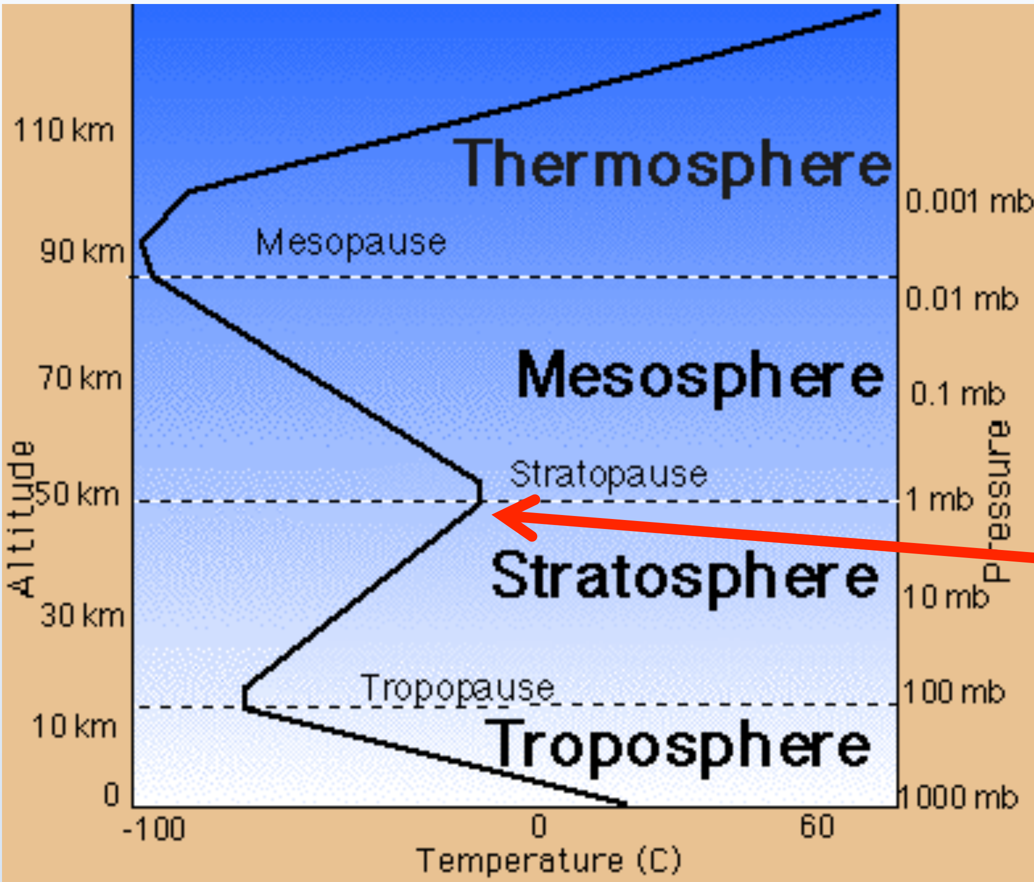
Atmospheric Chemistry

Lecture 10

Temperature Structure of the Atmosphere

$$h\nu + O_3 \rightarrow O_2 + O + k.e.$$



Kinetic energy shared with other molecules by collision; leads to heating of stratosphere

Photon Energetics

$$E(energy) = h\nu = \frac{hc}{\lambda}$$

$$hc = 6.6 \cdot 10^{-27}(erg\ sec) \cdot 3 \cdot 10^{8}(cm\ sec^{-1}) = 1.98 \cdot 10^{-18}(erg\ cm)$$

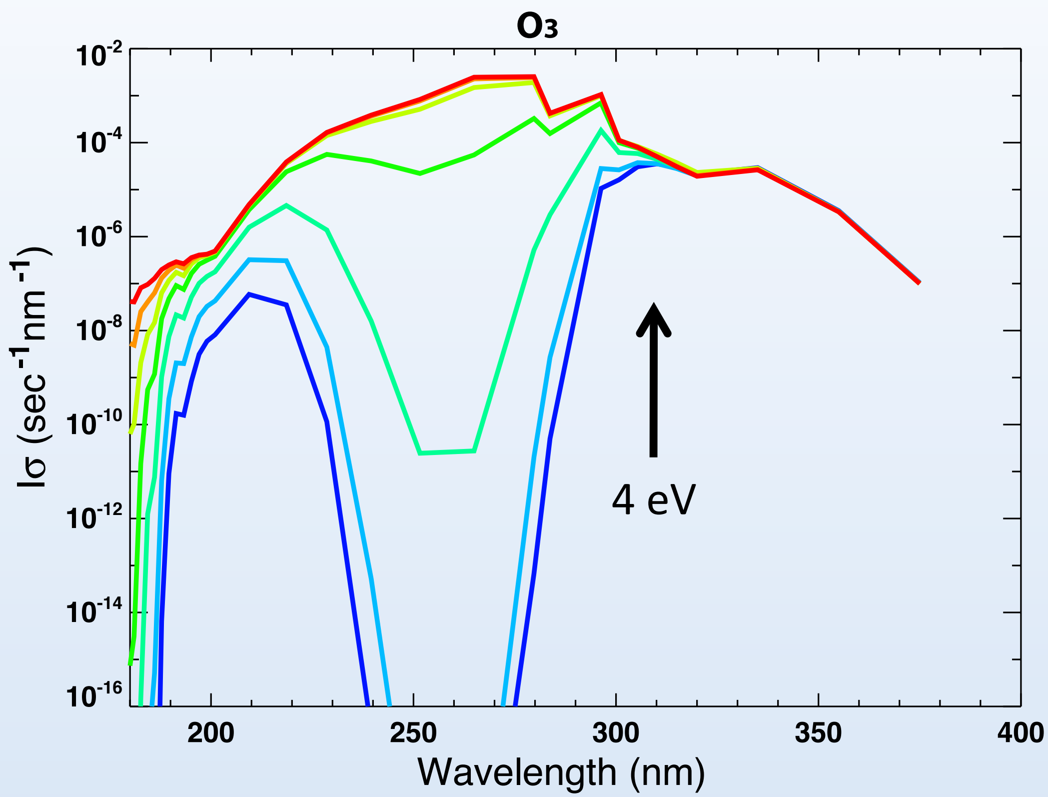
$$hc = \frac{1.98 \cdot 10^{-18}(erg\ cm)}{1.6 \cdot 10^{-12}(erg/eV)} = 1.24 \cdot 10^{-6}(eV\ \ cm) = 1240(eV\ \ nm)$$

