## PHY392S Physics of Climate

## Lectures 15 and 16

# Interaction of the radiation field with gases in the atmosphere

Types of transitions in the internal energy of the molecules

- Rotational
- Vibrational
- Electronic
- photodissociation

Order of increasing energy



## Interaction of the Radiation Field with Gases in the Atmosphere

- Solar interactions
  - Photoionization: extreme UV strips electrons from atoms
  - Photodissociation:
    UV breaks apart
    molecules
  - Electronic
- Thermal IR interactions
  - Electronic
  - Vibration
  - Rotation



Born-Oppenheimer Approx: Energy of a gas molecule  $E = E_{elec} + E_{vib} + E_{rot} + E_{trans}$ 

## **Absorption in Earth's Atmosphere**

- Earth's atmosphere mainly  $N_2$  and  $O_2$ .
- These two molecules are spectrally "dull"!
  - Have only photoionization, photodissociation, and atomic-like lines.
  - All of these are at high energies that involve interaction with short-wave UV radiation to produce atomic oxygen, ozone, and atomic nitrogen which in turn interact with UV.
- The two O or N nuclei can only move towards and away from each other during vibration.
  - They have one vibrational mode due to the symmetrical charge distribution, and so lack a permanent dipole moment.
  - As a result, they have little radiative activity in the visible and IR.

## **Potential Energy Curves for O<sub>2</sub>**



FIGURE 4.1 Potential energy curves for ground and first four excited states of  $O_2$ . S-R = Schumann-Runge system, H = Herzberg continuum, A-A = atmospheric bands (adapted from Gaydon, 1968).

#### B. J. Finlayson-Pitts, 2000.

### O<sub>2</sub> and O<sub>3</sub> Absorption Cross Section

10<sup>-17</sup> cm<sup>2</sup> is very strong absorption 10<sup>-16</sup> SECTION (10<sup>17</sup> cm<sup>2</sup>) 10<sup>-17</sup> SCHUMANN-RUNGE CONTINUUM OZONE 10 (cm<sup>2</sup>) 10<sup>-18</sup> (cm<sup>2</sup>) 10<sup>-19</sup> (cm<sup>2</sup>) 10<sup>-20</sup> (cm<sup>2</sup>) 10<sup>-18</sup>' IONIZATION CONTINUUM Hartley 0,8 bands 10-201 CROSS SCHUMANN-RUNGE BANDS 0,6 CROSS LYMAN a 10-21 ABSORPTION NOILduosan 10-22 0.4 10-231 02 0,2 HERZBERG CONTINUUM 0 260 10-25 220 240 280 300 200 50 100 150 200 250 WAVELENGTH(nm) WAVELENGTH (nm) 10<sup>-20</sup> ABSORPTION CROSS SECTION (cm<sup>2</sup>) OZONE OZONE CHAPPUIS BANDS HUGGINS BANDS SECTION (cm<sup>2</sup>) ABSORPTION CROSS **VIGROUX (1953)** UPPER CURVE 291 K LOWER CURVE 198 K -- INTERPOLATION 10-2 310 320 330 WAVELENGTH (nm) 10-2 500 600 700 800 900 WAVELENGTH (nm)

[From Brasseur and Solomon, 1986]

## Absorption by O<sub>2</sub> and O<sub>3</sub>



### **Spectrum of Solar Radiation vs. Altitude**



Fig. 10-2 Solar actinic flux at different altitudes, for typical atmospheric conditions and a 30° solar zenith angle. From DeMore, W. B., et al. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*. JPL Publication 97-4. Pasadena, Calif.: Jet Propulsion Lab, 1997.

### **Absorption of Solar Radiation**



FIGURE 14.1 Solar flux outside the atmosphere and at sea level, respectively. The emission of a blackbody at 6000 K is also shown for comparison. The species responsible for light absorption in the various regions ( $O_3$ ,  $H_2O$ , etc.) are also shown (adapted from Howard *et al.*, 1960).

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## **Solar Absorption – A Summary**

Interactions between solar radiation and the atmosphere:

- Photoionization and photodissociation in the upper atmosphere
- Atmospheric scattering
- Absorption in the lower atmosphere
  - In the ultraviolet, where ozone strongly absorbs
  - At the red end of the solar spectrum, primarily due to absorption by water which is concentrated in the troposphere
  - Absorption in the infrared by greenhouse gases

## **Infrared Absorption in Earth's Atmosphere**

- Earth's atmosphere also contains CO<sub>2</sub>, N<sub>2</sub>O, which are triatomic molecules having a linear symmetrical configuration.
- These molecules do have IR spectra.



See animation at http://chemmac1.usc.edu/bruno/java/Vibrate.html

## **Greenhouse Gases (GHGs)**

Greenhouse gases = gases with vib-rot absorption features at 5-50  $\mu$ m VIBRATIONAL MODES OF CO<sub>2</sub>



- Major greenhouse gases: H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, O<sub>3</sub>, N<sub>2</sub>O, CFCs,...
- <u>Not</u> greenhouse gases: N<sub>2</sub>, O<sub>2</sub>, Ar, ...

