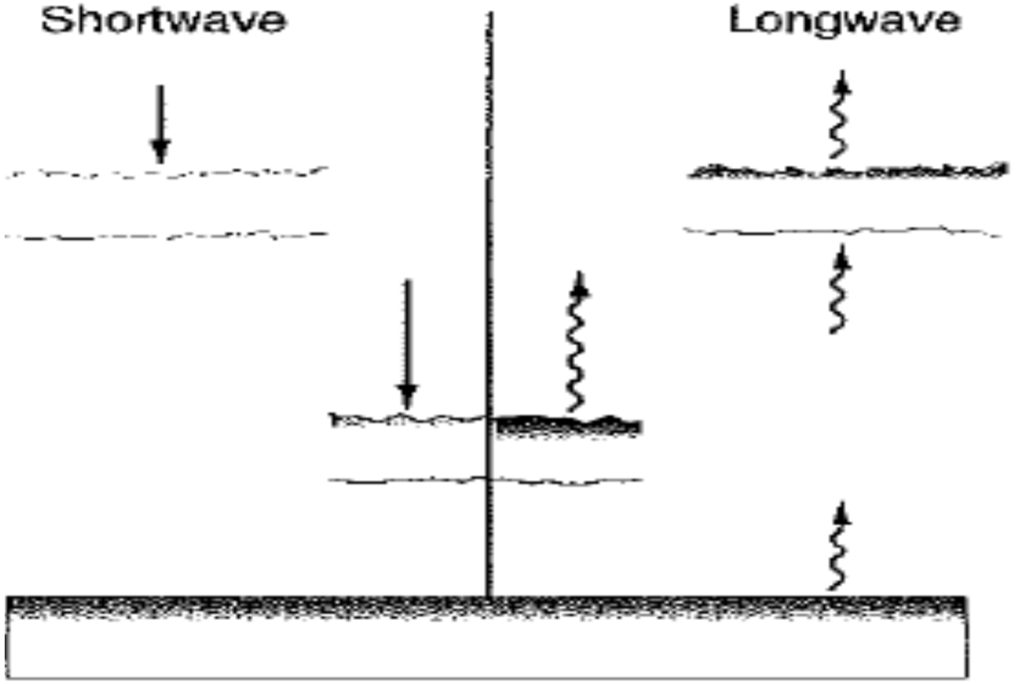
1. Atmospheric characteristics such as vertical profiles of T, P and density
2. The vertical profiles of IR radiatively active gases, clouds and aerosols

Heating rates by various
constituents as given in
Textbook
(both SW and LW
heatings
are illustrated)



ig. 4.29 Vertical profiles of the time rate of change of
emperature due to the absorption of solar radiation (solid
urves) and the transfer of infrared radiation (dashed
urves) by water vapor (blue), carbon dioxide (black), and
zone (red). The heavy black solid curve represents the com-
ined effects of the three gases. [Adapted from S. Manabe
nd R. F. Strickler, *J. Atmos. Sci.*, 21, p. 373 (1964).]

When clouds are present, the computations are more complicated.

