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

- **Plank function** can be expressed in wavelength, frequency, or wavenumber domains as

$$B_\lambda(T) = \frac{2hc^2}{\lambda^5(\exp(hc/k_B T\lambda) - 1)} \qquad [4.1]$$

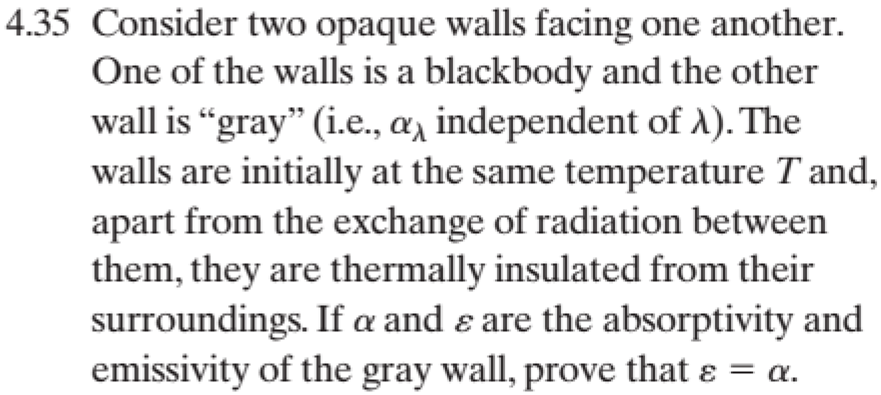
$$B_{\tilde{\nu}}(T) = \frac{2h\tilde{\nu}^3}{c^2(\exp(h\tilde{\nu}/k_B T) - 1)} \qquad [4.2]$$

$$B_\nu(T) = \frac{2h\nu^3 c^2}{\exp(h\nu c/k_B T) - 1} \qquad [4.3]$$

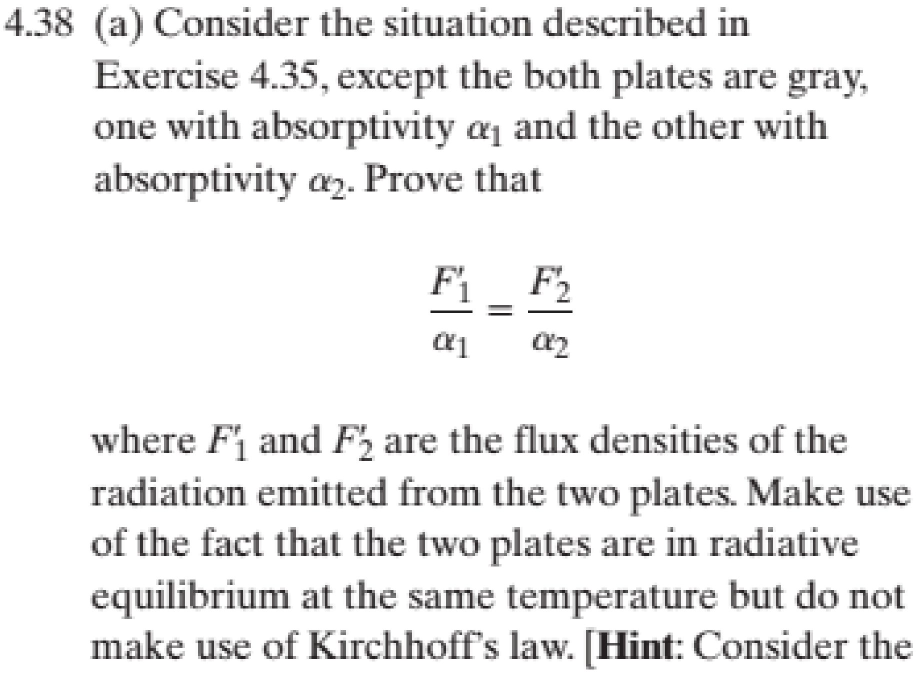
where **λ** is the wavelength; $\tilde{\nu}$ is the frequency; **ν** is the wavenumber;
h is the Plank's constant; ***k_B*** is the Boltzmann's constant ($k_B = 1.38\text{x}10^{-23}$ J K^{-1});
c is the velocity of light; and ***T*** is the absolute temperature of a blackbody.

