Radiation

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（特别是关于辐射的部分）。

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Outline

- Introduction
- Concepts
- Absorption
- Scattering
- Radiative transfer
- Radiative equilibrium temperature
- Radiative heating and cooling

思考题

普朗克定律可以以波长 λ、频率 f 或者波数 ν 形式来表达：

$$B(\lambda,T)=\frac{2c^2h}{\lambda^5}\left(e^{\frac{ch}{k\lambda T}}-1\right)^{-1}$$

$$B(f,T)=\frac{2f^3h}{c^2}\left(e^{\frac{fh}{kT}}-1\right)^{-1}$$

$$B(\nu,T)=2\nu^3c^2h\left(e^{\frac{\nu ch}{kT}}-1\right)^{-1}$$

A. 从波长形式推导其他两种形式

B. 当普朗克函数用波长、频率、波数表达时，都会得到一个极值点。若把极值点对应的波长、频率、波数都转换成对应的波长，这3个波长是否相等？

思考题

A. Consider two opaque walls facing one another. One of the walls is a blackbody and the other wall is “gray”. The walls are initially at the same temperature T and, apart from the exchanges of radiation between them, they are thermally insulated from their surroundings. If A and ε are the absorptivity and emissivity of the gray wall, use thermodynamic arguments to prove that $\varepsilon = A$.

B. Consider a similar situation with two “gray” walls, one with absorptivity A_1 and the other with absorptivity A_2. Prove that $\frac{F_1}{A_1} = \frac{F_2}{A_2}$

   where F_1 and F_2 are the flux densities of the radiation emitted from the two walls.

Modified from Michael Wallace book

Radiative Absorption and Scattering in the Atmosphere

Absorption

- ✓ Solar radiation: by O_2, O_3, H_2O, CO_2, aerosols, NO_2, HCHO, SO_2, CHOCHO, other gases
- ✓ Terrestrial radiation: by H_2O, CO_2, CH_4, O_3, N_2O, halocarbons, clouds

Scattering

- ✓ Solar radiation: by gases (O_2, N_2, etc.), aerosols, clouds
- ✓ Terrestrial radiation: by aerosols, clouds, rain droplets, snow

Radiative Absorption and Scattering in the Atmosphere

Processes following an interaction $AB + \gamma \rightarrow AB^*$

1. $AB^* \rightarrow AB + \gamma$	Radiative decay	**Scattering**
2. $AB^* + M \rightarrow AB + M + e$	Thermalization	**Absorption**
3. $AB^* \rightarrow A + B$	Dissociation	**Absorption**
4. $AB^* + C \rightarrow A + BC$	Reaction	**Absorption**

- ✓ Process 1 has a natural decay time independent of pressure
- ✓ Processes 2, 3, and 4 have a thermalization time that depends on pressure

Internal Energy of a Molecule Related to EMR

$E = E_t + E_v + E_r + E_e$ E_v, E_r, E_e are quantized 量子化

E_t : translation energy (energy of the molecule of due to its motion in a straight line); equivalent to wavenumber of ~ 400 cm^{-1} for T = 300 K

E_v : kinetic energy of vibration (energy of vibrating atoms about their equilibrium positions in a molecule); about 500 to 10^4 cm^{-1} (near- to far-IR)

E_r : kinetic energy of rotation (energy of the rotation of a molecule as a unit body); about 1-500 cm^{-1} (far-infrared to microwave region)

E_e : electronic energy (potential energy of electron arrangement); about 10^4-10^5 cm^{-1} (UV and visible)

- ✓ Rotational energy change will accompany a vibrational transition. Therefore, vibration-rotation bands are often formed.
- ✓ Kinetic collisions, by changing the translation energy, influence rotational levels strongly, vibrational levels slightly, and electronic levels scarcely at all.

Absorption with Change in Quantized Electronic Energy

$$\Delta E = h\nu$$

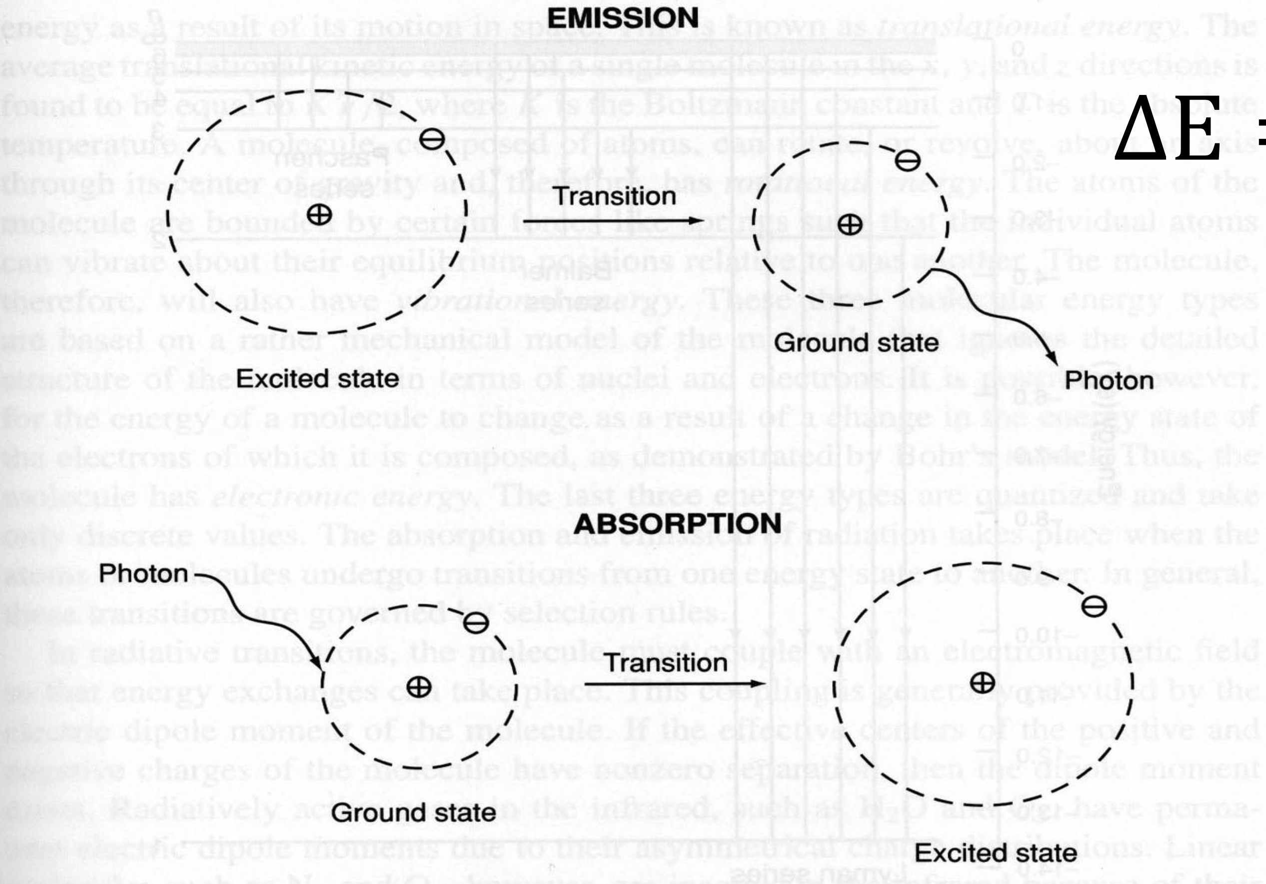


Figure 1.8 Illustration of emission and absorption for a hydrogen atom that is composed of one proton and one electron. The radius of the circular orbit r is given by $n^2 \times 0.53$ Å, where n is the quantum number, and 1 Å $= 10^{-8}$ cm.