## **Greenhouse Gases**

## • Water vapour (H<sub>2</sub>O)

- most common greenhouse gas
- increases as surface temperature rises
- Carbon dioxide (CO<sub>2</sub>)
  - released by plant and animal life, decay, and burning of fuels
  - removed by plant photosynthesis and absorption by the oceans
- Methane (CH<sub>4</sub>)
  - not as common in volume as  $H_2O$  or  $CO_2$
  - very effective at trapping heat powerful greenhouse gas
  - wetlands, rice paddies, animal digestion, fossil fuel extraction, decaying garbage
- Nitrous oxide (N<sub>2</sub>O)
  - soils and the oceans, some from burning fossil fuels and fertilizer use
- Ozone (O<sub>3</sub>)
  - most ground level ozone is from chemical reactions involving pollutants
- Halocarbons
  - anthropogenic chemicals containing bromine, chlorine, or fluorine, and carbon
  - extremely powerful greenhouse gases

## **Molecular Vibrational Frequencies**

Species	Parameter	Vibrational modes		
		<b>v</b> <sub>1</sub>	<b>v</b> <sub>2</sub>	$\nu_3$
CO	Hz	6.43 x 10 <sup>13</sup>	-	-
	μm	4.67	-	-
	cm <sup>-1</sup>	2143	-	-
CO <sub>2</sub>	Hz	-	2.00 x 1013	7.05 x 10 <sup>13</sup>
	μm	-	15.0	4.26
	cm <sup>-1</sup>	-	667	2349
N <sub>2</sub> O	Hz	3.86 x 10 <sup>13</sup>	1.77 <b>x</b> 10 <sup>13</sup>	6.67 x 10 <sup>13</sup>
	μm	7.78	17.0	4.49
	cm <sup>-1</sup>	1285	589	2224
H <sub>2</sub> O	Hz	1.10 x 10 <sup>14</sup>	4.79 x 1013	1.13 x 1014
	μm,	2.73	6.27	2.65
	cm	3657	1595	3776
O <sub>3</sub>	Hz	3.33 x 10 <sup>13</sup>	2.12 x 10 <sup>13</sup>	3.13 x 10 <sup>13</sup>
	μm,	9.01	14.2	9.59
	cm <sup>-1</sup>	1110	705	1043
NO	Hz	5.71 x 10 <sup>13</sup>	-	-
	μm	5.25	-	-
	cm <sup>-1</sup>	1904	-	-
NO <sub>2</sub>	Hz	3.92 x 1013	2.26 x 1013	4.86 x 1013
	μm	7.66	13.25	6.17
	cm	1306	755	1621
$\mathrm{CH}_4$	Hz	8.75 x 10 <sup>13</sup>	4.60 x 10 <sup>13</sup>	9.06 x 10 <sup>13</sup>
	μm	3.43	6.52	3.31
	cm <sup>-1</sup>	2917	1534	3019
		$v_4$		
CII	11-	5.71 1012	-	
$CH_4$	HZ	$5./1 \times 10^{15}$		

5.25

1904

μղ

cm

TABLE 2. VIBRATIONAL FREQUENCIES, WAVELENGTHS AND WAVENUMBERS OF RADIATIVELY ACTIVE ATMOSPHERIC MOLECULES (TAKEN FROM McCartney, 1983).

#### [From Saunders, ECMWF, 2002]

## **Atmospheric Absorption**



through the atmosphere and reaches the surface

## **Band Spectra of Molecules**

Molecule:



vibrational and rotational transitions - band emission spectra

## **Infrared Absorption Bands**

- The energy diagram shows that:
  - a spectral line on the low wavenumber (energy) side is caused by a decrease in rotational energy (∆J = -1, where J is the rotational quantum number)
  - a spectral line on the high wavenumber (energy) side is caused by an increase in rotational energy  $(\Delta J = +1)$
- Each band is due to the allowed values of the vibrational quantum number v.



### **Infrared Absorption Bands**

- Typical infrared absorption bands are characterized by:
- a central peak due to the molecule changing its vibrational state (this may or may not exist)
- "humps" due to the molecule changing both its vibrational and rotational states (composed of many lines).





### **Infrared Absorption Bands**

• The energy absorption can be written as:



- All the bands of a given gas have similar bands, as they share the same rotational wavenumbers  $\,\overline{v}_{_{rot}}\,$
- The large central peak is caused by the  $v_{\rm vib.}$  being slightly affected by the rotational state and therefore even if the rotational state does not change there are slight differences in the absorption energy for different vibrational states.

## **Infrared Line Shapes**

- In order to perform any calculations with an infrared line, we need to define its <u>line shape function</u> (f) and <u>line strength</u> (S).
- These are independent properties of a line.
  - Line shape is determined by atmospheric broadening mechanisms.
  - Line strength is determined by quantum mechanical considerations of the strength of the interactions between the molecule and the photon field.
- The absorption coefficient is thus:  $k(\overline{v}) \propto S f(\overline{v})$

## **Line-Broadening Processes**

Every infrared line has a line width, which results from 3 processes:

- (1) <u>Natural line broadening</u> due to uncertainties in the energy levels associated with the lifetime of the excited state.
  - Only important in the upper stratosphere and mesosphere.
- (2) <u>Pressure (or Lorentz) broadening</u> due to collisions between molecules which distort them and cause absorption at slightly different frequencies.
  - Most relevant to the lower atmosphere below 40 km.
- (3) <u>Doppler broadening</u> due to the random motion of molecules.
  - If a molecule moves with thermal velocity V and emits at  $\bar{v}_o$ :

 $\overline{V} = \overline{V}_o (1 \pm V / c)$  with  $V \ll c$ 

 Most relevant to the atmosphere above about 40 km, becoming comparable to Lorentz broadening at 40 km.