问题1：从4. 1推导4. 2和4. 3
问题2：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



4.35 Consider two opaque walls facing one another. One of the walls is a blackbody and the other wall is "gray" (i.e., α_λ independent of λ). The walls are initially at the same temperature T and, apart from the exchange of radiation between them, they are thermally insulated from their surroundings. If α and ε are the absorptivity and emissivity of the gray wall, prove that $\varepsilon = \alpha$.



4.38 (a) Consider the situation described in Exercise 4.35, except the both plates are gray, one with absorptivity α_1 and the other with absorptivity α_2. Prove that

$$\frac{F'_1}{\alpha_1} = \frac{F'_2}{\alpha_2}$$

where F'_1 and F'_2 are the flux densities of the radiation emitted from the two plates. Make use of the fact that the two plates are in radiative equilibrium at the same temperature but do not make use of Kirchhoff's law. [**Hint**: Consider the

Michael Wallace book

大气中的吸收、散射

吸收：

- ✓ 太阳短波辐射：O_2、O_3、H_2O、CO_2、气溶胶、NO_2、HCHO、SO_2、CHOCHO、其它痕量气体
- ✓ 地球长波辐射：H_2O、CO_2、CH_4、O_3、N_2O、halocarbons、云

散射：

- ✓ 太阳短波辐射：气体分子（O_2、N_2等）、气溶胶、云
- ✓ 地球长波辐射：气溶胶、云、雨滴、雪花

Absorption, Scattering, Transmission 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

✓ P2,3,4 have a thermalization time that depends on pressure

Internal Energy of a Molecule

$E = E_t + E_v + E_r + E_e$

E_e, E_v, E_r are quantized 量子化

E_t: translation energy (energy of the molecule of due to its motion in a straight line); about 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.