1 eV = 23 kCal/mol

310 nm photon = ~ 4 eV energy

1 eV = 96 kJ/mol

Ozone Photodissociation vs Wavelength



Ozone Enthalpy of formation (bond strength) = 143 kJ/mol = ~1.5 eV/molecule

Needs wavelength of about 800nm (near IR) for photodissociation. Chappuis bands dissociate ozone in the visible, but are forbidden transitions with small cross section.

Heating vs Altitude

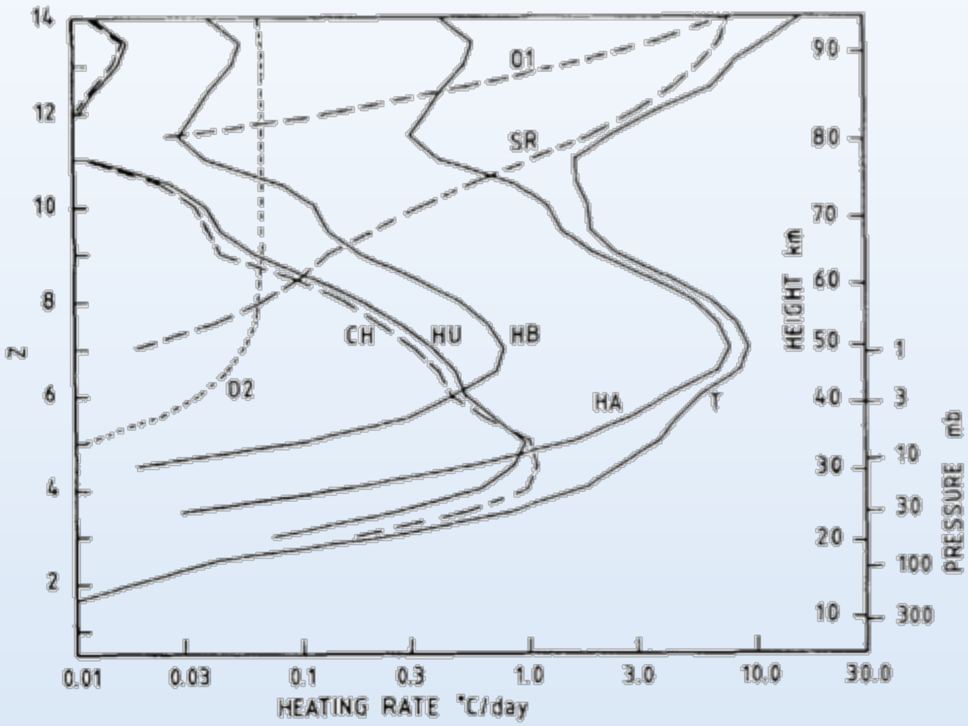
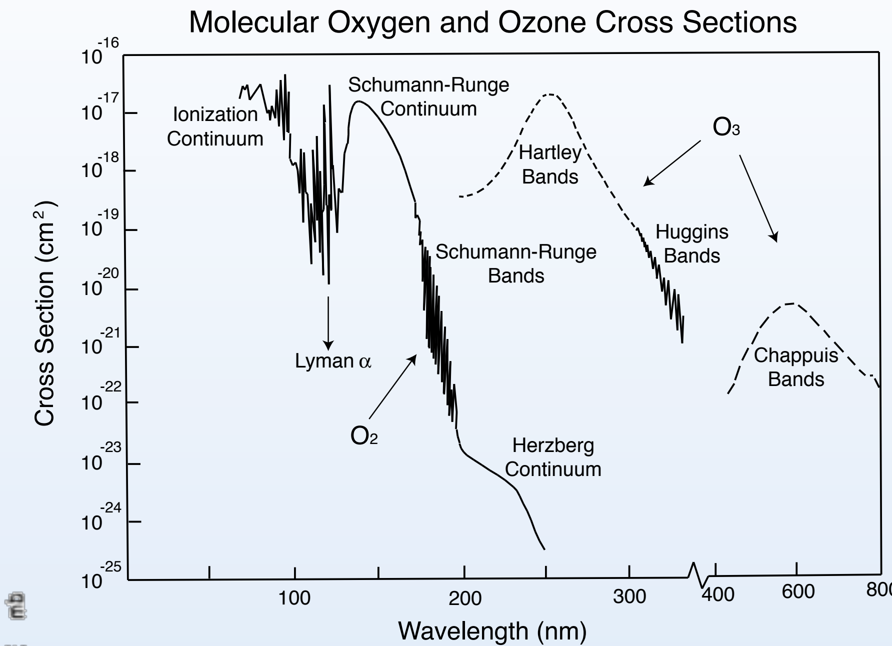
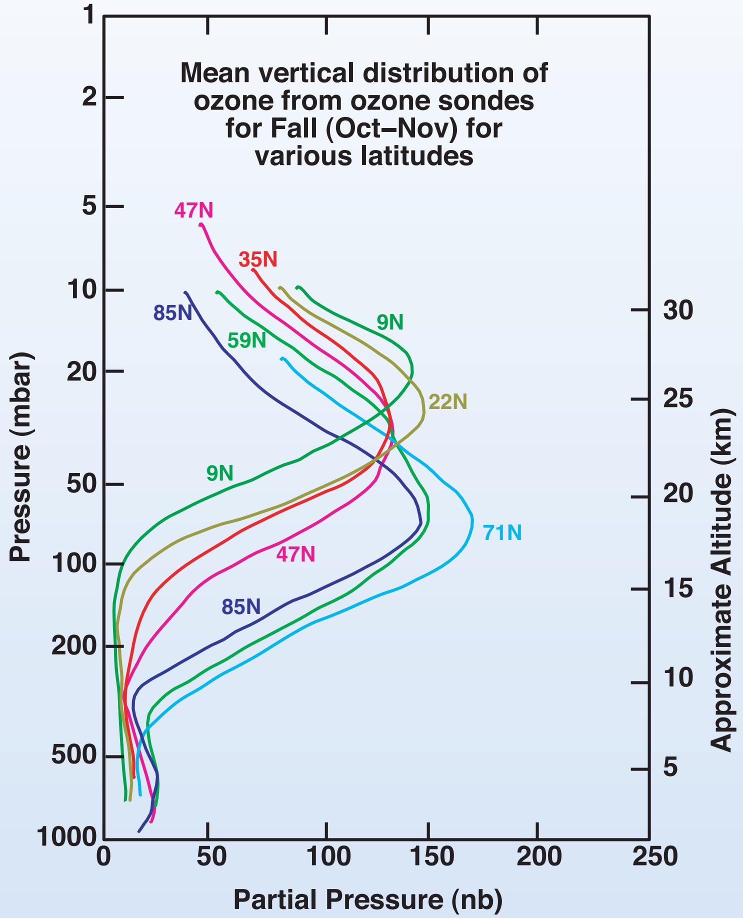