Bohr's Hydrogen Atom Spectrum

- Transition of state (j, k are integers)

$$E_k - E_j = h\nu c$$

- Wavenumber of emission/absorption lines

$$\upsilon = R_H\left(\frac{1}{j^2} - \frac{1}{k^2}\right)$$

Rydberg constant $R_H = 1.097 \times 10^5\ \mathrm{cm}^{-1}$

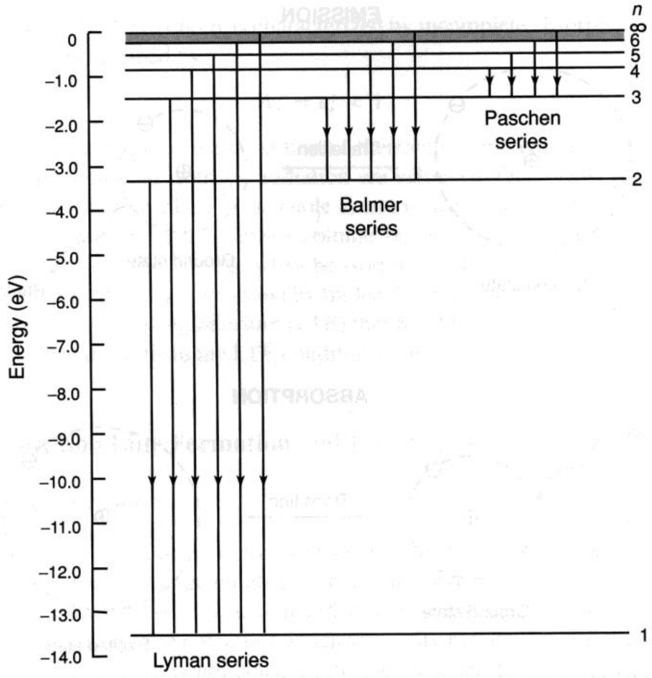
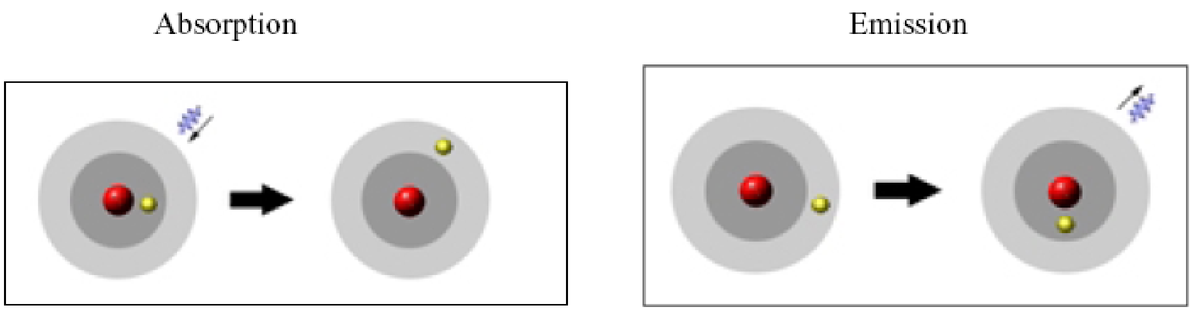
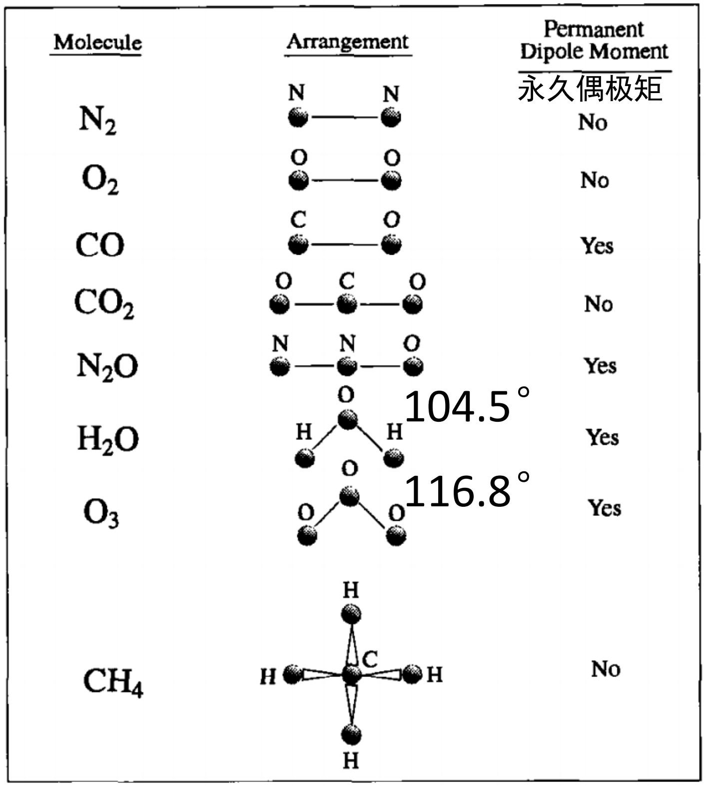
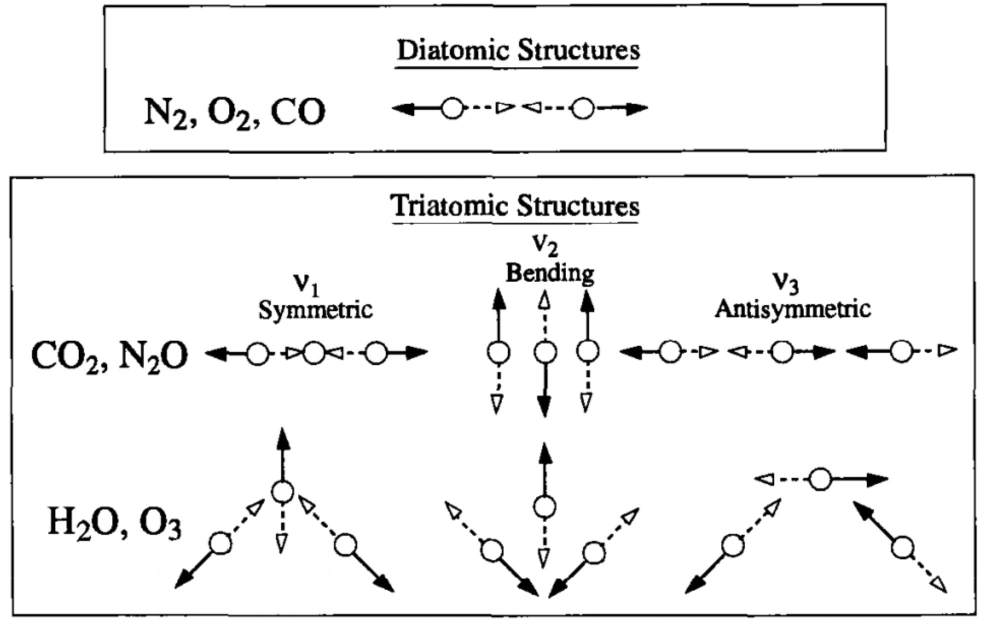


Figure 1.9 Energy level diagram for a hydrogen atom showing the quantum number n for each level and some of the transitions that appear in the spectrum. An infinite number of levels is crowded in between the levels marked $n = 6$ and $n = \infty$.