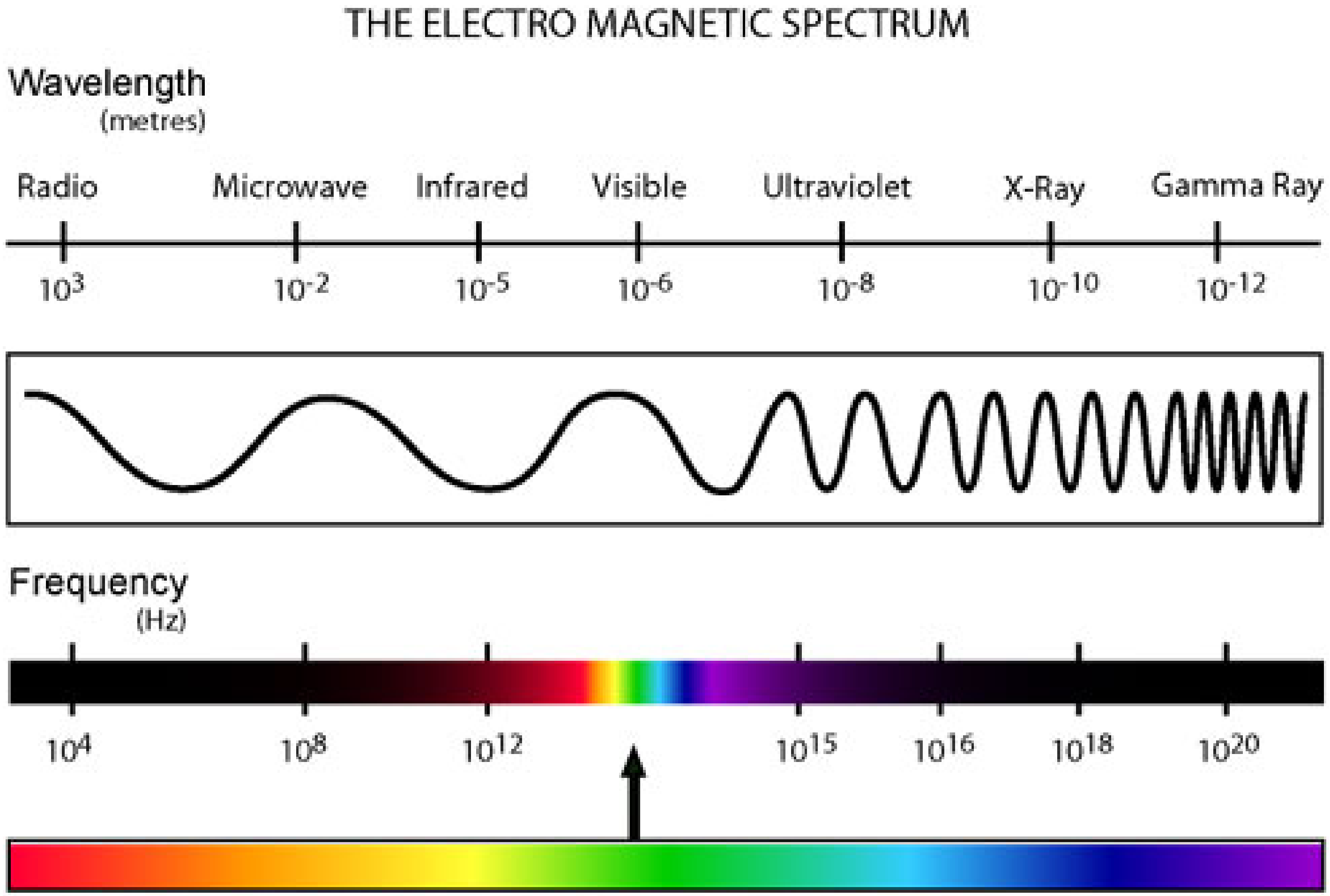


Schematic of vertical profiles of heating in cloud
arious heights in the atmosphere as indicated.
ding indicates warming and blue shading indicates
ects of shortwave radiation are represented on the
ects of longwave radiation on the right.

Passive Remote Sensing by Satellites

Monitoring of radiation emitted by and reflected from the Earth system by satellite-borne radiometers provides information on weather and climate. Fields that are currently routinely monitored from space include: temperature, cloud cover, cloud droplet concentrations and sizes, rainfall rates, humidity, radiative fluxes, surface wind speed and direction, **concentrations of trace constituents and aerosols,** and lightning. Discussed will be just a few of the many applications of remote sensing in **atmospheric science.**

Remember: units in microwave are HZ of GHz:

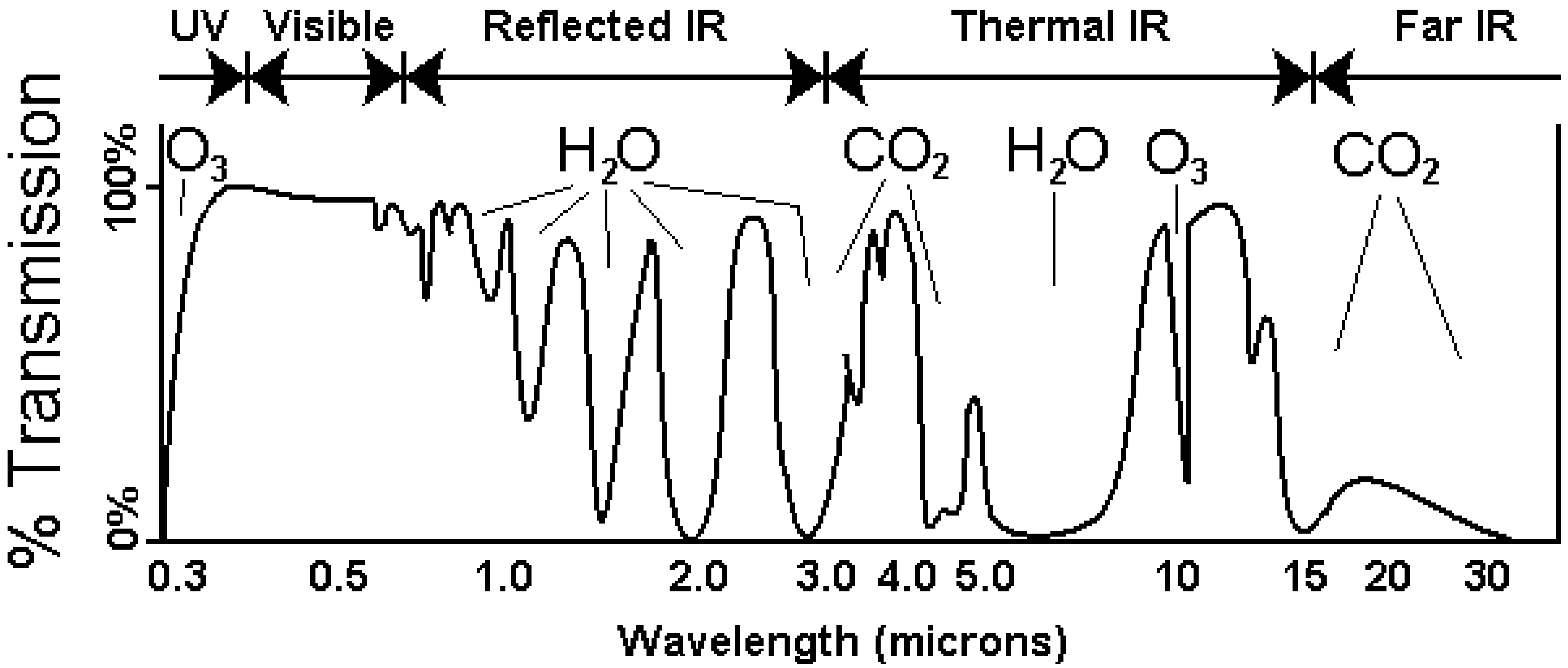


Spectral Intervals in (VIS, IR, MW) of interest in Remote Sensing

Several spectral regions are considered useful for remote sensing from satellites.

Windows to the atmosphere (regions of minimal atmospheric absorption) exist near 4 µm, 10 µm, 0.3 cm, and 1 cm *(see next slide)*.

