Radiation

Jintai Lin

致谢：本课件中部分资料来自李成才老师（特别是关于辐射的部分）。



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 υ 形式来表达：

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

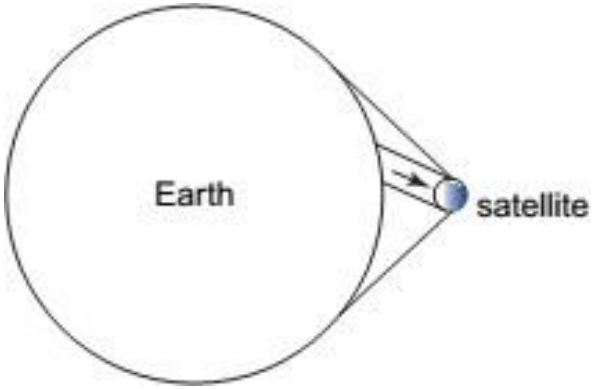
$$B(f,T)=\frac{2f^3h}{c^2}\left(e^{\frac{fh}{kT}}-1\right)^{-1}$$ 单位频率

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

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. A small, perfectly black, spherical satellite is in orbit around the Earth at an altitude of 2000 km. What angle does the Earth subtend when viewed from the satellite?

B. If the Earth radiates as a blackbody at an equivalent blackbody temperature Te = 255 K, calculate the radiative equilibrium temperature of the satellite when it is in the Earth's shadow.

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 $\frac{\mathrm{F}_1}{\mathrm{A}_1} = \frac{\mathrm{F}_2}{\mathrm{A}_2}$

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

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, NH_3, clouds

Scattering

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

Radiative Absorption and Scattering in the Atmosphere

Processes following an interaction $\mathrm{AB} + \gamma \rightarrow \mathrm{AB}^*$ **higher-energy state**

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

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

E_t : translation energy (energy of the molecule due to its motion in a straight line); its mean energy is equivalent to ~ 313 cm^{-1} (far-IR) for T = 300 K

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

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_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.

Absorption with Change in Quantized Electronic Energy

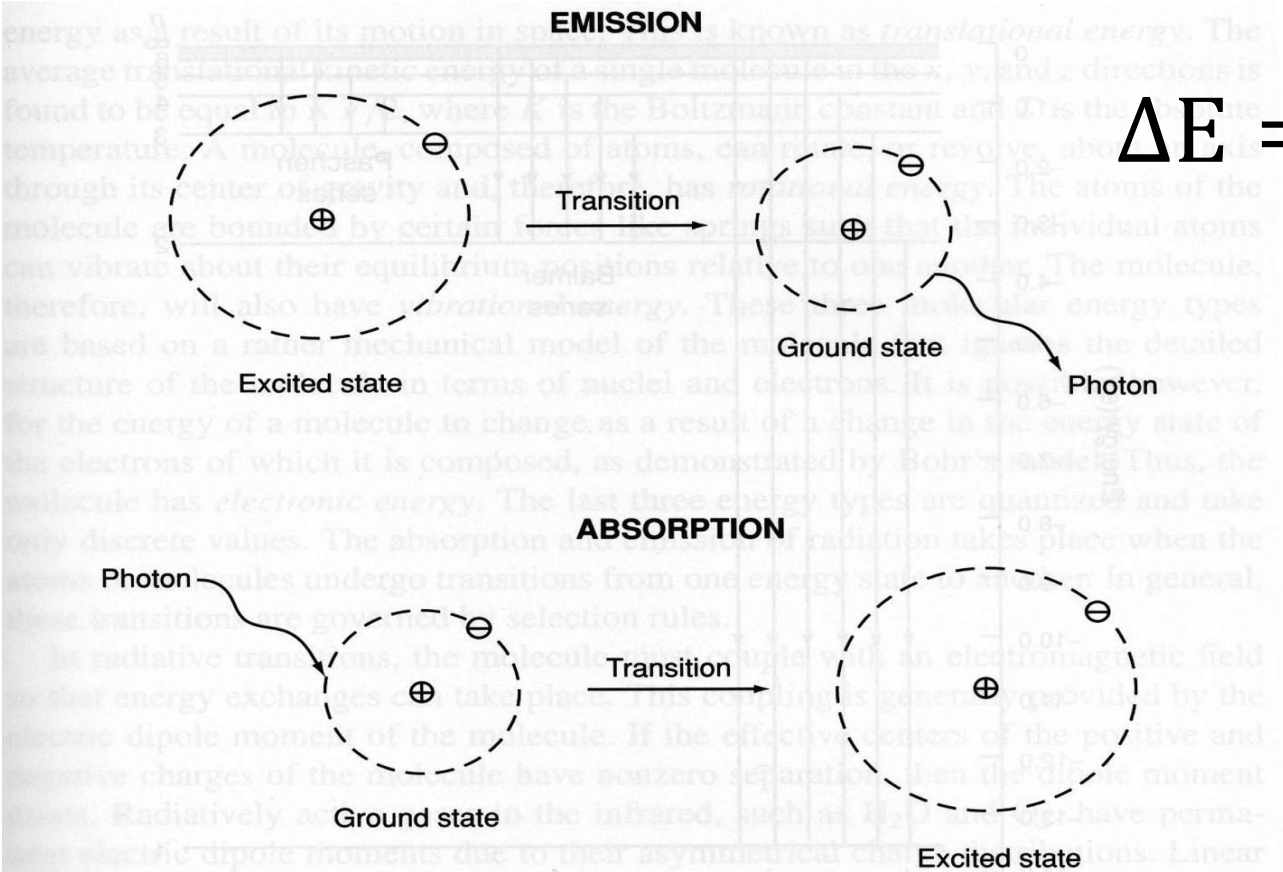


Figure 1.8 Illustration of emission and absorption for a hydrogen atom that is composed of one proton and one electron. The radius of the circular orbit r is given by $n^2 \times 0.53$ Å, where n is the quantum number, and 1 Å $= 10^{-8}$ cm.

$$\Delta E = h\nu$$

Bohr's Hydrogen Atom Spectrum

- Transition of state (j, k are integers)