Figure 4. The solar heating contributed by each absorption band for ascent II.
CH: Chappuis band
HA: Hartley band 240–300 nm 01: Oxygen absorption 180–200 nm
HB: Hartley band 200–240 nm 02: Oxygen absorption 200–240 nm
HU: Huggins band 300–350 nm SR: Schumann Runge bands
T: Total

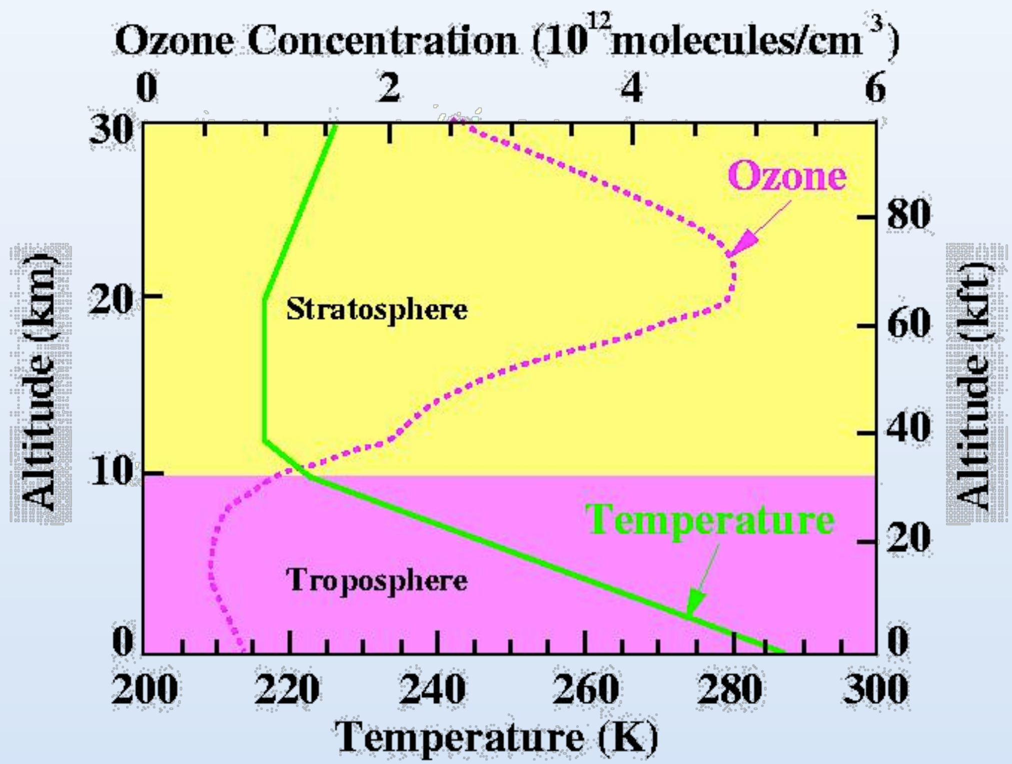


Maximum Heating Near 1 hPa; Well Above the Ozone Maximum



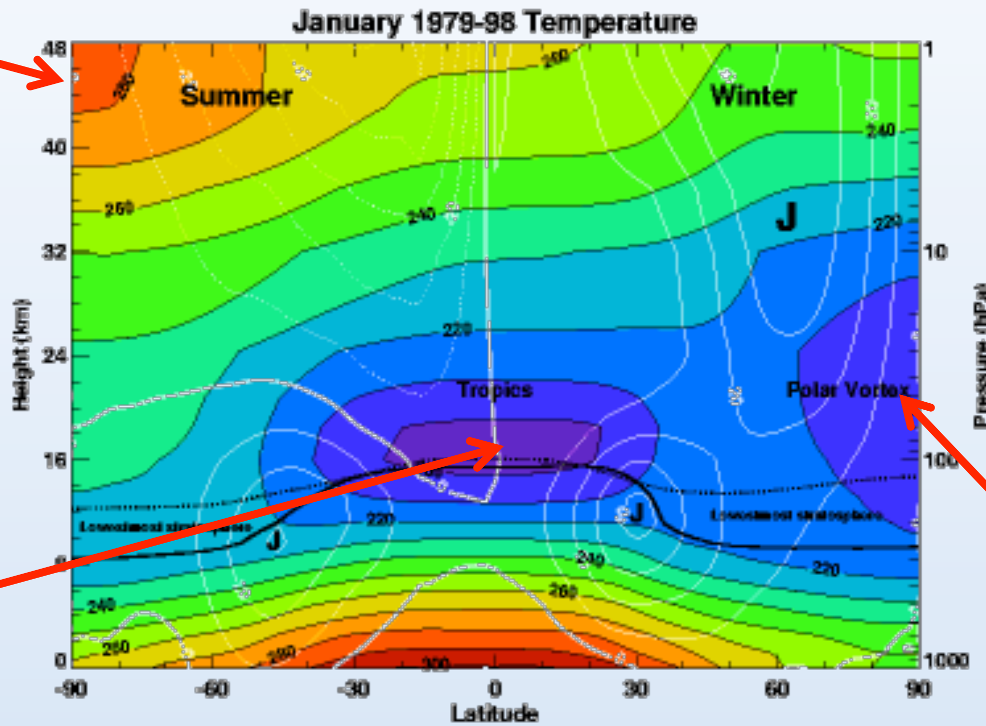
from Dütsch, Advances in Geophysics, 1971