Absorption with Change in Quantized Vibrational Energy





- Change in vibrational energy is associated with IR absorption
- Normal modes of vibration: 3N-6 or 3N-5 (for a linear molecule like CO_2)
- IR active ? It depends on the change in dipole moment
- Molecular vibration： http://www.chem.purdue.edu/gchelp/vibs/o2.html

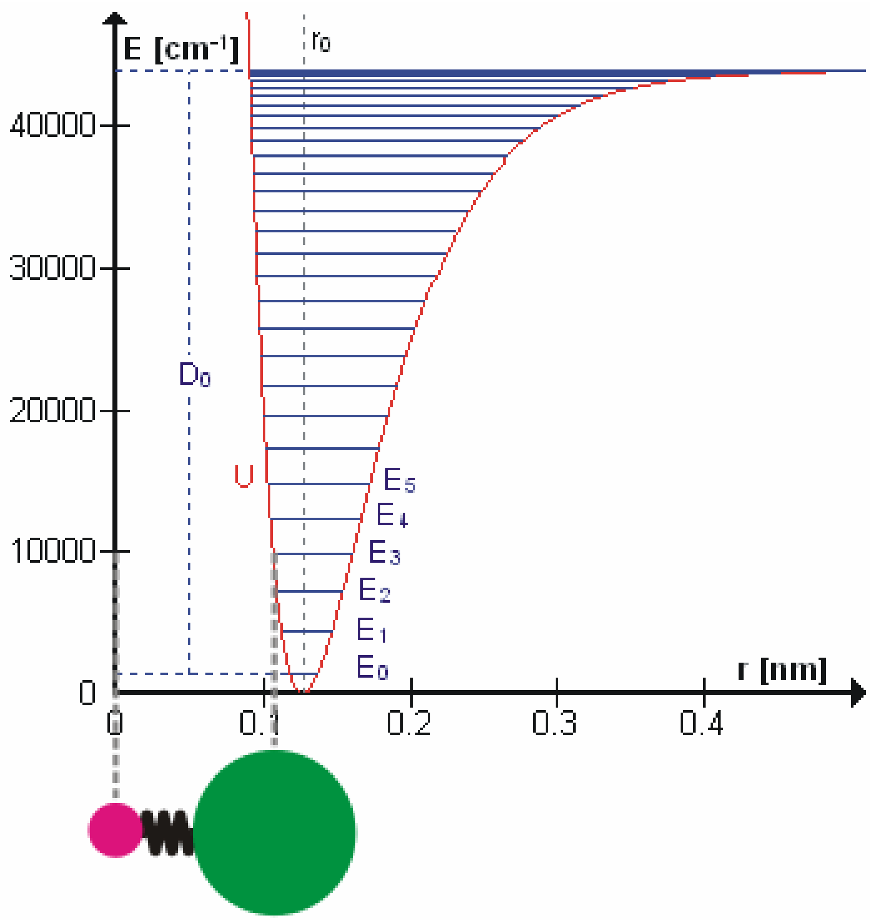
Examples of Vibration Modes

Wavelengths of Vibrational Modes of Some Important Atmospheric Molecules

	Vibrational modes		
Species	ν_1	ν_2	ν_3
CO	4.67		
CO_2		15.0	4.26
N_2O	7.78	17.0	4.49
H_2O	2.73	6.27	2.65
O_3	9.01	14.2	9.59
NO	5.25		
NO_2	7.66	13.25	6.17
CH_4	3.43	6.52	3.31
CH_4	5.25		

Units are in micrometers (μm). [From Herzberg and Herzberg (1957), © McGraw Hill, Inc. and from Shimanouchi (1967a, 1967b, 1968)].

Vibration of HCl



https://en.wikipedia.org/wiki/Molecular_vibration

吸收线、吸收系数、吸收截面

- 吸收线：吸收波长位置。吸收伴随着分子或原子内部能级的跃迁，因此，吸收线与分子或原子内部的能级结构有关
- 不是频率合适的每一个光子都能被吸收，这里遵循一个概论分布，它决定了吸收系数的大小
- 对一个吸收分子来说，吸收系数的大小常用吸收截面 σ_{ab} 来表示，即对这个吸收分子而言，它能把多大一个截面上的辐射能吸收
- 当单位体积中有 N 个分子时，体积吸收系数

$$k_{ab} = \sigma_{ab} \cdot N$$

单位	
σ_{ab}	$m^2/molecule$
N	$molecules/m^3$
k_{ab}	m^{-1}

独立吸收？

谱线增宽

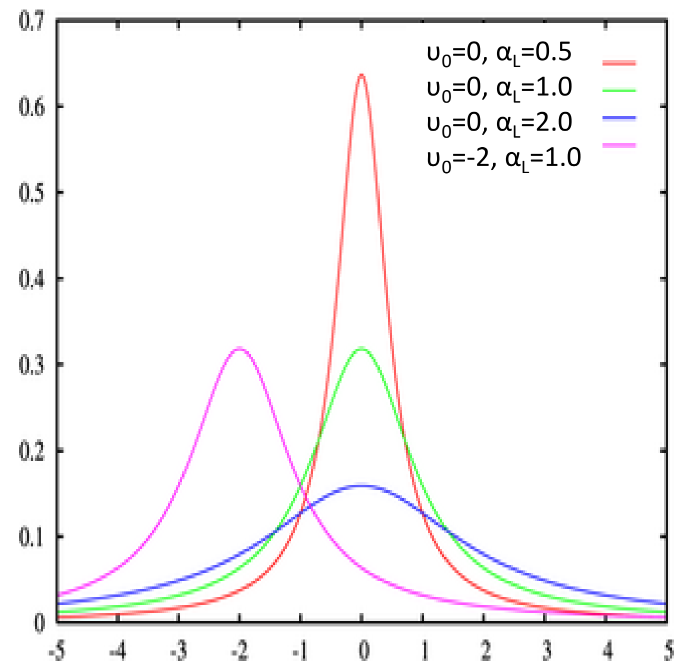
- 一根吸收线与一个能级跃迁相对应，但是，
- 存在三种谱线增宽方式：
  - 自然增宽：测不准原理（影响很小）
  - 压力增宽：粒子碰撞产生能量交换，影响到能级差。气体压力大，分子密度大，碰撞的机会就增加，从而使谱线的加宽增大。
  - 多普勒增宽：分子处于无规则的热运动之中。运动的分子吸收的电磁波频率与其在静止时所吸收的电磁波频率有一个差别，称为多普勒频偏，导致多普勒增宽。

  类似地，火车由远及近声音的变化？

压力增宽（Lorentz增宽）

- 压力增宽可以用Lorentz公式来表示：

$$k_v = \frac{S}{\pi}\frac{\alpha_L}{(v-v_0)^2+\alpha_L^2}$$



- S 是谱线的强度，即为吸收线增宽后的总面积

$$S = \int_{-\infty}^{+\infty} k_v dv \qquad 量纲: k_{ab}$$

- $v_0 = (E_U - E_L)/hc$ 是吸收线的中心波数，E_L和E_U是分子吸收光子前后的能量

压力增宽（Lorentz增宽）

- α_L 是洛伦茨谱宽，在这里正好是吸收线的半宽度：

  在 $v = v_0$处，$k_{v0} = S/(\pi\alpha_L)$，

  在$v = v_0 \pm \alpha_L$处， $k_v = \frac{1}{2}k_{v0} = S/(2\pi\alpha_L)$

- α_L与分子碰撞频率成正比，因此与气压P成正比，与气温平方根$T^{1/2}$成反比：

$$\alpha_L(P,T) = \alpha_{L0}\frac{P}{P_0}\left(\frac{T_0}{T}\right)^{1/2}$$

- 大气中温度变化在190K 到 320K 之间，而气压从1000 hPa 变化到0.1 hPa，因此气压对 α_L 的影响最重要

- 大气中几种主要吸收气体的 α_L大约0.1~0.2 cm^{-1}（1~2 nm at λ=10 μm； 0.01~0.02 nm at λ=1 μm ）

多普勒增宽

- 多普勒频偏：分子处于无规的热运动之中。因此，

$$\upsilon=\upsilon_0\left(1+\frac{v}{c}\right)$$

v 为相对于观测者的运动速度

- 多普勒增宽：

$$k_\upsilon=\frac{S}{\alpha_D\sqrt{\pi}}exp\left[-\frac{(\upsilon-\upsilon_0)^2}{{\alpha_D}^2}\right]$$