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

- Wavenumber of emission/absorption lines

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

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

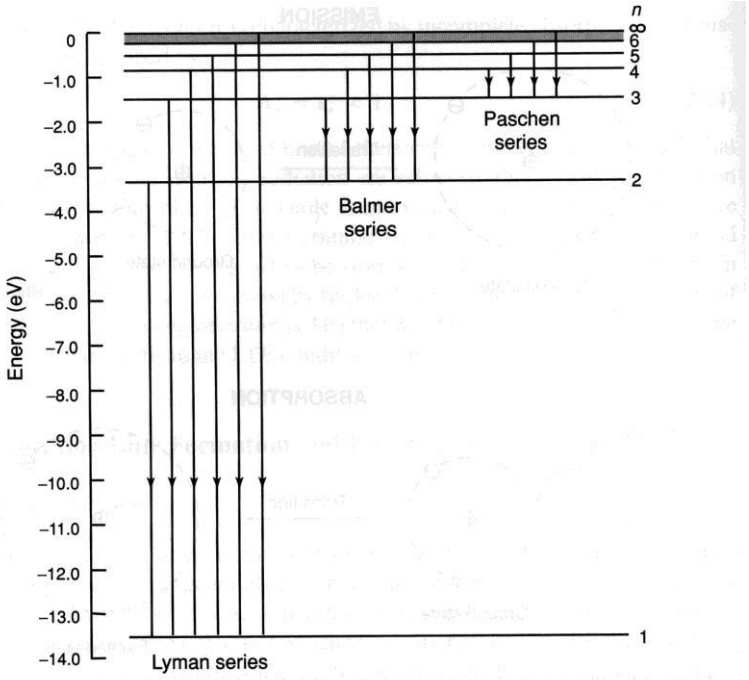
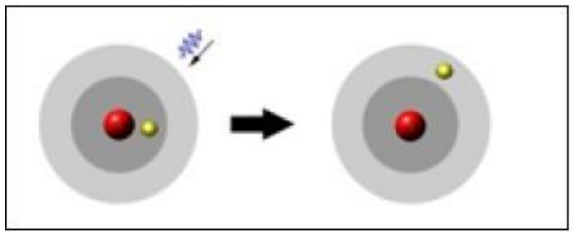
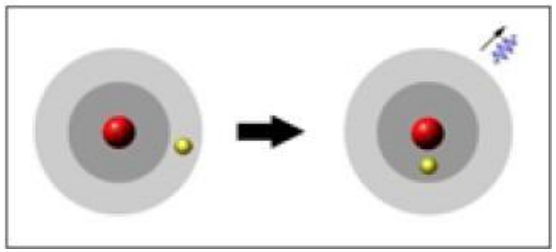


Figure 1.9 Energy level diagram for a hydrogen atom showing the quantum number n for each level and some of the transitions that appear in the spectrum. An infinite number of levels is crowded in between the levels marked $n = 6$ and $n = \infty$.

Absorption

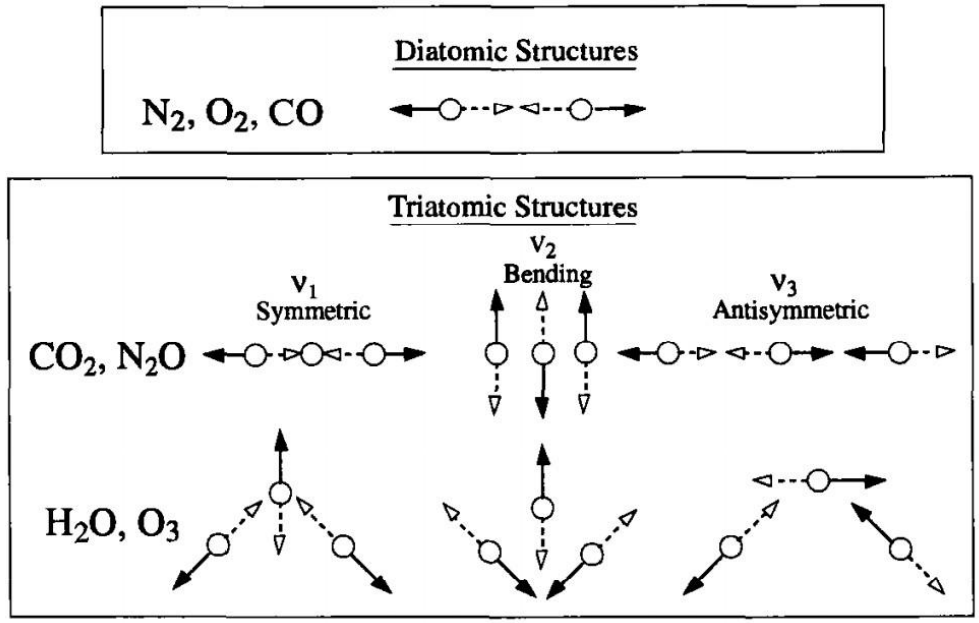


Emission



Absorption with Change in Quantized Vibrational Energy

Molecule	Arrangement	Permanent Dipole Moment 永久偶极矩
N_2	N N	No
O_2	O O	No
CO	C O	Yes
CO_2	O C O	No
N_2O	N N O	Yes
H_2O	H O H, 104.5°	Yes
O_3	O O O, 116.8°	Yes
CH_4	H C H, H, H	No