Altitude of peak heating by ozone



Two-dimensional atmospheric temperature structure

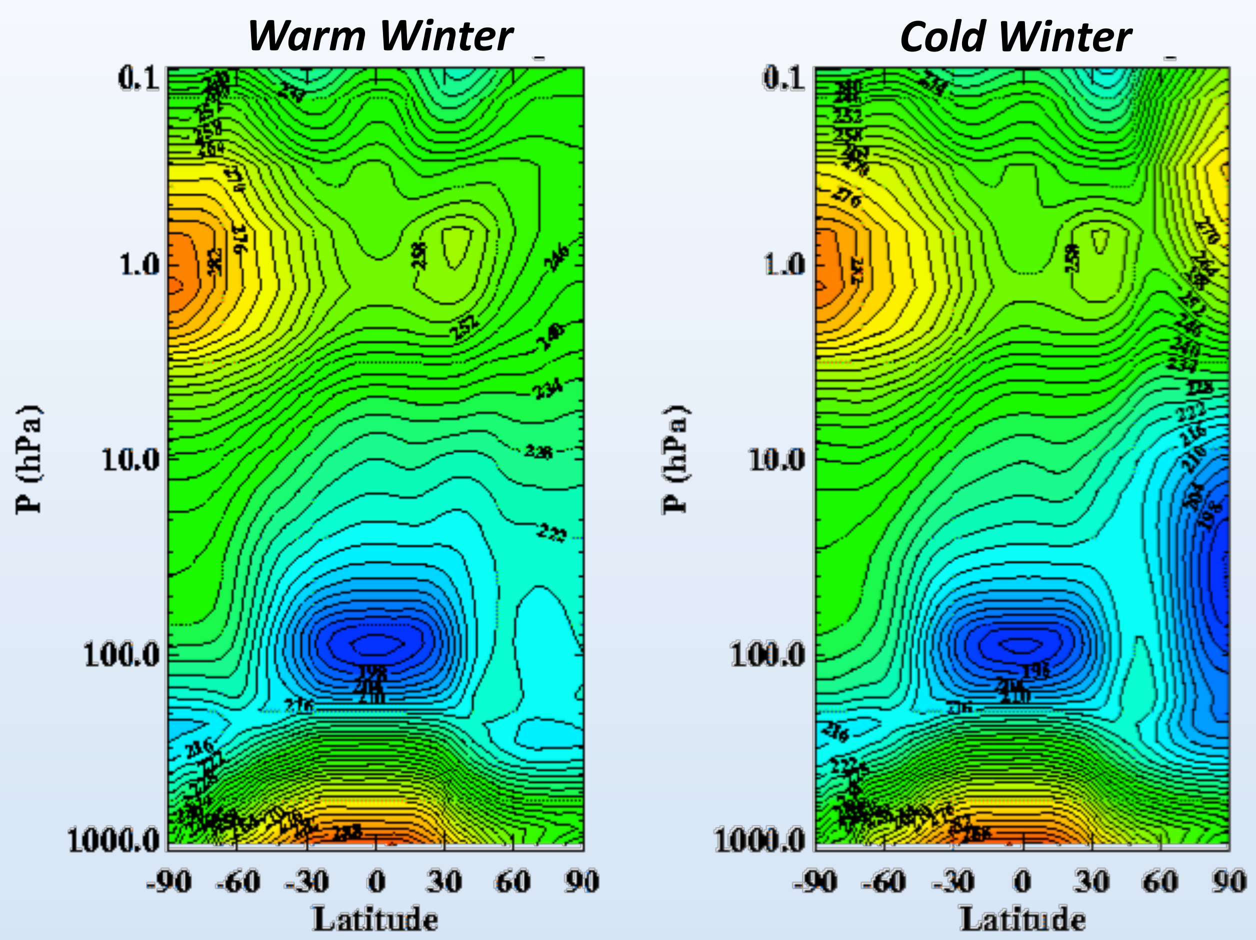
Warm summer stratopause



Cold tropical tropopause

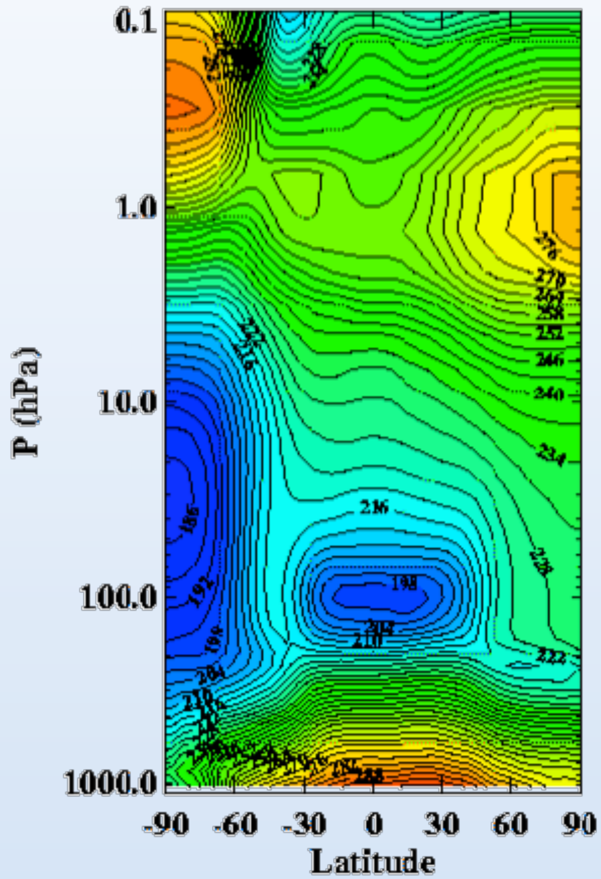
Cold winter polar lower stratosphere