在 $\upsilon=\upsilon_0$处，$k_{\upsilon 0}=S/\left(\alpha_D\sqrt{\pi}\right)$

在 $\upsilon=\upsilon_0\pm\alpha_D$ 处，$k_\upsilon=S/\left(\alpha_D\sqrt{\pi}\right)\cdot e^{-1}$

- α_D是多普勒谱宽，与气压P无关，与$T^{1/2}$成正比，与$m^{1/2}$成反比

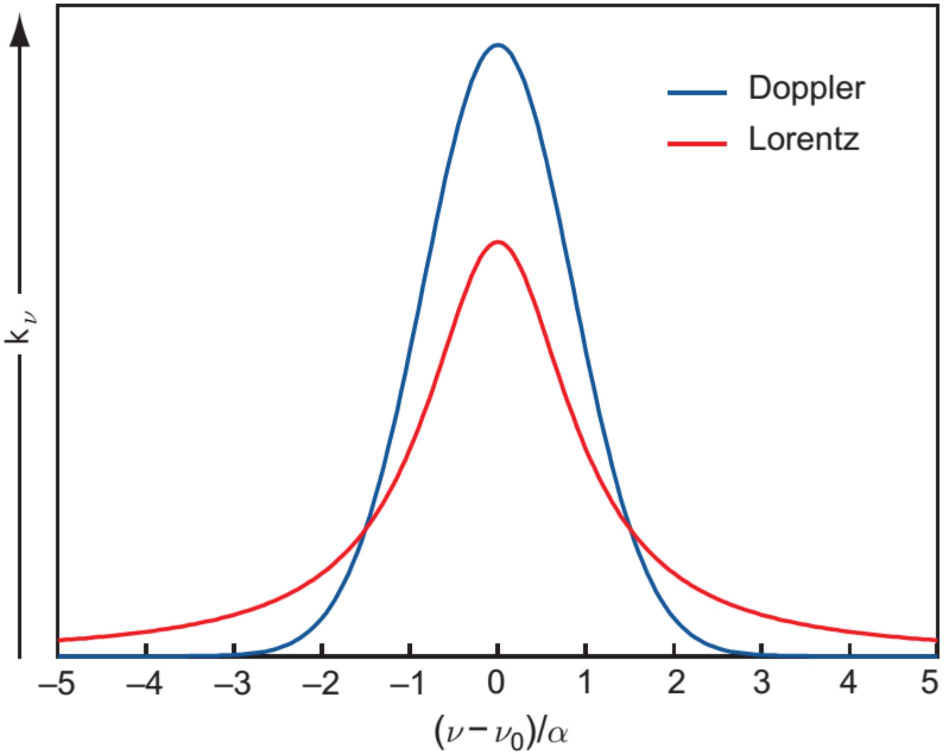
$$\alpha_D=\frac{\upsilon_0}{c}(2kT/m)^{1/2}$$

分子相对于观测者的运动速度的麦克斯韦分布：

$$p(v)dv=\left(\frac{m}{2\pi kT}\right)^{1/2}exp\left(-\frac{mv^2}{2kT}\right)dv$$

压力增宽 versus 多普勒增宽

- ✓ α_D随高度的变化比 α_L慢得多
- ✓ 在对流层，$\alpha_L \gg \alpha_D$
- ✓ 但到某一高度，$\alpha_L = \alpha_D$
- ✓ 高度再增加时，多普勒增宽就变得重要了



压力增宽 versus 多普勒增宽

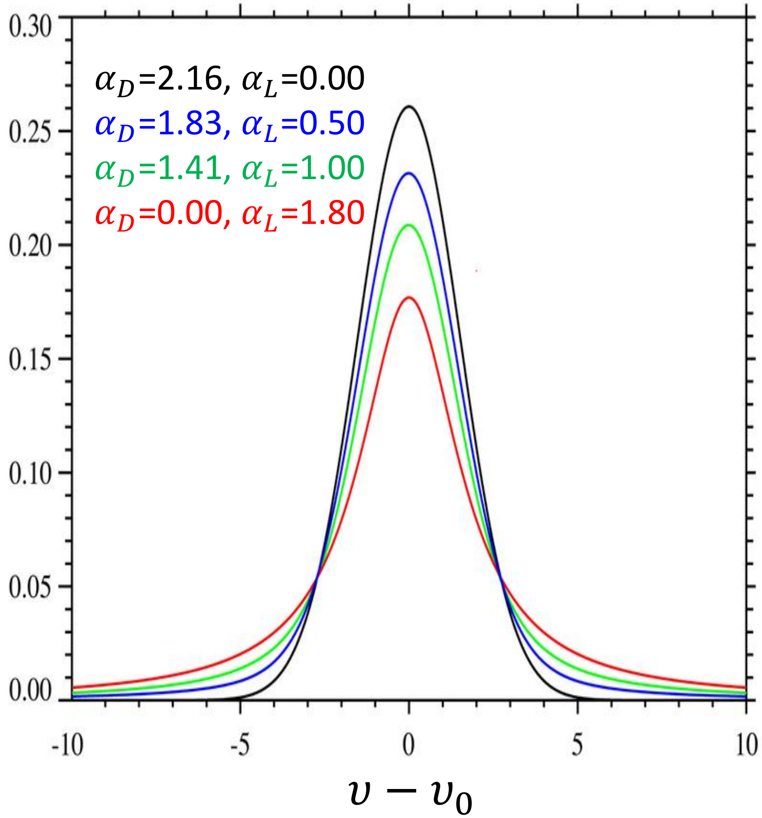
吸收气体	波长(μm)	标准状态 α_D (cm^{-1})	标准状态 α_L(cm^{-1})	$\alpha_L = \alpha_D$ 时的气压 (hPa)
H_2O	6.3	0.0022	0.11	20.0
H_2O	20	0.0007	0.11	6.4
H_2O	40	0.00035	0.11	2.8
CO_2	4.3	0.0021	0.15	14.0
CO_2	15	0.0006	0.15	4.2
O_3	4.7	0.002	0.16	12.0
O_3	9.6	0.00087	0.16	5.3
O_3	14.1	0.0006	0.16	4.2

Voigt Profile: Combining Lorentz & Doppler Broadening

Convolution (卷积) of Lorentz and Doppler Broadening:

$$V(v|\alpha_D,\alpha_L) = \int_{-\infty}^{\infty} D(v_1 - v_0|\alpha_D)\cdot L(v - v_1|\alpha_L)\cdot dv_1$$

$$k_v = S\cdot V(v|\alpha_D,\alpha_L)$$



- ✓ Doppler profile:

$$D(v_1 - v_0|\alpha_D) = \frac{1}{\alpha_D\sqrt{\pi}} exp\left[-\frac{(v_1 - v_0)^2}{{\alpha_D}^2}\right]$$