- 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

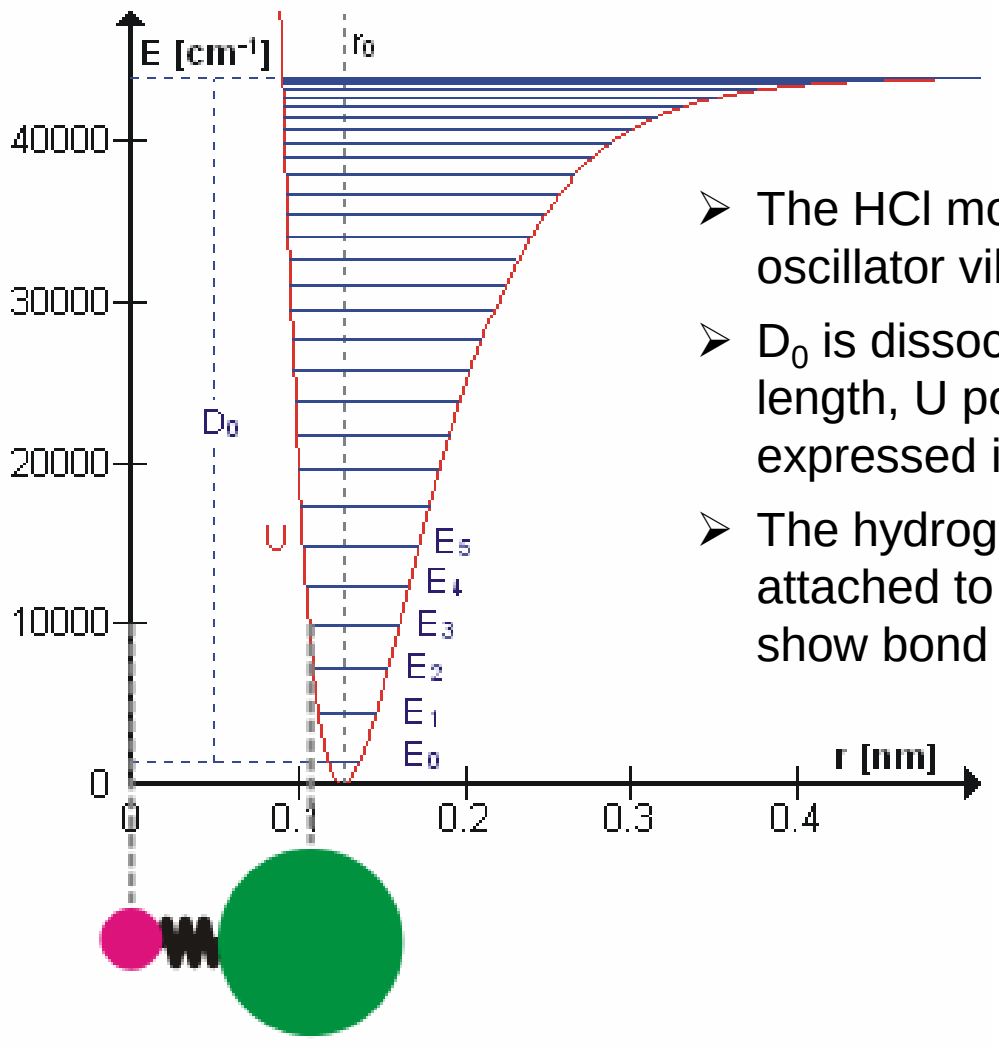
Examples of Vibration Modes

Wavelengths of Vibrational Modes of Some Important Atmospheric Molecules

Species	Vibrational modes		
	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



- The HCl molecule as an anharmonic oscillator vibrating at energy level E3.
- D_0 is dissociation energy here, r_0 bond length, U potential energy. Energy is expressed in wavenumbers.
- The hydrogen chloride molecule is attached to the coordinate system to show bond length changes on the curve.

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，这里遵循一个概率分布，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

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

独立吸收？

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

谱线增宽

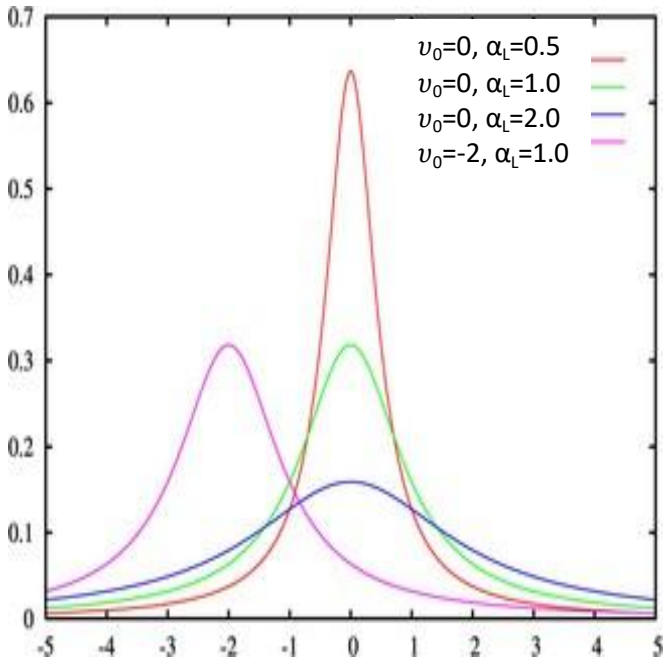
- 一根吸收线与一个能级跃迁相对应，但是，
- 存在三种谱线增宽方式：
  - 自然增宽：测不准原理（影响很小）
  - 压力增宽：粒子碰撞产生能级/相位/相干性的变化，影响到有效相位扰动碰撞频率。气体压力大，分子密度大，碰撞频率就增加，从而使谱线的加宽增大。
  - 多普勒增宽：分子处于无规则的热运动之中。运动的分子吸收的电磁波频率与其在静止时所吸收的电磁波频率有一个差别，称为多普勒频偏，导致多普勒增宽。

    类似地，火车由远及近声音的变化？

压力增宽

- 压力增宽可以用 Lorentz 线型来表示：

$$k_\upsilon = \frac{S}{\pi}\frac{\alpha_L}{(\upsilon - \upsilon_0)^2 + \alpha_L^2}$$



- S 是谱线的强度，即为吸收线增宽后的总面积

$$S = \int_{-\infty}^{+\infty} k_\upsilon d\upsilon \qquad \text{量纲: } k_{\mathrm{ab}}$$

- $\upsilon_0 = (E_U - E_L)/hc$ 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 $\upsilon = \upsilon_0$处，$k_{\upsilon 0} = S/(\pi\alpha_L)$

在$\upsilon = \upsilon_0 \pm \alpha_L$处，$k_\upsilon = \frac{1}{2}k_{\upsilon 0} = S/(2\pi\alpha_L)$

- 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，

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

v 为分子沿着光传播方向的运动速度分量

- 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，$k_{\upsilon 0} = S/(\alpha_D\sqrt{\pi})$

在 $\upsilon = \upsilon_0 \pm \alpha_D$ 处，$k_\upsilon = k_{\upsilon 0}\cdot e^{-1}$