January Temperature Structure

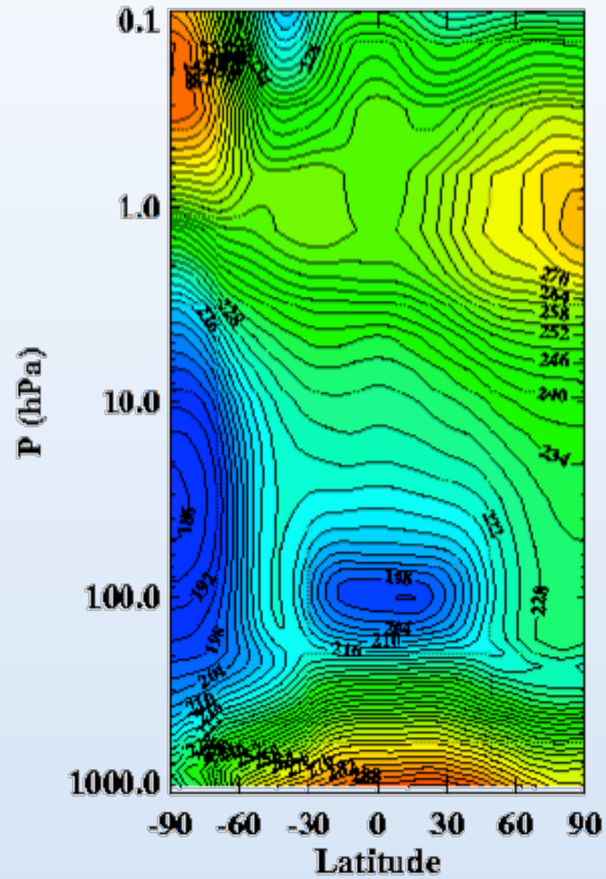


July Temperature Structure

Warm Winter



Cold Winter



Stratospheric Heat Balance Equation

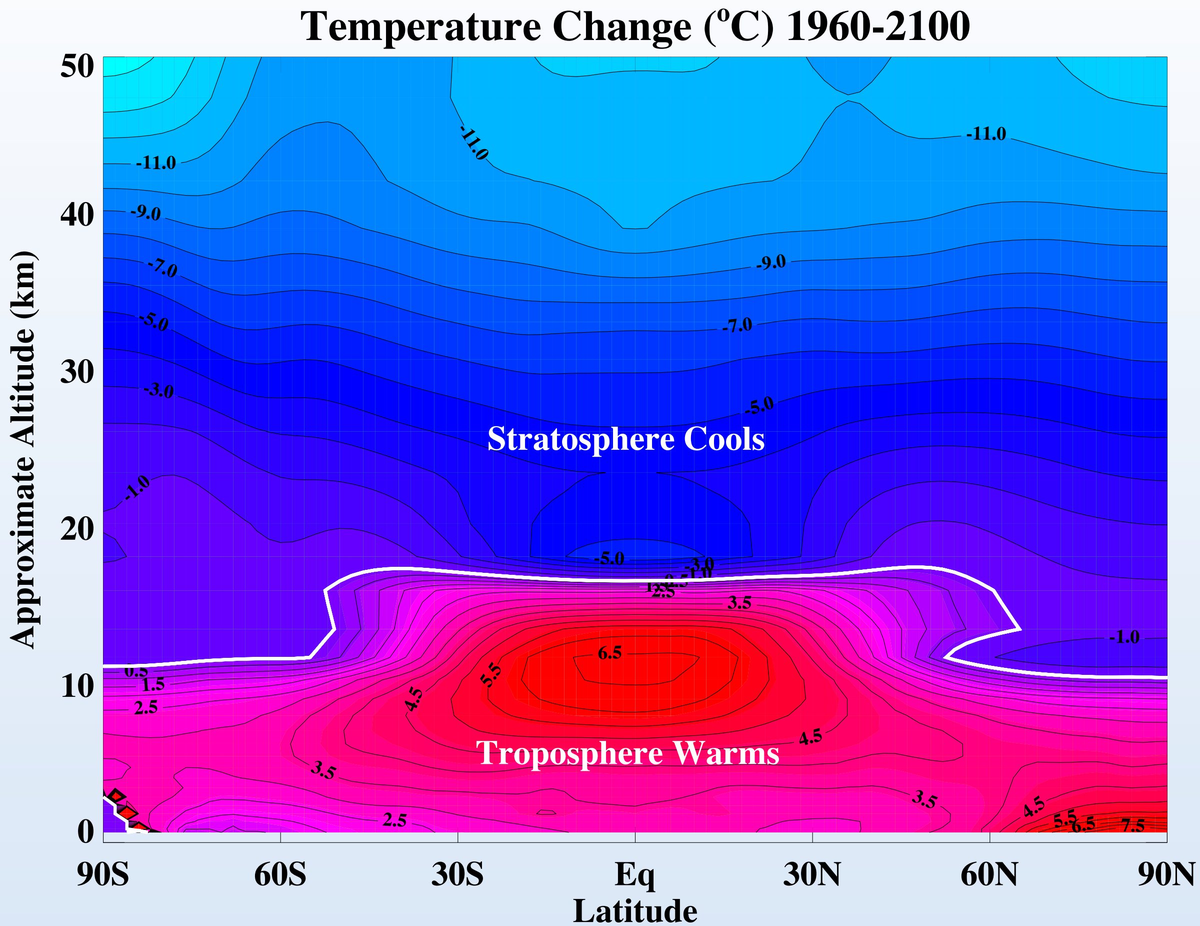
$$\frac{\partial T}{\partial t} + Transport\ of\ heat = Heating(O_3) - Cooling(CO_2)$$

Cooling often approximated by linear response proportional to temperature

Cooling = aT +b

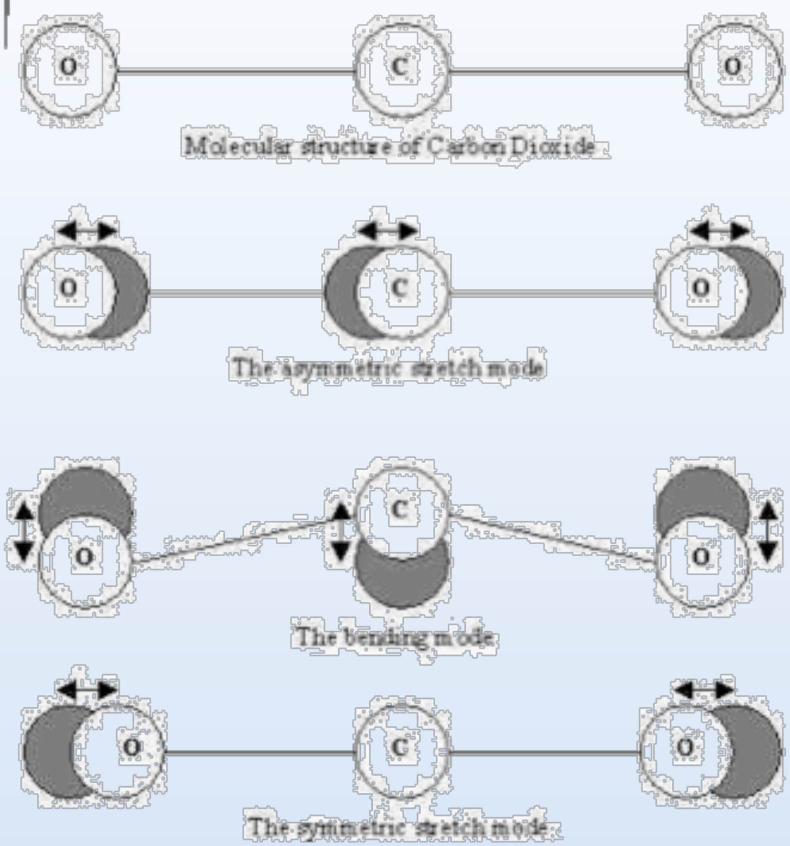
where a has units of inverse time with 1/a of the order of a few days to a week