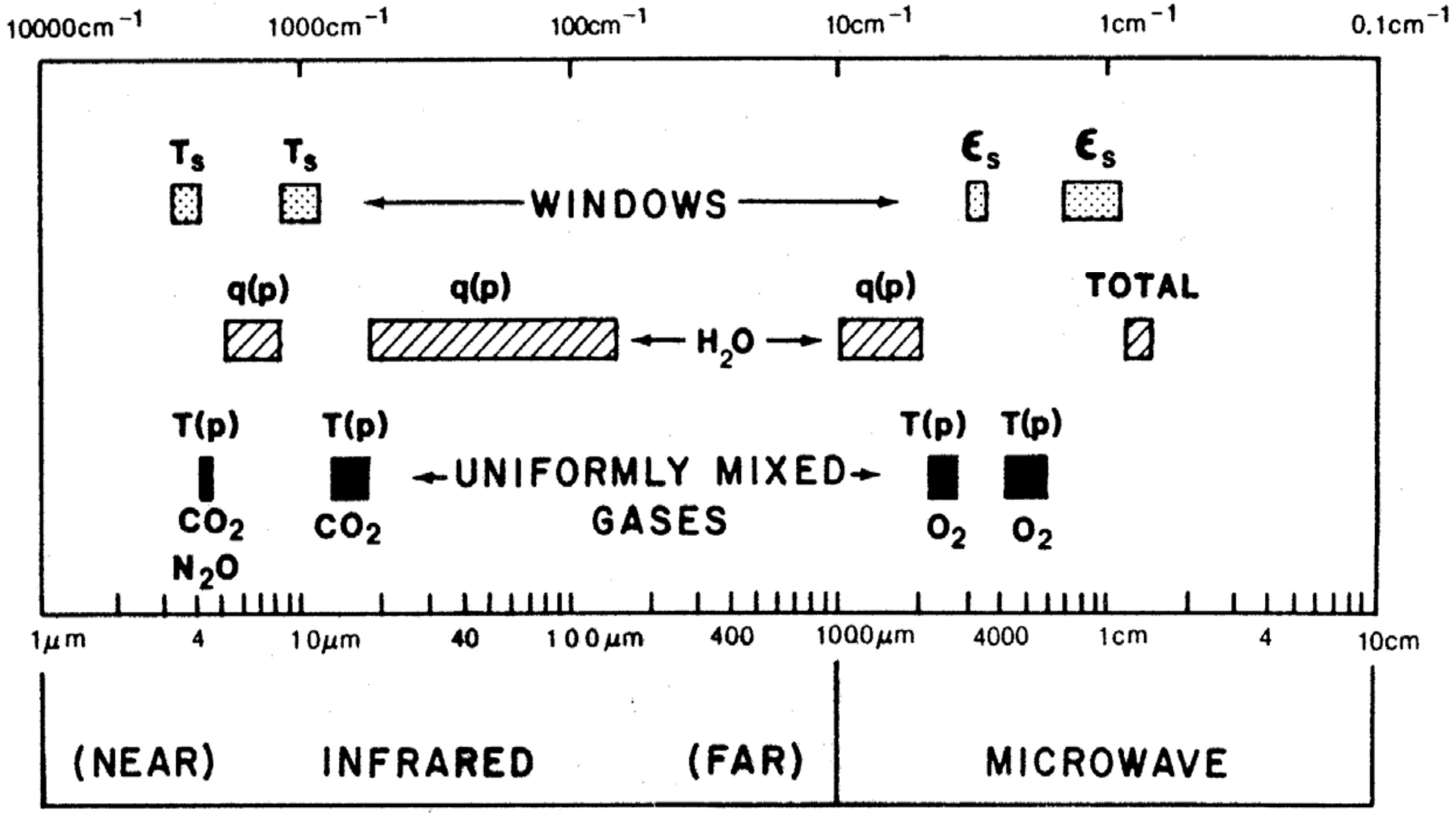
Infrared windows are used for sensing the temperature of the earth surface and clouds, while microwave windows help to investigate the surface emissivity and the liquid water content of clouds.



High transmission means low absorption. There is significant transmission of radiation at 0.5 microns, 2.5 microns, and 3.5 microns, but a great deal of atmospheric absorption at 2.0, 3.0, and about 7.0 microns.

The CO_2 and O_2 absorption bands at 4.3 μm, 15 μm, 0.25 cm, and 0.5 cm are used for temperature profile retrieval; because these gases are uniformly mixed in the atmosphere in known portions they lend themselves to this application. The water vapor absorption bands near 6.3 μm, beyond 18 μm, near 0.2 cm, and near 1.3 cm are sensitive to the water vapor concentration in the atmosphere.

Spectral regions used for remote sensing of the earth atmosphere and surface from satellites. ε indicates emissivity, q denotes water vapor, and T represents temperature.



Supplement on Water vapour continuum

From:

http://www.met.reading.ac.uk/caviar/water_continuum.html

British use vapour for vapor.