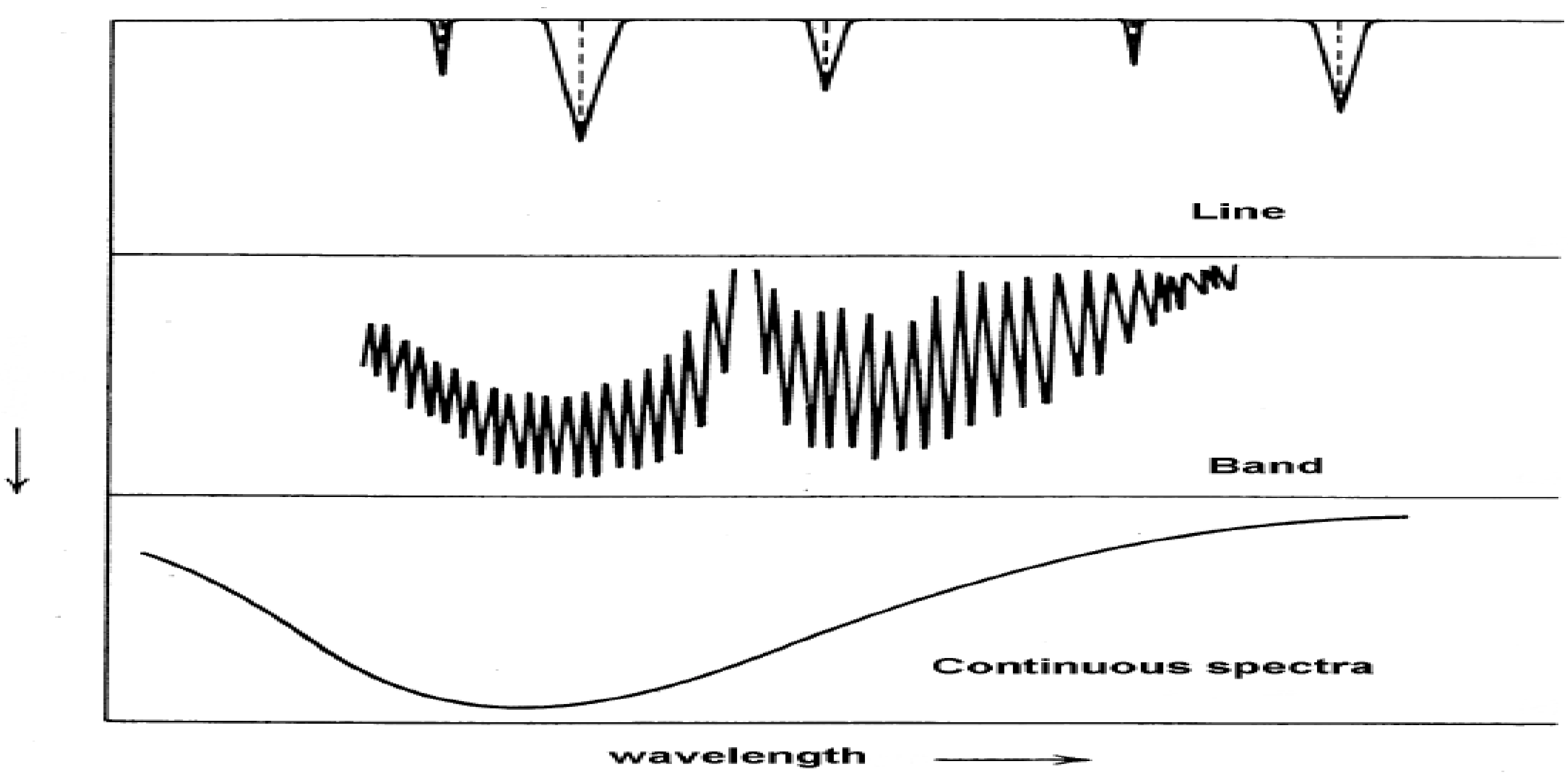
- ✓ Lorentzian profile:

$$L(v - v_1|\alpha_L) = \frac{\alpha_L}{\pi\left((v - v_1)^2 + \alpha_L^2\right)}$$

Absorption Line, Band and Continuum

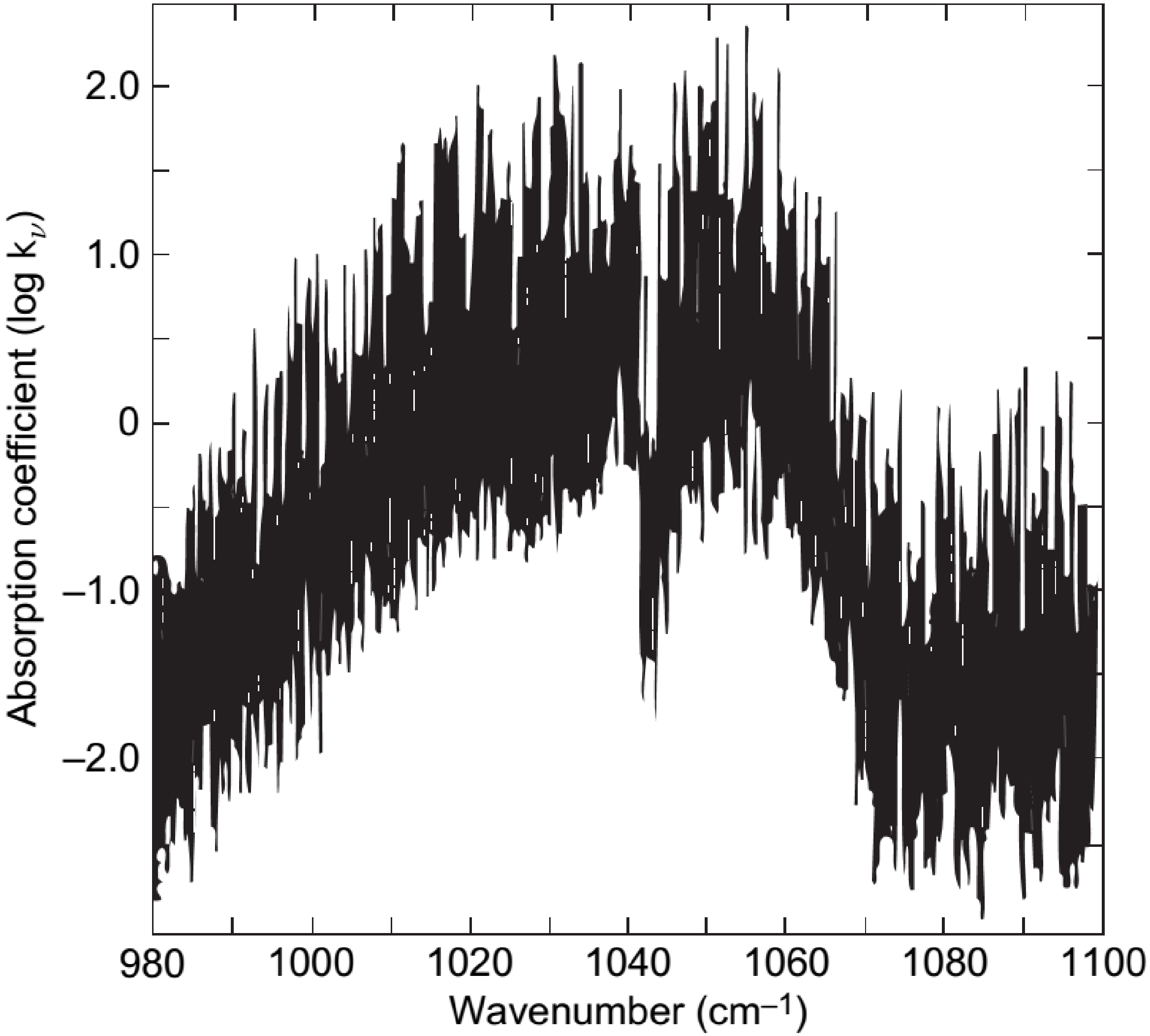
Three types of absorption/emission spectra:

- ✓ Sharp lines of finite widths
- ✓ Aggregations (series) of lines called bands
- ✓ Spectral continuum extending over a broad range of wavelengths

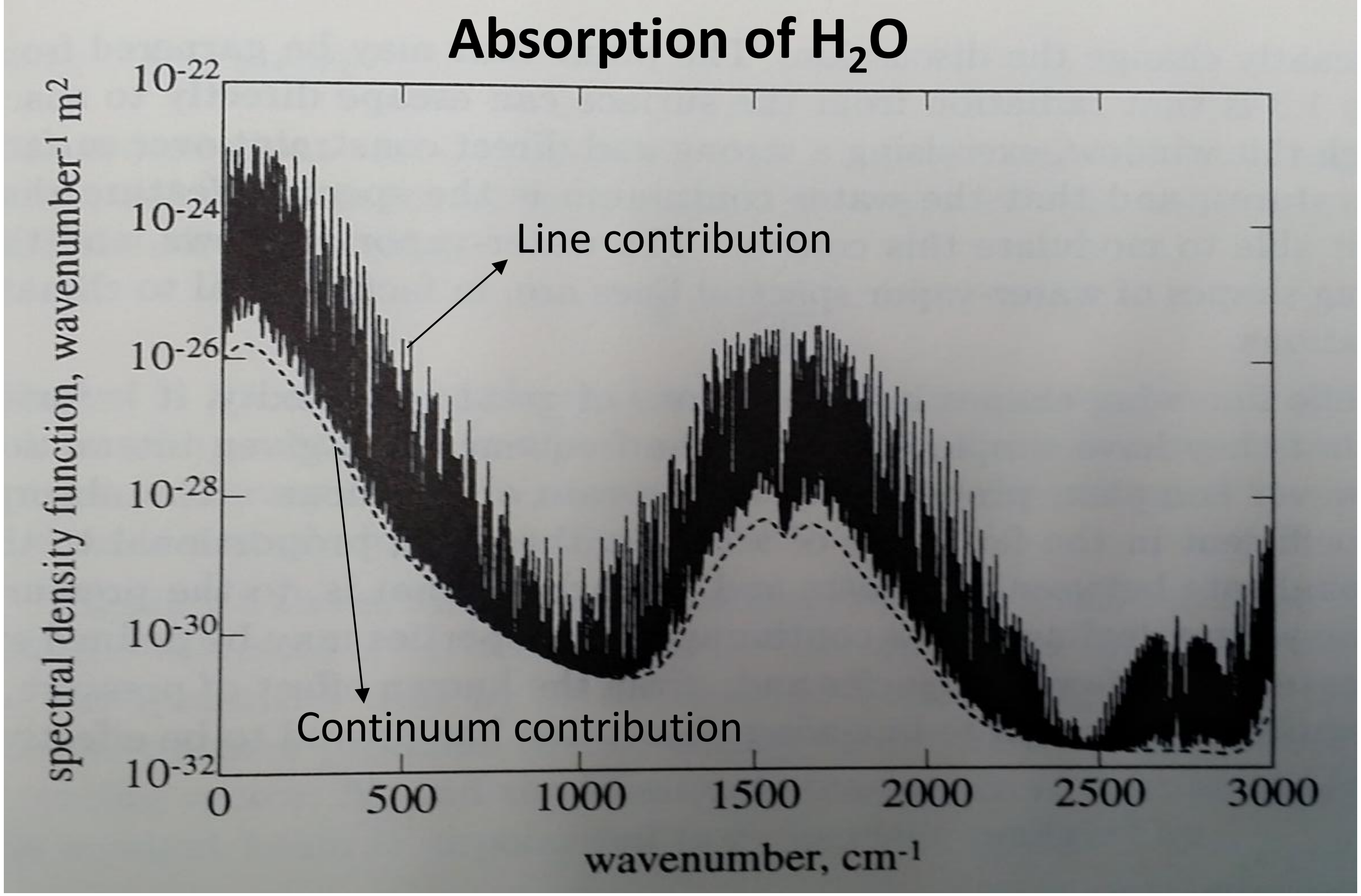


High-res Absorption at the 1000 cm^{-1} Line

There are many vibrational-rotation lines



Line and Continuum Contributions to Absorption



The tail of the shape profile may be very important!

Absorption of Visible and Near-IR Radiation

Absorption of visible and near-IR radiation in the gaseous atmosphere is primarily due to H_2O, O_3, and CO_2.

NOTE: Atmospheric gases absorb only a small fraction of visible radiation.

