AT622 Section 10 The Atmospheric Absorption Spectrum

The aim of this section is introduce the characteristics of the atmospheric absorption spectrum as summarized in Fig. 10.1.



Fig. 10.1 (a) The broad characteristics of the atmospheric absorption spectrum. (b)The spectrum of solar flux between the ultraviolet and infrared with molecular absorption features indicated.

10.1 Visible - UV

Atmospheric absorption calculations in the visible and UV spectrum are commonly done on the basis of empirical data and at a level without requiring the degree of understanding applied to vibration-rotation

bands. Figure 10.2 shows the absorption by O_2 and O_3 by electronic transitions. It doesn't show the near UV Huggins bands of the visible Chappuis bands of O_3 . Both of these electronic bands are of some importance to solar absorption but the absorption is weak.



Fig. 10.2 Depth of penetration, defined as altitude at which $\tau = 1$ of solar radiation in the ultraviolet spectrum as a function of wavelength. The line shows the altitude of unit optical depth. The vertical arrows indicate ionization limits. The broken line represents predissociation for molecular oxygen. After Herzberg (1965).

10.2 The Near IR

The predominant absorption of near infrared wavelengths (0.7-4.0 μ m) is by several vibrational-rotational H₂O absorption bands. CO₂ also contributes to near IR absorption by bands centered at 2.7 and 2.0 μ m and weak bands at 1.6 and 1.4 μ m. These features appear in Fig. 10.1b.

10.3 The Far IR

Again the most dominant absorption in the far IR is that of water vapor. Figure 10.3 shows the H₂O absorption spectra based on use of a theoretical line shape. Superimposed on this absorption is the absorption centered at 15 μ m and at 4.4 μ m by CO₂ and weaker bands at 10 and 5 μ m. Ozone has a strong vibration-rotation band centered at 10.6 μ m and a weaker band at 14 μ m.

10.4 'Greenhouse Gases'

A variety of trace gases absorb in the far infrared and may be considered as greenhouse gases (e.g., CH4, ... etc.) and the prevalence of the absorption by these gases is highlighted in Fig. 10.4.



Fig. 10.3 Theoretical absorption coefficients of pure water vapor at 1 bar and 296 K. The vertical axis is the molecular absorption coefficient divided by a "radiation term", $f(v/c) = (v/c) \tanh(hv/2k\theta)$, which is approximately equal to v/c (the frequency in wave numbers) for v/c > 500 cm⁻¹. After Clough et al. (1980).



Fig. 10.4 Some general properties of absorption by greenhouse gases.

Molecule	Lifetime	Concentration	Spectral Range	Band Strength
	(years)	(ppbv)	(cm^{-1})	$(cm^{-2}atm^{-1})$ at 296K
CO ₂	2	3.39×10^3	550-800	220
O ₃	0.1-0.3	variable	950-1200	312
N_2O	120	300	1200-1350	218
CH ₄	5-10	1650	950-1650	134
$CFCl_3(CFC11)$	65	0.18	800-900	1828
$CF_2Cl_2(CFC12)$	110	0.28	875-950	1446
CF ₃ Cl (CFC13)	400	0.007	1075-1125	1758

10.5 Water Vapor Continuum Absorption

An especially important form of absorption for atmospheric problems is the more or less continuous absorption in regions where line absorption is weak. The continuum occurs at all frequencies (Fig. 10.3) but is most important in window regions in which continuum absorption exceeds line absorption.

The absorption in these windows has special properties such that

$$k_{\nu} = k_1 p + k_2 e$$

where p = atmospheric pressure, e = water vapor partial pressure, and $k_2 > k_1$. Thus,

$$k_{\nu} \sim k_2 e$$
$$\tau_{\nu} \sim \int k_2 e du$$

This is called "e-type" absorption. The mechanism for this absorption is not decisively known at this time.

Mechanism?

• Overlapping foreign broadened lines, but

$$k_{\nu} \sim \frac{S\alpha_L^f / T}{\left(\nu - \nu_a\right)^2} \sim k_2 e$$

in wings. This was the historical explanation. It was discovered however that continuum absorption was much stronger than this (especially in the tropics)

• Overlapping self broadened lines (water-water collisions)?

$$k_{\nu} \sim \frac{S \alpha_L^s / \pi}{\left(\nu - \nu_o\right)^2} \sim k_2 e$$

since α_L^s proportional to *e*.

• Dimer absorption?

Temperature variation is the reverse of line absorption and has the approximate form

$$\Phi(T) = \exp(1800/T)$$

Roberts provides a parameterization of k_{ν} such that

$$k_{v}(p,T) = \frac{\Phi(T)}{\Phi(T_{o})} \Psi(v,T_{o})e$$

where

$$\Psi = 4.18 + 5578 \exp(-0.00787\nu)g^{-1} \text{ cm}^{-2}$$

for $T_o = 296$ K with v in crn⁻¹.



Fig. 10.5 Absorption coefficients for water-water collisions in the 1000 cm⁻¹ window. n_s is Loschmidt's number.