Water vapour continuum

In addition to the spectral lines, it has long been recognized that water vapour possesses a continuum absorption which varies relatively slowly with wavelength and pervades the entire IR and microwave spectral region. This has a marked impact on the Earth's radiation balance with consequences for understanding present day weather and climate and predicting climate change. It is also important for remote sensing of the Earth and its atmosphere.

Discovered by Hettner (1918) as a low-frequency component of water vapour absorption in atmospheric transparency window 8-14 mcr, this phenomenon remained unexplained for 20 years, until Elsasser (1938) suggested that the continuum is an accumulated far-wing contribution of strong water vapour spectral lines from neighbour bands. This hypothesis was generally accepted until the end of 70th years when the strong quadratic pressure dependence of the continuum absorption (which could not be explained by Lorentz (1906) line profile) as well as the strong negative temperature dependence have been detected (Bignell et al.,1963; Penner and Varanasi,1967). In this connection Penner and Varanasi (1967) and Varanasi et al. (1968) suggested that the main contribution to the self-continuum could be caused not by far wings of water monomer lines but rather by water dimers. Similar assumption was made also by Viktorova and Zhevakin (1967) for microwave spectral region.

The dimer model have explained quite easily the pressure and temperature dependencies of the self-continuum absorption observed since then in many experiments (Mc Coy et al. 1969; Bignell, 1970; Burch, 1970; etc.). Since that time a long scientific discussion has started between adherents of the "monomer" (or "far-wings") and the "dimer" nature of the water vapour self-continuum, which is continuing up to the current time.

On the one hand, more sophisticated (than Lorentz theory) ab-initio (Tvorogov et al. 1994; Ma and Tipping 1999, 2002; etc.) and semi-empirical (Clough et al. 1989, 1995, etc; Mlawer et al. 1999; etc.) line shape models have been developed, which could explain quite well the experimental facts mentioned above, and due to which the dominating role of the far wings of water vapour lines in the continuum absorption, especially in atmospheric conditions, is most commonly accepted today.

On the other hand, water dimers have been and are being often discussed as a possible component of the water self-continuum absorption (Lowder, 1971; Penner, 1973; Roberts et al. 1976; Arefev and Dianov-Klokov 1977; Montgomery, 1978; Dianov-Klokov et al. 1981; Varanasi, 1988; Devir et al. 1994; Vigasin et al. 1989, 2000; Cormier et al. 2005, etc.).

Finally, collision-induced absorption, resulting from the generation of a short-lived complex of water vapour and colliding molecules, has been proposed as a dominant within water vapour bands in the recent MT_CKD continuum model (Mlawer et al., in preparation, http://rtweb.aer.com/continuum_frame.html).

The possibility of both collision-induced and water dimer marked contribution to the water continuum absorption is however highly disagreed by Tipping (personal communication; Brown and Tipping, 2003). This point of view is shared by Vigasin only in respect to the free pair states, which negligible role as compared to the metastable or true bound water dimers at near-room temperatures has been shown by Vigasin (1991) and by Epifanov and Vigasin (1997) on the basis of preliminary statistical partitioning of the pair states in water vapour.

Thus, **a deep controversy** on the nature of the **water vapour continuum** still remains unresolved. The atmospheric science community has largely sidestepped this controversy, and has adopted a pragmatic approach. Most radiative transfer codes used in climate modelling, numerical weather prediction and remote sensing use a semi-empirical formulation of the continuum - CKD-model (Clough et al. 1989). This formulation was tuned to available (mostly laboratory) observations in rather limited (far-infrared) spectral regions.

The CKD model has served the community extremely well but we lack confidence that its semi-empirical formulation works at wavelength, or in atmospheric conditions, away from those in which it has been tested. This lack of confidence is exacerbated by the recent up-to-date theoretical (Schofield and Kjaergaard, 2003; Daniel et al. 2004; Scribano et al. 2006) and experimental (Vigasin et al. 2000, 2005; Ptashnik et al. 2004, 2005, 2006; Cormier et al. 2005; Paynter et al. 2007) studies that very well correlate and supplement each other, indicating all together the marked water dimer contribution to the water vapour self-continuum in some spectral regions.