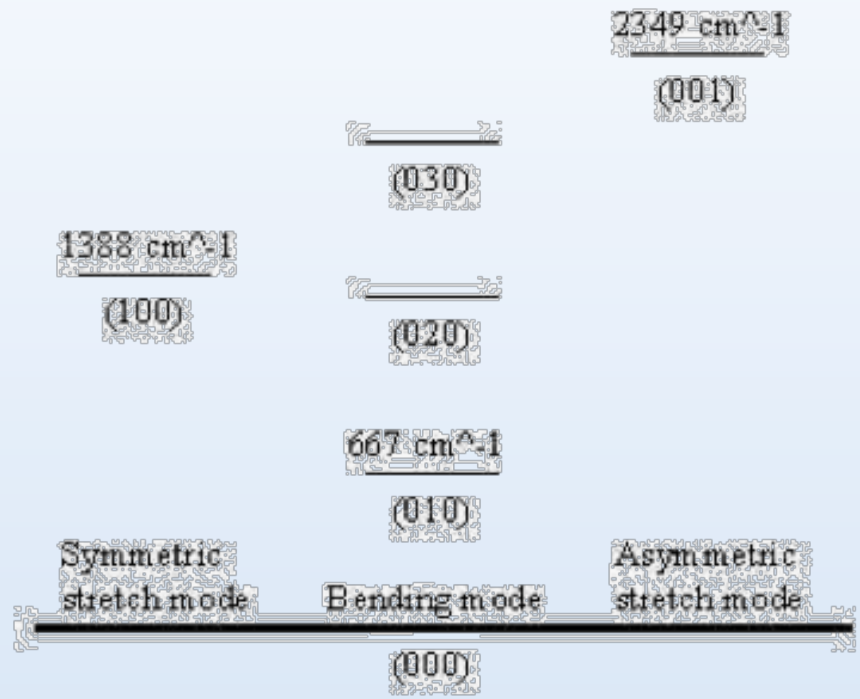
Model Calculation of Temperature Change



Why does the troposphere warm while the stratosphere cools with the addition of CO_2 to the atmosphere?

Stratospheric Cooling: CO_2 IR Bands





Observed IR Spectrum at Top of Atmosphere

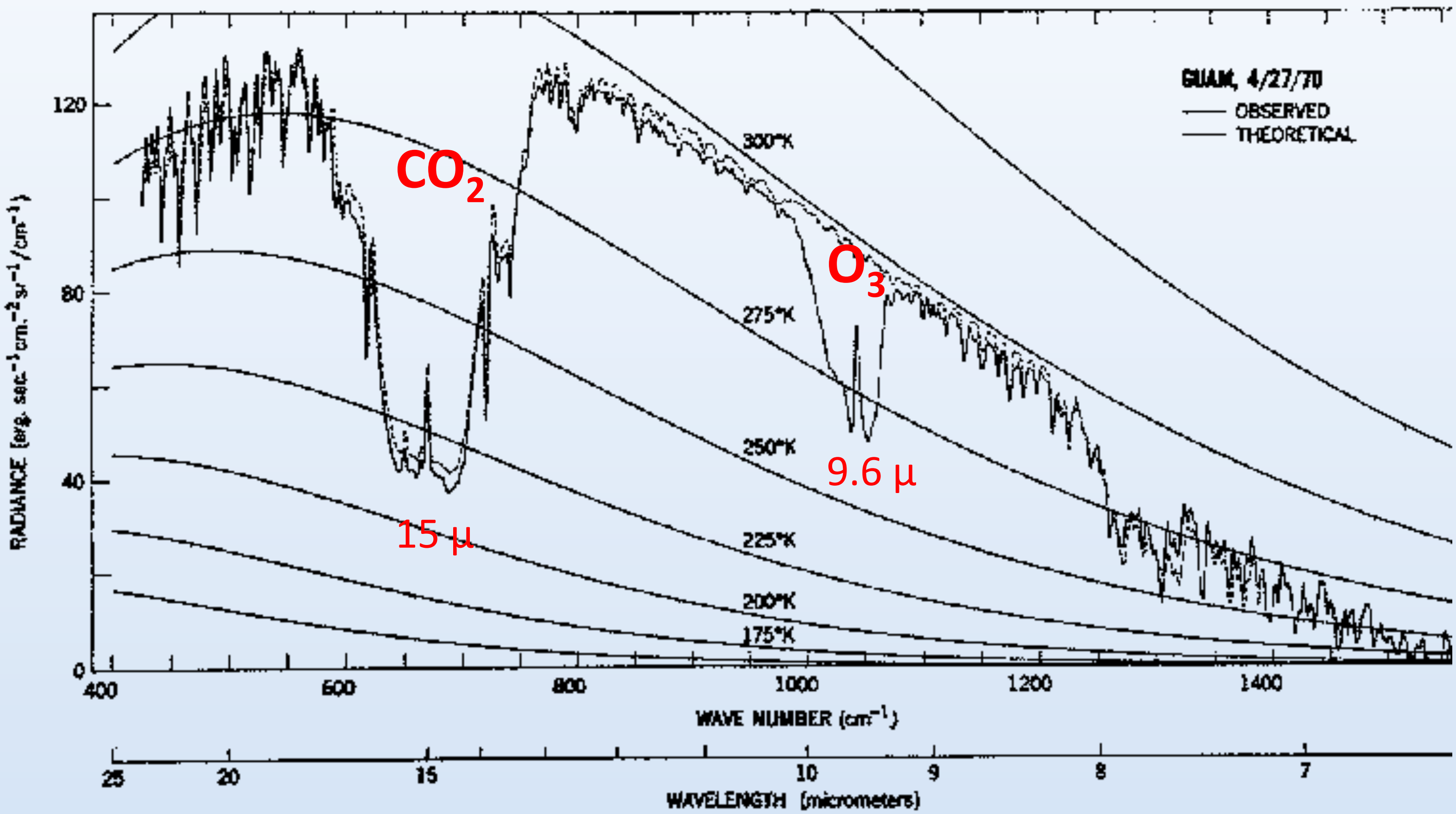
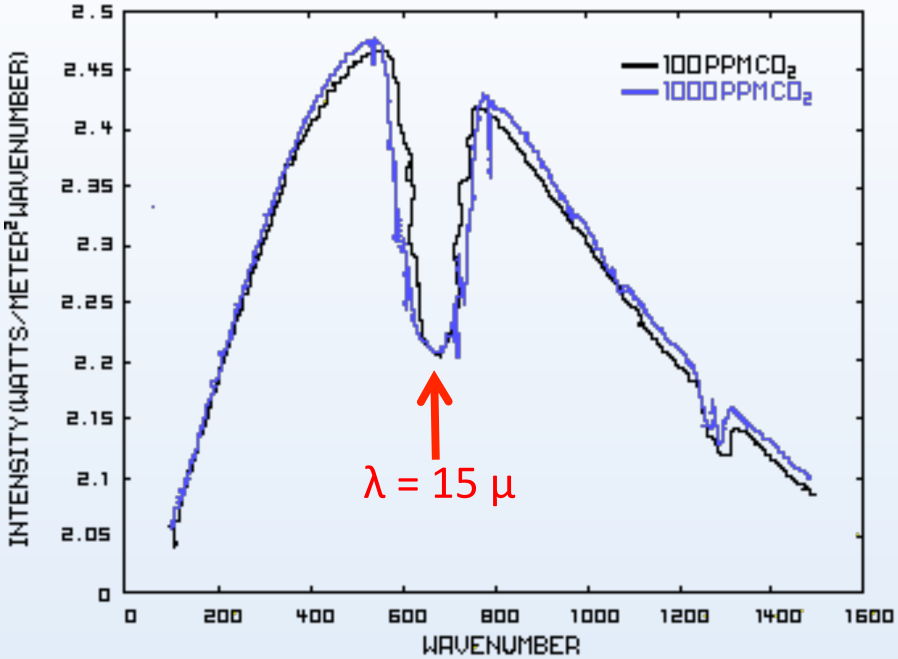