## **Lorentz-Broadened Lines**

• The line shape function for a Lorentz-broadened line is:

$$f_L(\overline{\nu} - \overline{\nu}_o) = \frac{1}{\pi} \frac{\alpha_L}{(\overline{\nu} - \overline{\nu}_o)^2 + \alpha_L^2}$$

where

- $\bar{v}_o$  = central wavenumber
- $\alpha_{L} = \underline{\text{Lorentz half-width}} (\text{HW at HM}) \quad \alpha_{L}(T,p) = \alpha_{L}^{o}(T_{o},p_{o}) \frac{p}{p_{o}} \left(\frac{T_{o}}{T}\right)^{N}$
- $\alpha_{\rm L}^{0}$  ranges from 0.01 to 0.1 cm<sup>-1</sup> for most gases
- $T_o$  and  $p_o$  = reference T and p (273.15 K, 1013.25 mbar)
- N = exponent of temperature dependence = 0.5 to 1 (usually use 0.5)
- The absorption coefficient of a Lorentz-broadened line is thus:

where

$$k_a(\overline{\nu}) = \frac{S}{\pi} \frac{\alpha_L}{\left(\overline{\nu} - \overline{\nu}_o\right)^2 + \alpha_L^2}$$

- S = line strength, a function of T and lower state energy E''
- Every Lorentz-broadened line can be specified by four parameters:  $\bar{v}_{o}, S, \alpha_{L}^{o}, E''$

## **Doppler-Broadened Lines**

• The line shape function for a Doppler-broadened line is:

$$f_D(\overline{\nu} - \overline{\nu}_o) = \frac{1}{\sqrt{\pi}\alpha_D} \exp\left(-\frac{(\overline{\nu} - \overline{\nu}_o)^2}{\alpha_D^2}\right)$$

where

- $\alpha_{\rm D} = \underline{\text{Doppler line-width}}$  (HWHM /  $\sqrt{\ln 2}$ )  $\alpha_{\rm D}(T) = \sqrt{\frac{2k_{\rm B}T}{M}} \frac{\overline{v_o}}{c}$
- $k_{\rm B}$  = Boltzmann's constant
- -M = molecular mass
- The absorption coefficient of a Doppler-broadened line is thus:

$$k_a(\overline{\nu}) = \frac{S}{\sqrt{\pi}\alpha_D} \exp\left(-\frac{(\overline{\nu} - \overline{\nu}_o)^2}{\alpha_D^2}\right)$$

### **Lorentz and Doppler Lines**





Frequency

Note: Doppler lines are more intense at the centre and weaker in the wings

than Lorentz lines. *From Saunders (ECMWF, 2002].*  The shape of a Doppler-broadened line reflects the Maxwell distribution of speeds in the sample at the temperature of the experiment. Notice that the line broadens temperature increases.

From: http://www.raunvis.hi.is/~agust/dopp.htm

## **The Voigt Line Shape**

- The influence of Lorentz and Doppler broadening can be combined in a convolution function called the <u>Voigt line shape</u>.
  - This is useful when both effects are important, e.g., near 40 km in the Earth's atmosphere.
  - Requires numerical calculations.

$$f_{Voigt}\left(\widetilde{v} - \widetilde{v}_{0}\right) = \int_{-\infty}^{\infty} f_{L}\left(\widetilde{v}' - \widetilde{v}_{0}\right) f_{D}\left(\widetilde{v} - \widetilde{v}'\right) dv' = \frac{\alpha}{\alpha_{D}\pi^{3/2}} \int_{-\infty}^{\infty} \frac{1}{\left(\widetilde{v}' - \widetilde{v}_{0}'\right)^{2} + \alpha^{2}} \exp\left[-\left(\frac{\widetilde{v} - \widetilde{v}'}{\alpha_{D}}\right)^{2}\right] dv'$$

- At high pressures: the Doppler profile is narrow compared to the Lorentz → the Voigt profile is the same as the Lorentz profile.
- At low pressures: the Voigt profile is a "hybrid" line with a Doppler center and Lorentz wings.

## Atmospheric Spectroscopy: A Practical Application

- Using an appropriate line shape function, the absorption coefficient can be calculated at any point in spectral space.
- This can then be used to derive the total absorption of the line, the atmospheric transmission, etc.
- Calculation of the line shape function requires knowledge of the relevant spectral line parameters.
  - HITRAN is the most widely used spectroscopic database with information (intensity, half-width, and so on) for more than 1,000,000 spectral lines for about 36 different molecules.

### **Example: Solar IR Absorption Spectra**