- 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

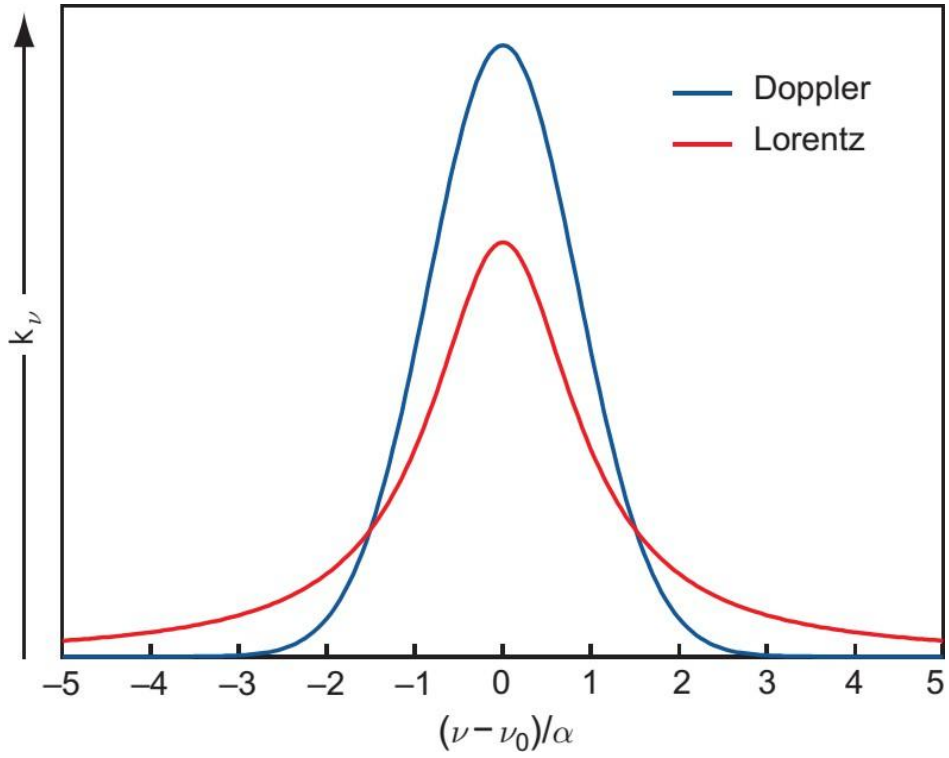
$$\alpha_D = \frac{\upsilon_0}{c}(2kT/m)^{1/2}$$

分子沿着光传播方向的运动速度分量呈现高斯分布（速率为麦克斯韦分布）：

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

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)	标准状态下的多普勒增宽半高半宽(cm^{-1}) $HWHM = 0.83\alpha_D$	标准状态下的压力增宽半高半宽(cm^{-1}) $HWHM = \alpha_L$	两种HWHM相同时的气压 (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	3.2
CO_2	4.3	0.0021	0.15	14.0
CO_2	15	0.0006	0.15	4.0
O_3	4.7	0.002	0.16	12.5
O_3	9.6	0.00087	0.16	5.4
O_3	14.1	0.0006	0.16	3.8

Voigt Profile 沃伊特线型:
Convolution (卷积) of Lorentz and Doppler Broadening

$$V(\upsilon|\alpha_D,\alpha_L)=\int_{-\infty}^{+\infty} D(\upsilon_1-\upsilon_0|\alpha_D)\cdot L(\upsilon-\upsilon_1|\alpha_L)\cdot d\upsilon_1$$

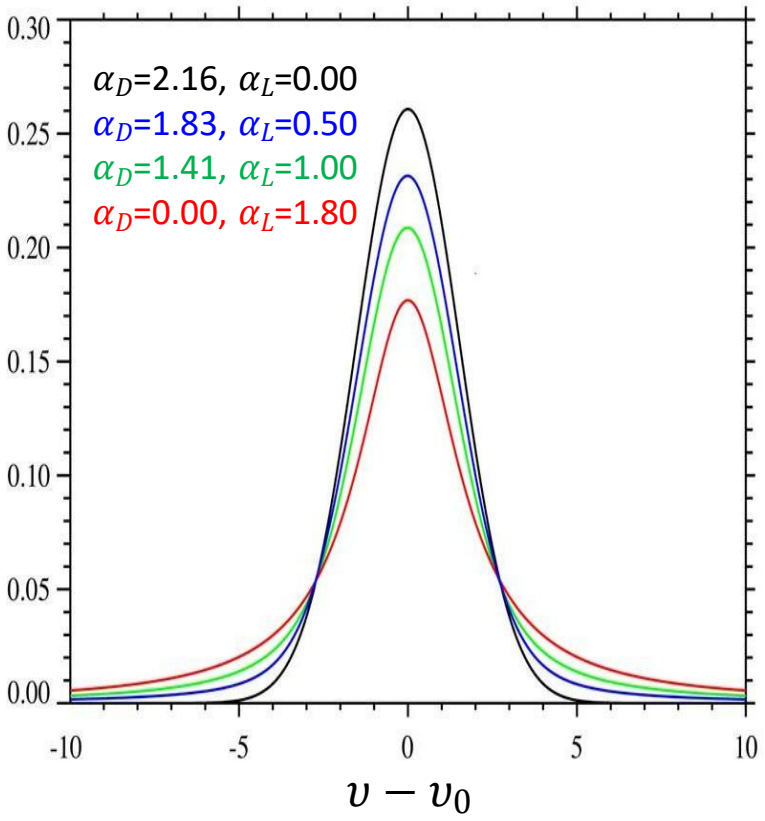
$$k_\upsilon = S\cdot V(\upsilon|\alpha_D,\alpha_L)$$

✓ Doppler profile:

$$\mathrm{D}(\upsilon_1-\upsilon_0|\alpha_D)=\frac{1}{\alpha_D\sqrt{\pi}}\exp\left[-\frac{(\upsilon_1-\upsilon_0)^2}{\alpha_{\mathrm{D}}^2}\right]$$

✓ Lorentzian profile:

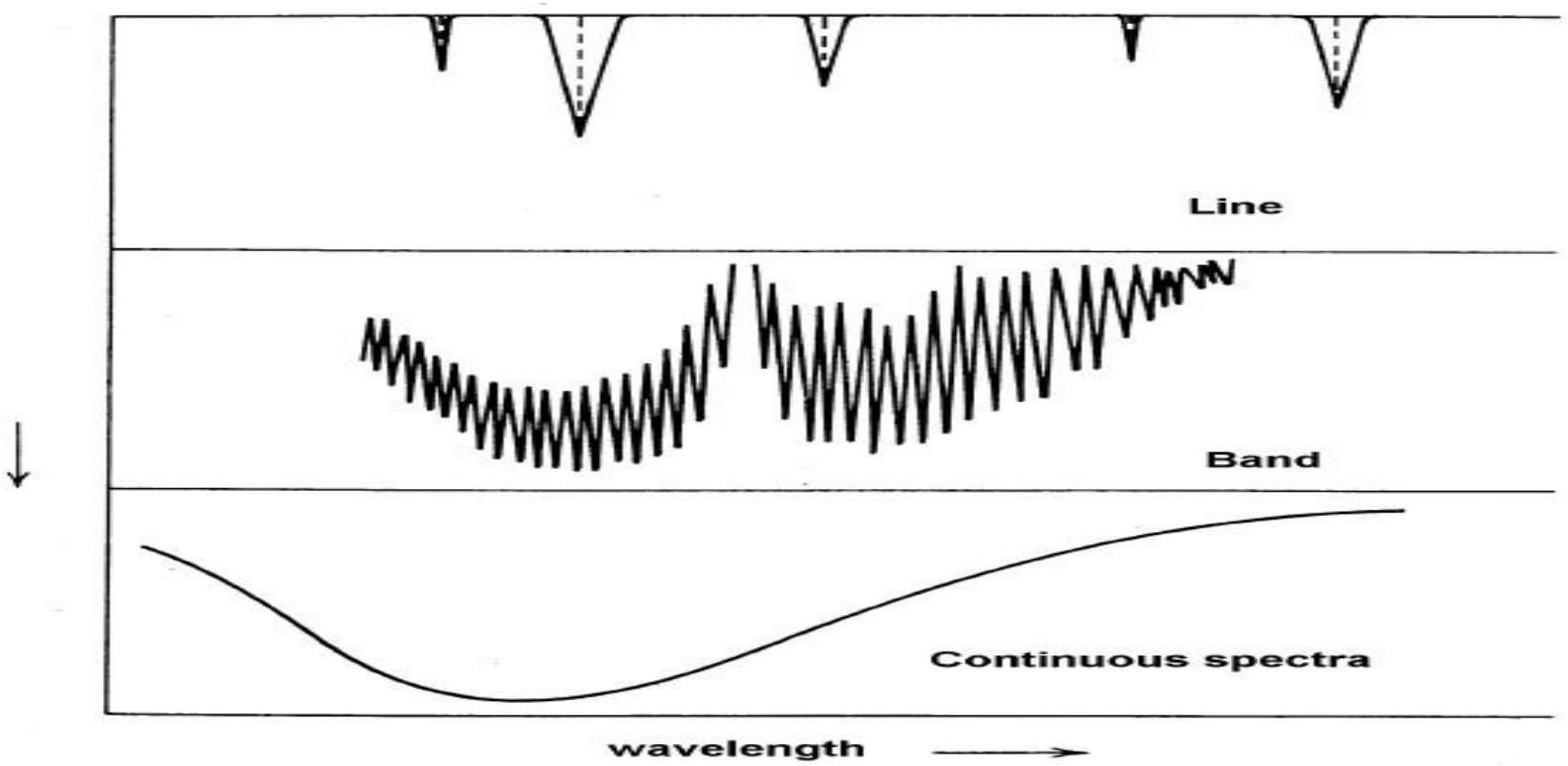
$$L(\upsilon-\upsilon_1|\alpha_L)=\frac{\alpha_L}{\pi\left((\upsilon-\upsilon_1)^2+\alpha_L^2\right)}$$



Absorption Line, Band and Continuum

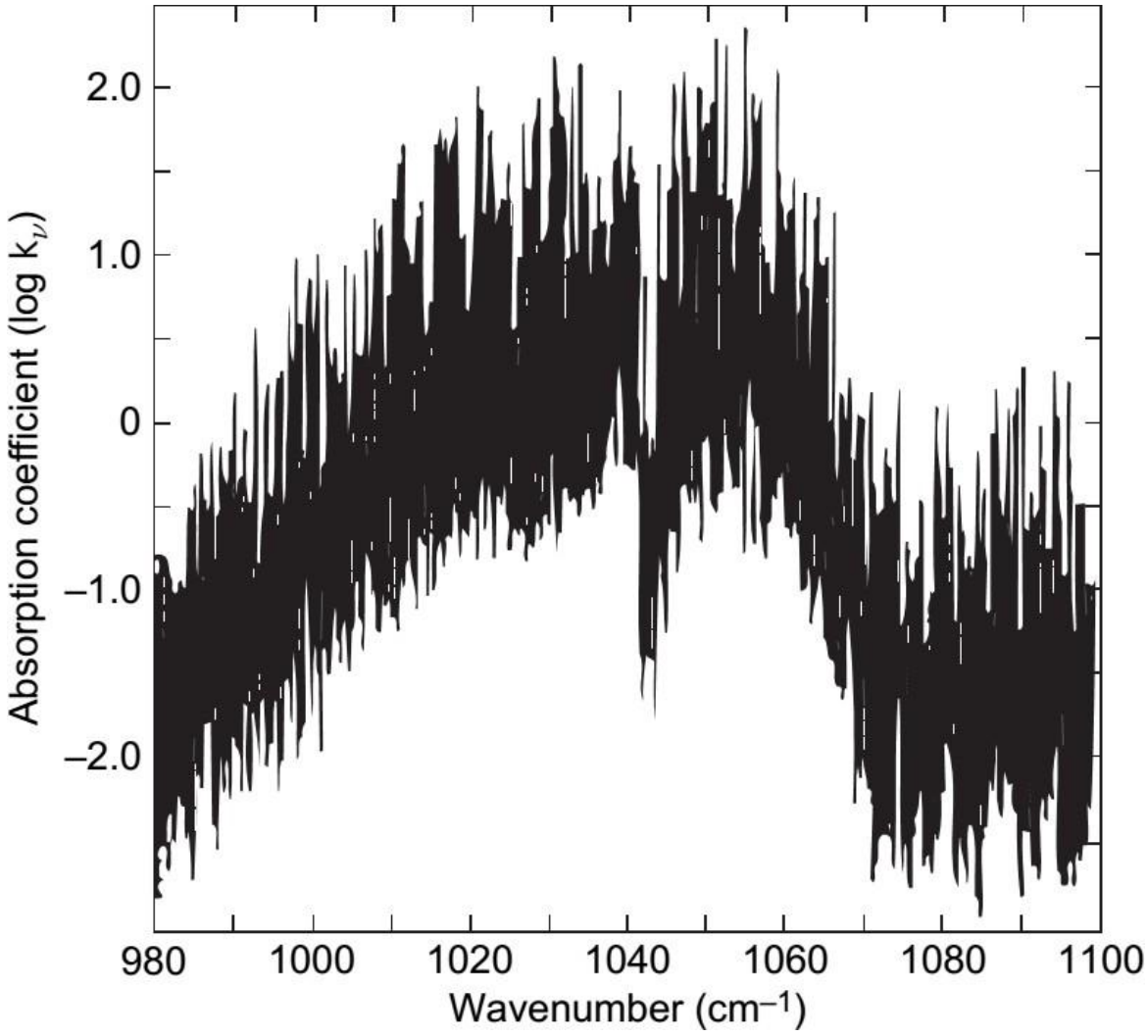
Three types of absorption/emission spectra:

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

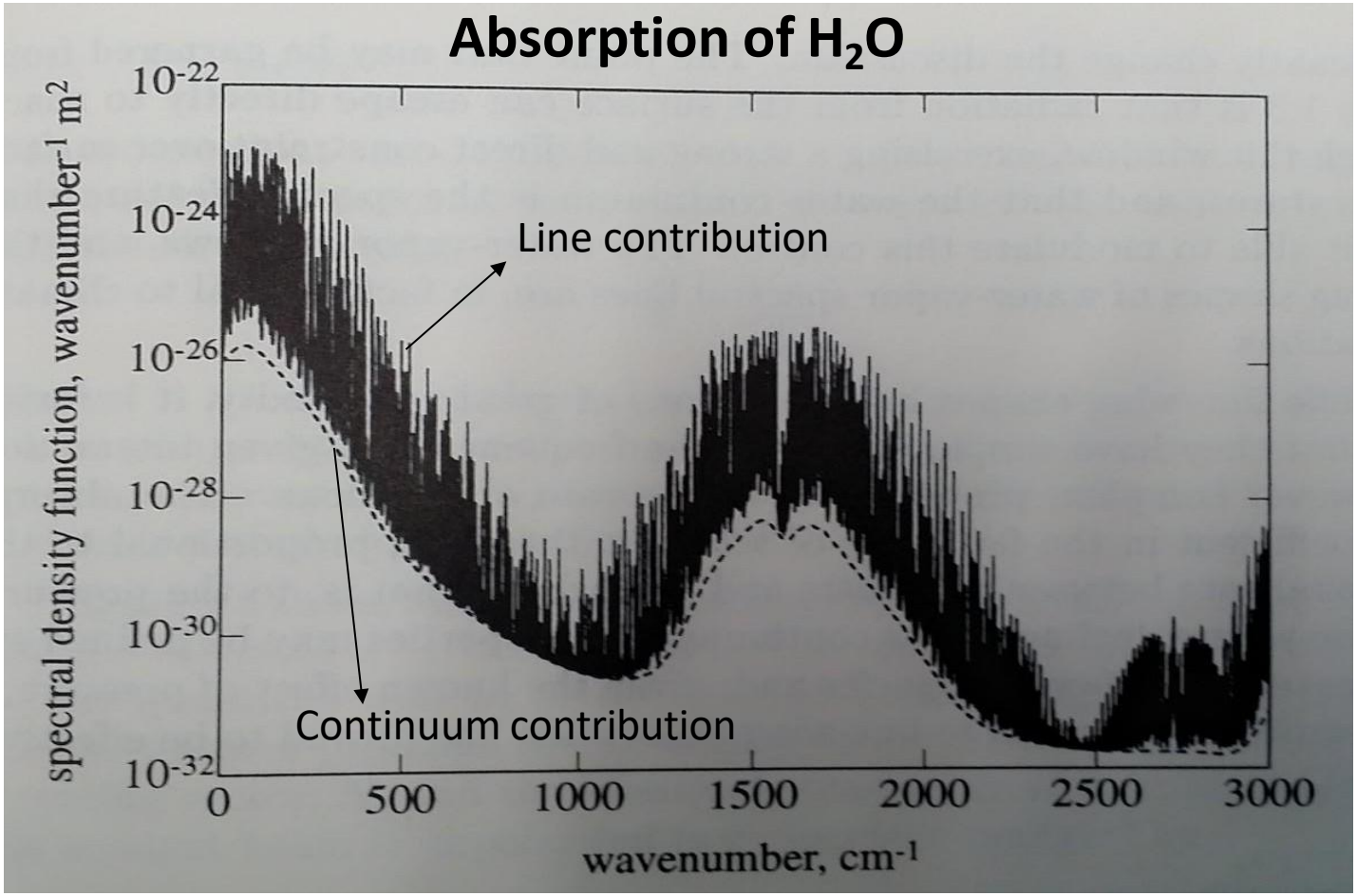


High-res Absorption around 1000 cm^{-1}

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.