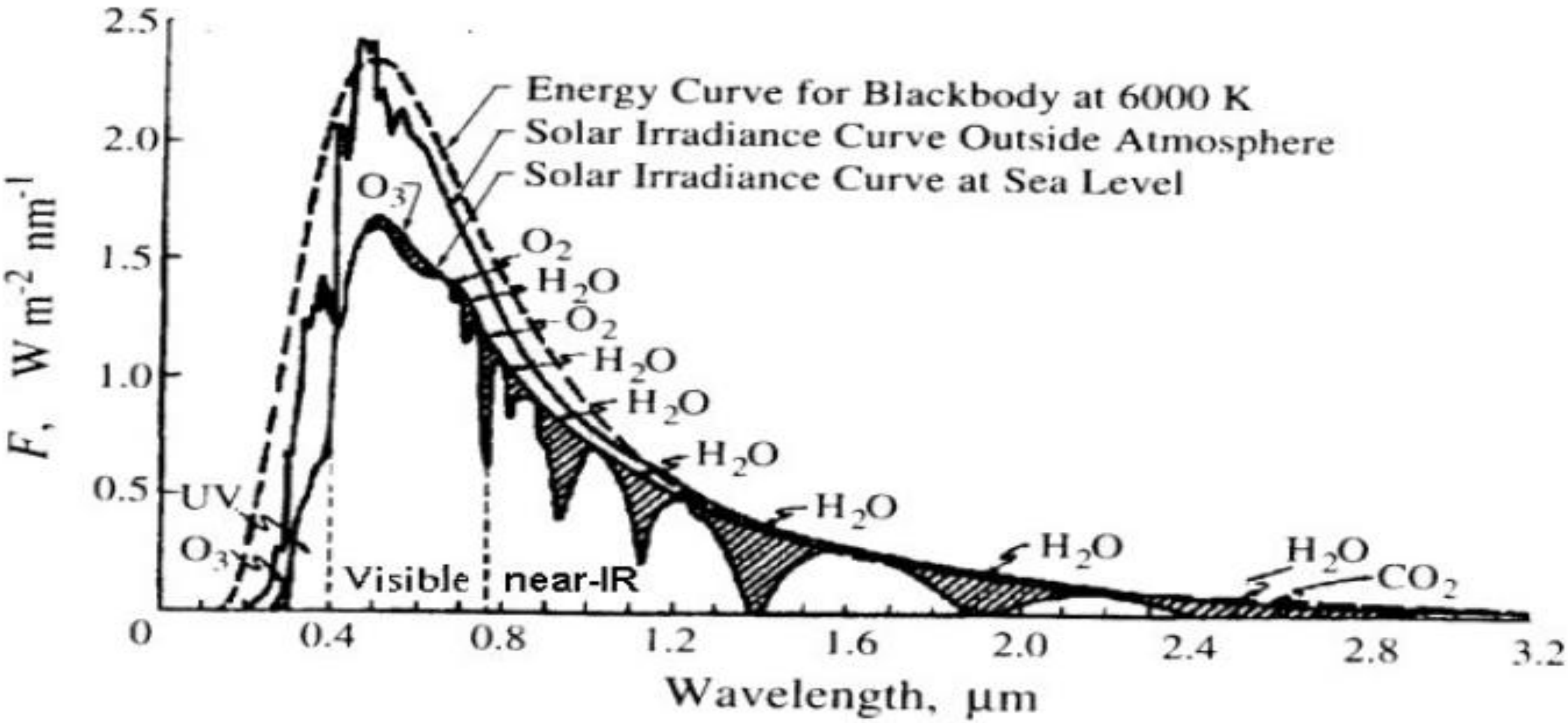


Figure 7.4 Solar spectral irradiance (flux) at the top of the atmosphere and at the surface.

Absorption of UV Radiation (by O_2 and O_3)