Fig. 3. Comparison of observed and theoretical radiances for a clear atmosphere near Guam at 15.1°N and 215.3°W, on April 27, 1970.

Response of Outgoing Radiation to Increased CO_2



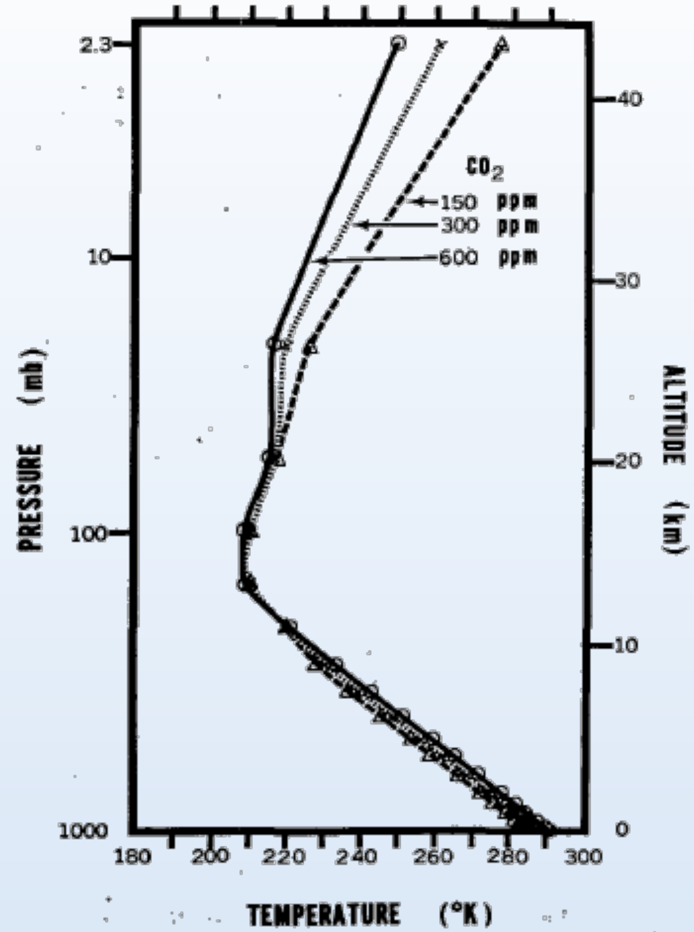


FIG. 16. Vertical distributions of temperature in radiative convective equilibrium for various values of CO_2 content.

Outgoing radiation from troposphere has absorption feature from 15μ CO_2 band. In stratosphere, collisions repopulate the excited state (CO_2) bending mode, which can then radiate upward to space, leading to a decrease in the energy locally.