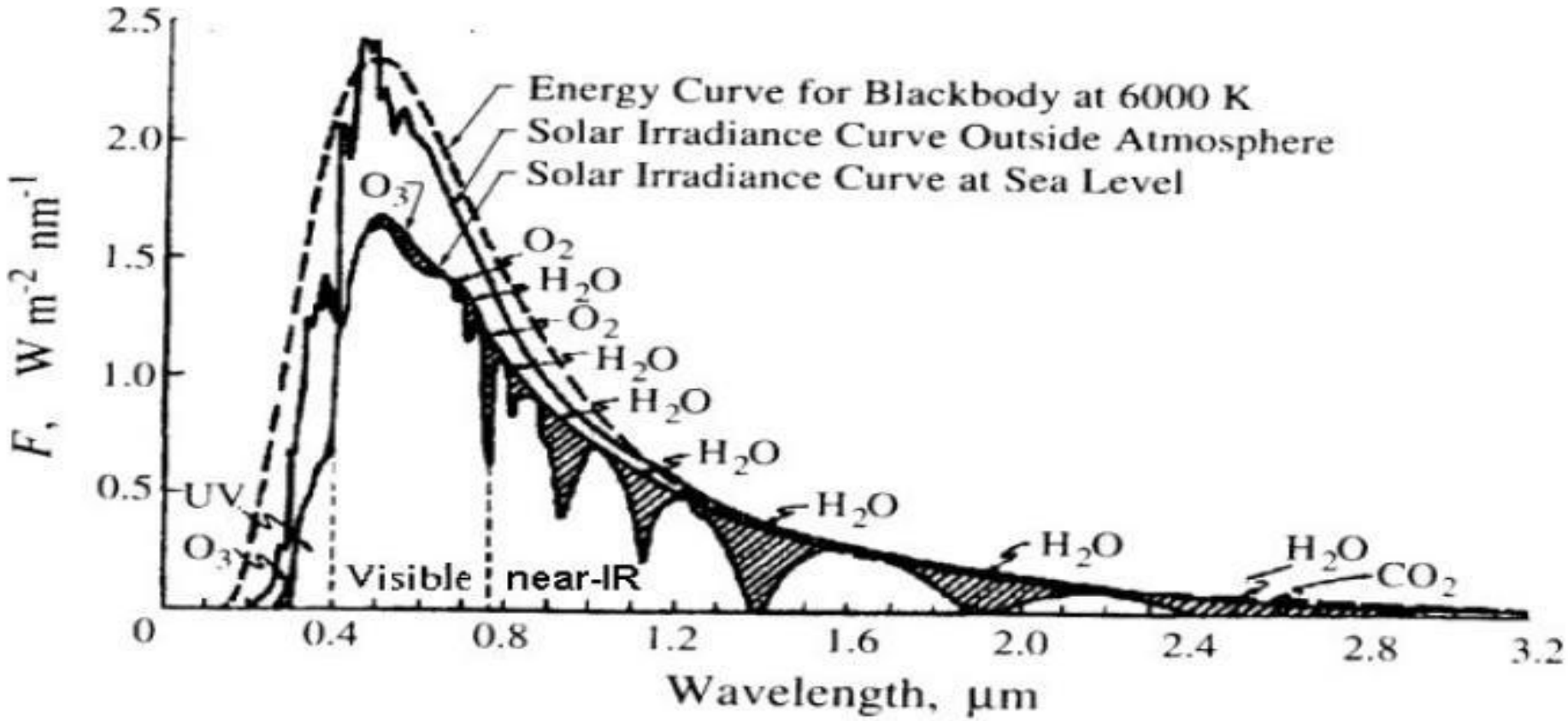
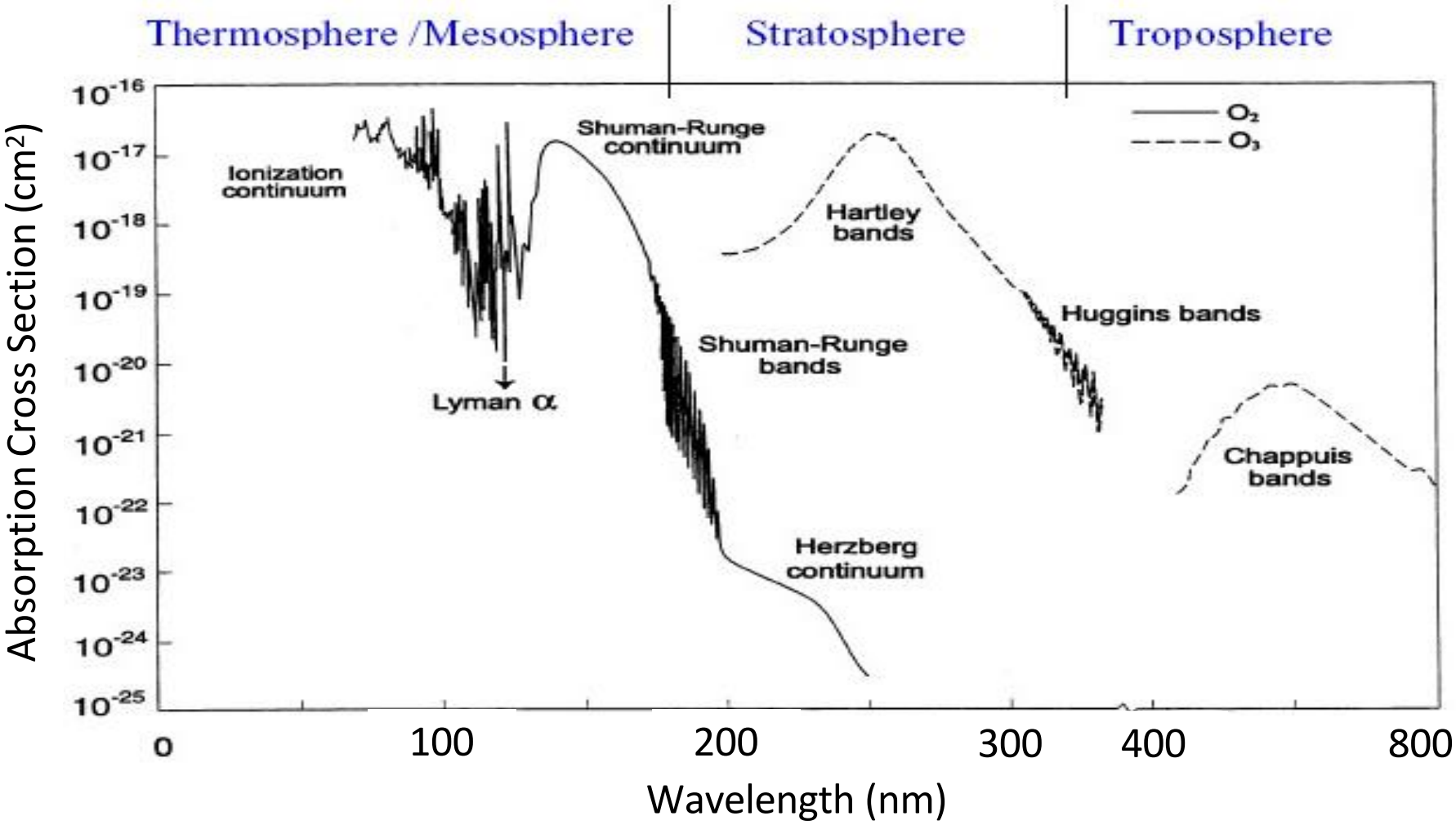


Figure 7.4 Solar spectral irradiance (flux) at the top of the atmosphere and at the surface.

Absorption of UV Radiation (by O_2 and O_3)