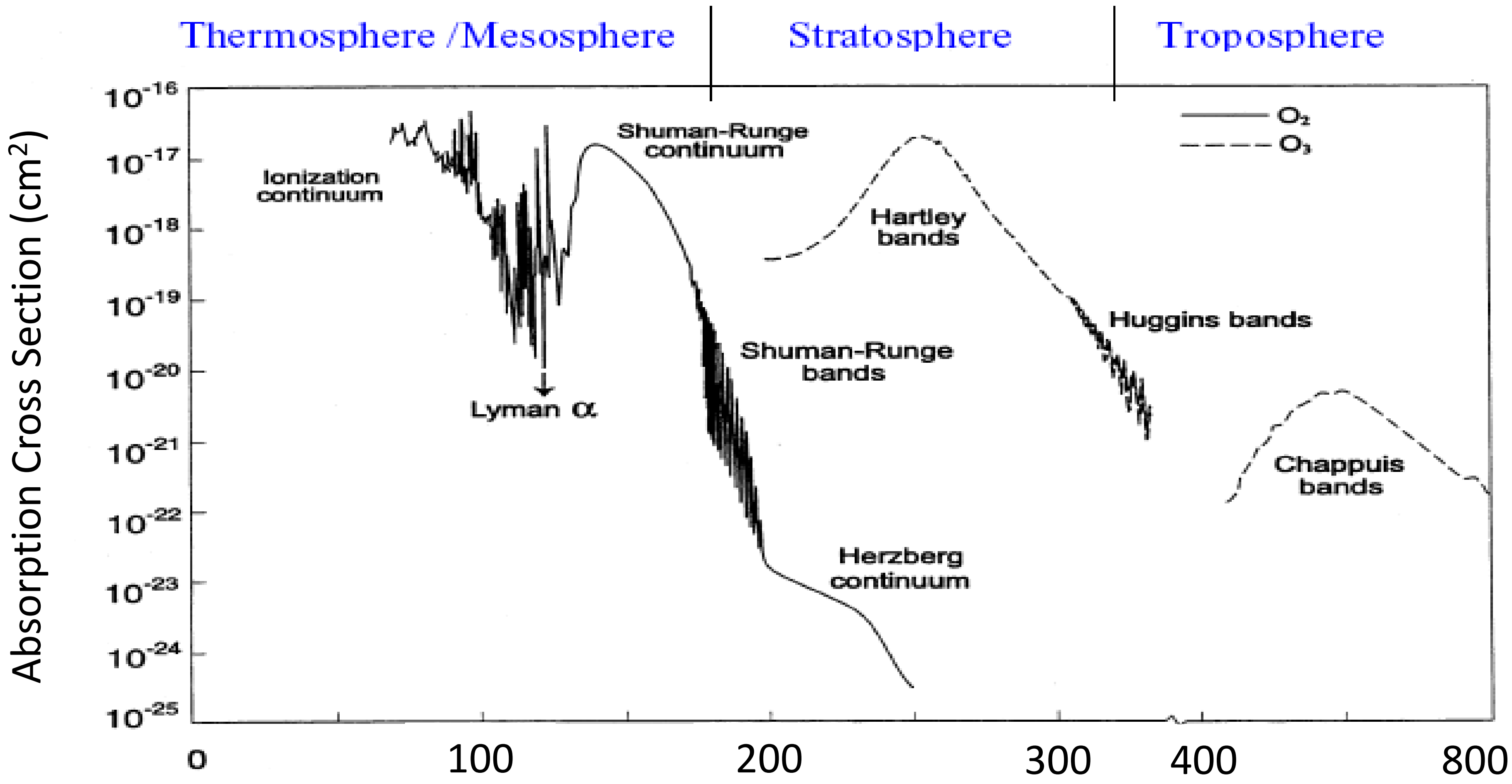


Figure 7.5 Spectral absorption cross-sections of O_2 and O_3

Absorption of Infrared Radiation

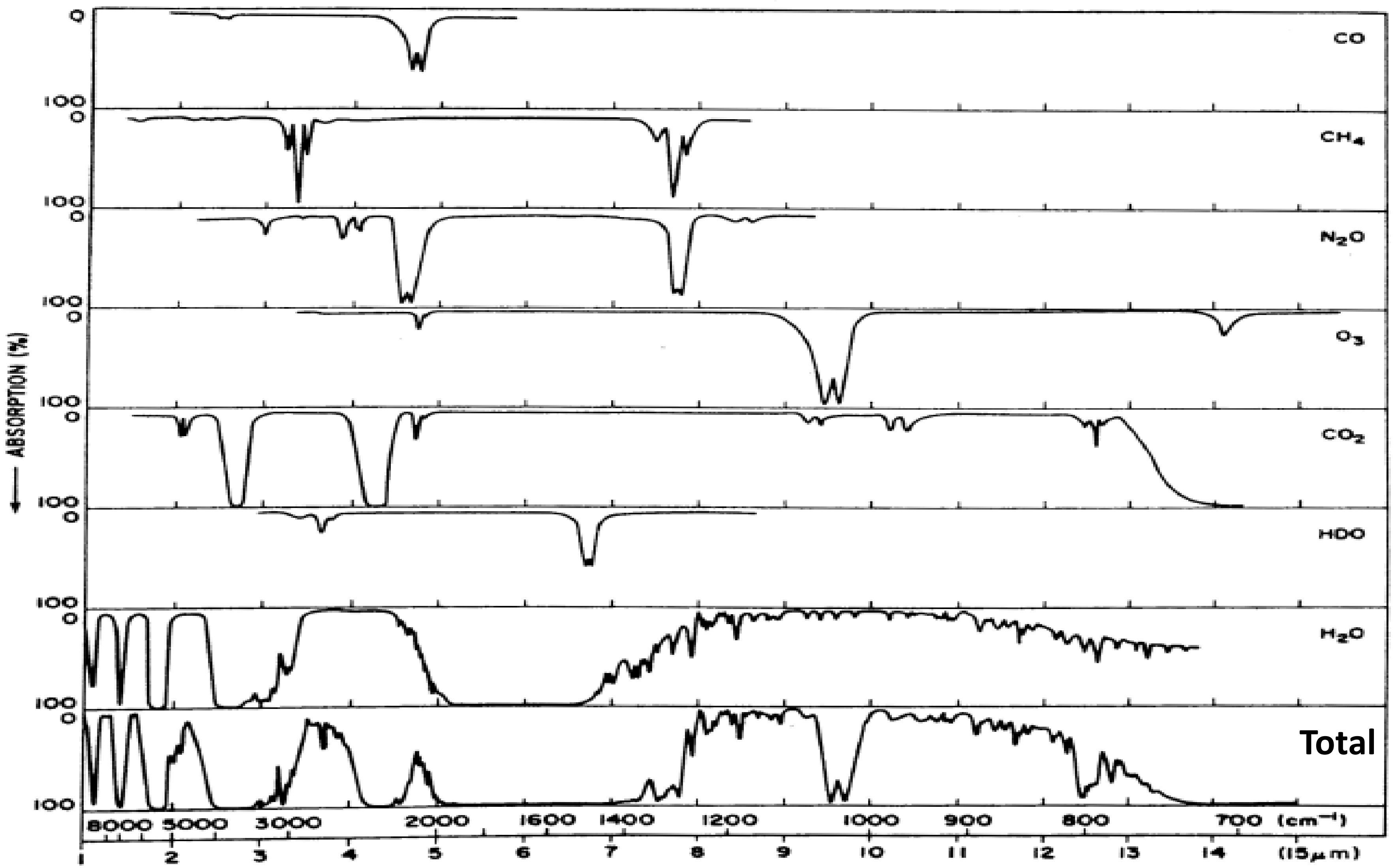


Figure 7.3 Low-resolution IR absorption spectra of the major atmospheric gases.

HITRAN

- HITRAN (High Resolution Transmission) is a compilation of spectroscopic parameters that a variety of computer codes use to predict and simulate the transmission and emission of light in the atmosphere.
- The original version was compiled by the Air Force Cambridge Research Laboratories (1960s). It is maintained and developed at the Harvard-Smithsonian Center for Astrophysics, Cambridge MA, USA.
- HITRAN is the worldwide standard for calculating or simulating atmospheric molecular transmission and radiance from the microwave through ultraviolet region of the spectrum. The current version contains 42 molecular species along with their most significant isotopologues. These data are archived as a multitude of high-resolution line transitions. There are in addition many molecular species collected as cross-section data. These latter include anthropogenic introduced constituents in the atmosphere such as the chlorofluorocarbons.

Rothman et al., "The *HITRAN* 2008 molecular spectroscopic database," *Journal of Quantitative Spectroscopy & Radiative Transfer*110, 533-572 (2009)

思考题

- 随着温室气体的不断增加，其对地球辐射的吸收率可能发生什么变化？
- 分子的吸收曲线存在显著的高光谱特征，那么如何定量表征这些吸收导致的（波长积分）辐射传输？不同方法的优缺点是什么？（line-by-line、correlated-k method）

吸收数据的获取

吸收谱线强度与温度有关：

$$S(T)=S(296)\frac{Q_v(296)\,Q_r(296)}{Q_v(T)\,Q_r(T)}$$

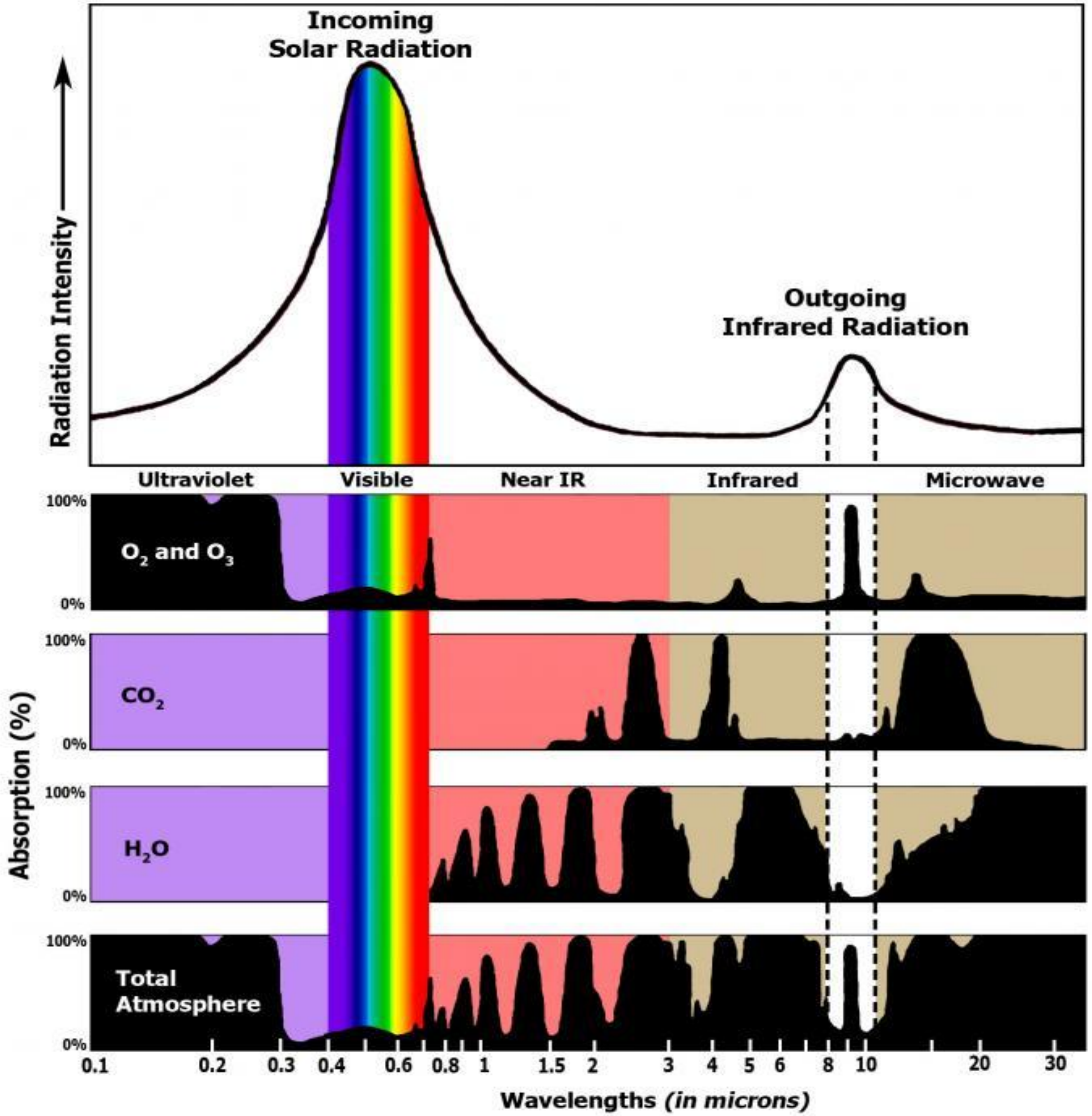
$$\times\exp\left[\frac{1.434\,E_L\,(T-296)}{296\,T}\right]$$

$$Q_r(T)=\left(\frac{T}{296}\right)^n$$

Q_r 和 Q_v 分别称为转动和振动的配分函数

n $Q_v(T)$ **可以查表**

Absorption of Solar and Terrestrial Radiation



http://www.ces.fau.edu/nasa/module-2/how-greenhouse-effect-works.php

几种能级跃迁对应的波长

能级跃迁	电子跃迁 ΔEe	振动 ΔEv	转动 ΔEr
能量差 (eV)	1 ~ 20	0.05~1	<0.1
吸收线中心 波数 υ_0 (cm^{-1})	8064~16129	403~8064	<806
吸收线中心 波长 λ(μm)	0.06~1.24	1.24~25	>12.5