Absorption of Infrared Radiation

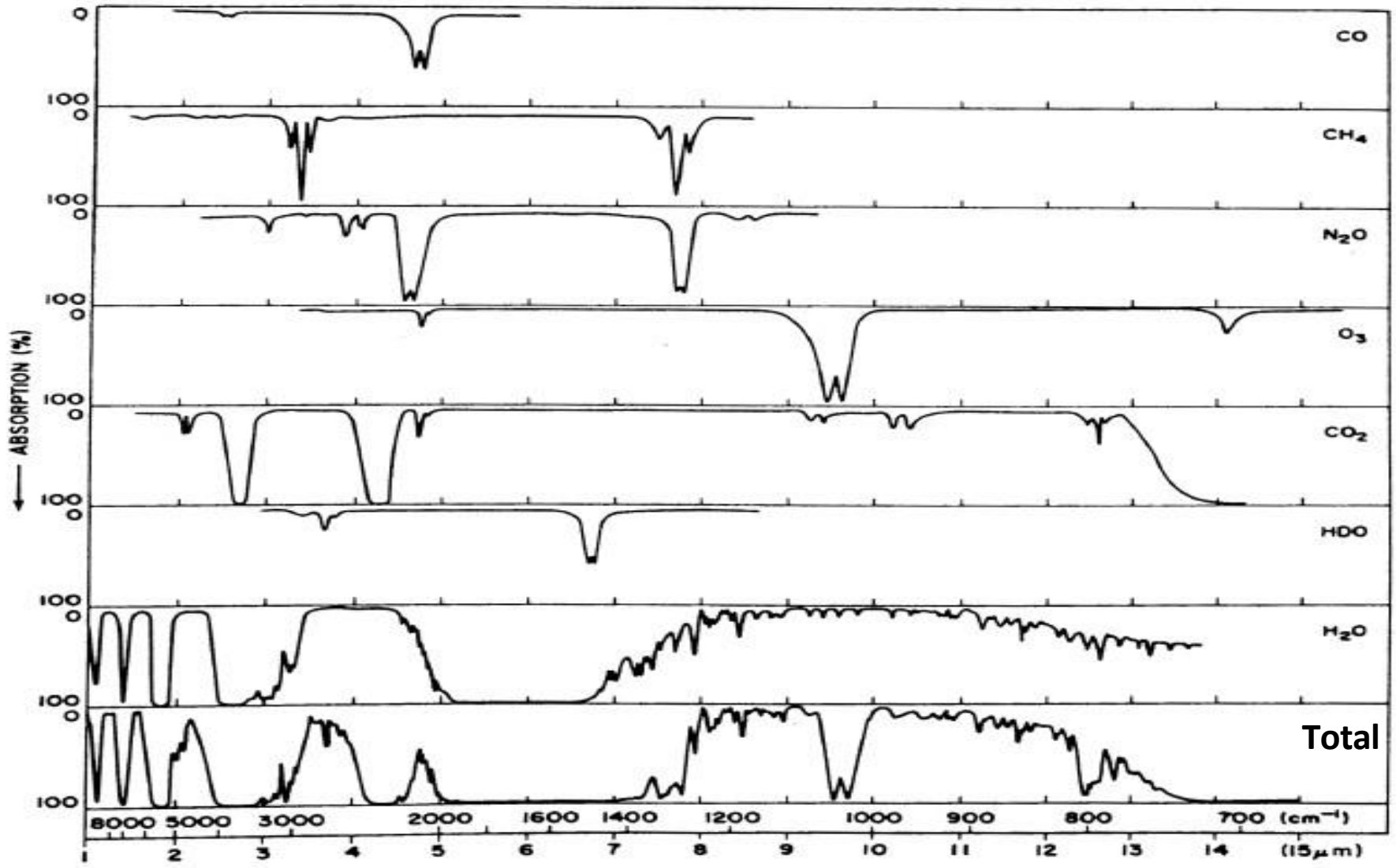


Figure 7.3 Low-resolution IR absorption spectra of the major atmospheric gases.

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：

$$S(T) = S(296)\frac{Q_{\mathrm{v}}(296)Q_r(296)}{Q_{\mathrm{v}}(T)Q_r(T)} \times exp\left[\frac{1.439E_L(T-296)}{296T}\right]$$

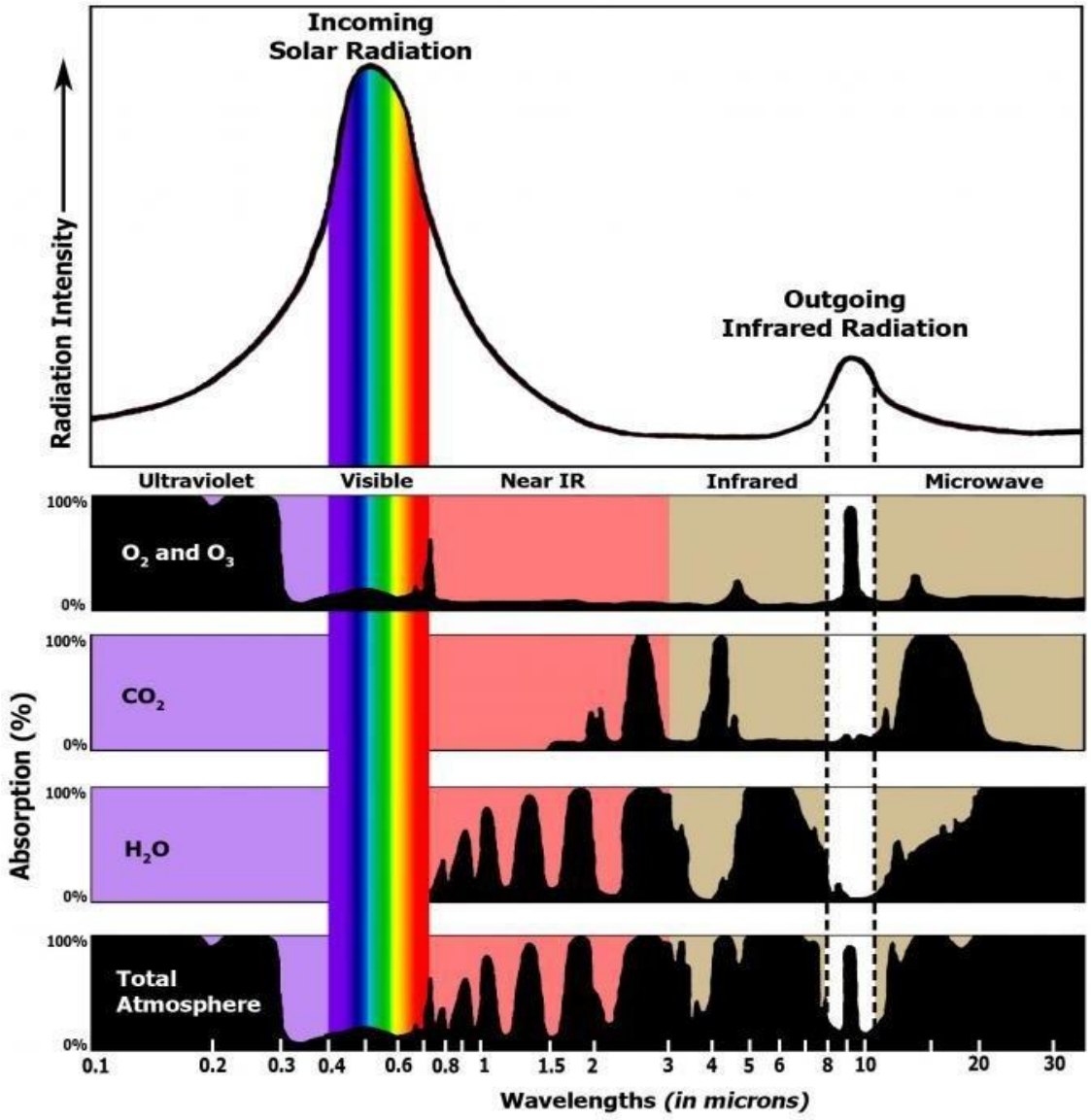
未考虑受激辐射修正因子

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

Q_r和 Q_v分别称为转动和振动的配分函数

n 和 $Q_v(T)$ 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})	8064~161290	403~8064	<806
吸收线中心波长 λ(μm)	0.06~1.24	1.24~25	>12.5