Quantized Electronic Energy

$$\Delta E = h\nu$$

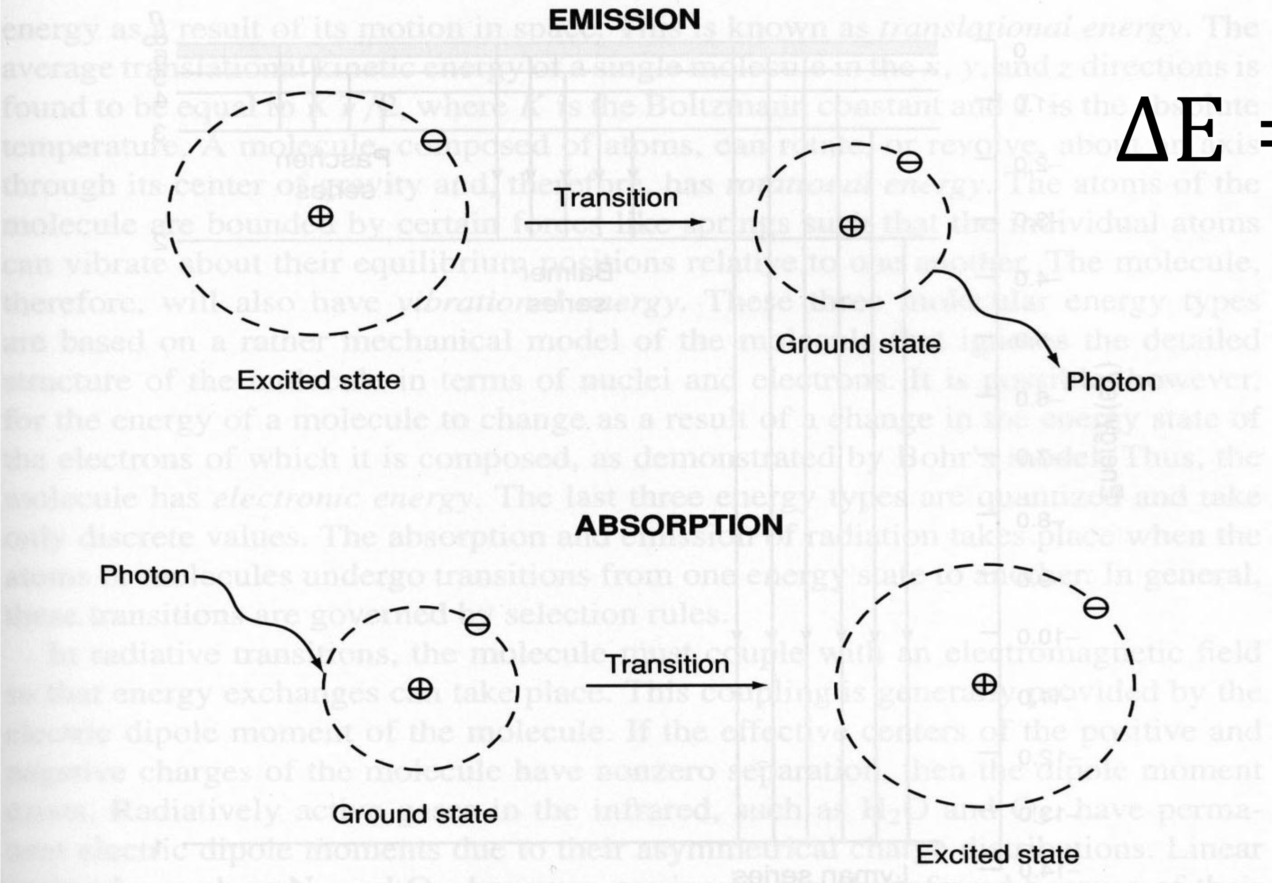


Figure 1.8 Illustration of emission and absorption for a hydrogen atom that is composed of one proton and one electron. The radius of the circular orbit r is given by $n^2 \times 0.53$ Å, where n is the quantum number, and $1\ \text{Å} = 10^{-8}$ cm.

Bohr’s Hydrogen Atom

- Transition of state (k,j: integers)

$$E_k - E_j = h\nu$$

- Wavenumber of emission/absorption lines

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

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

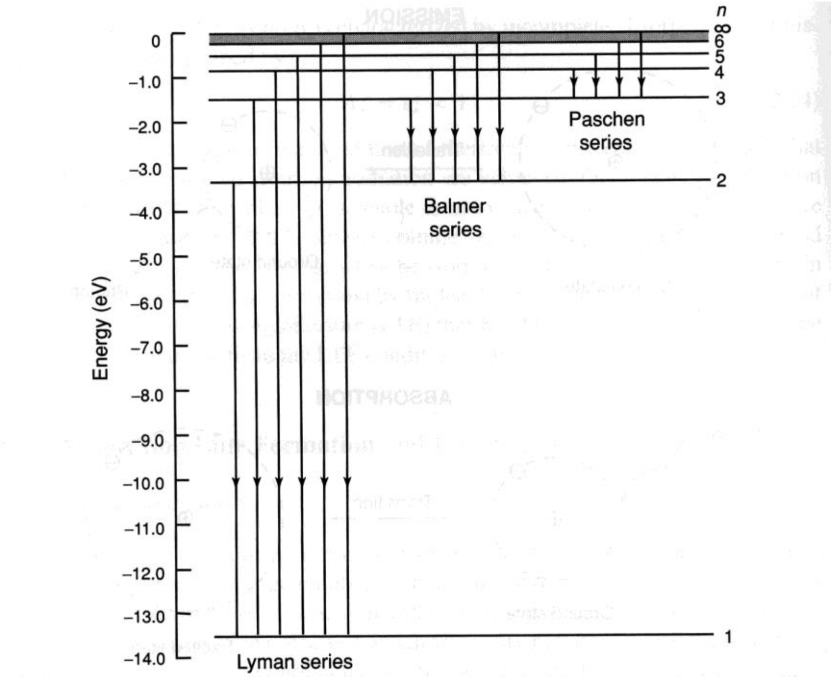
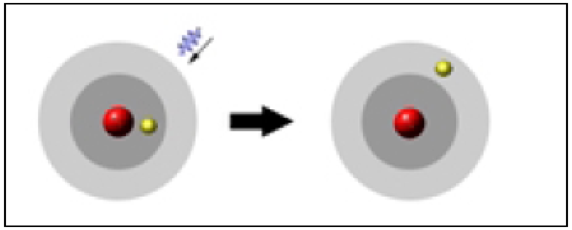
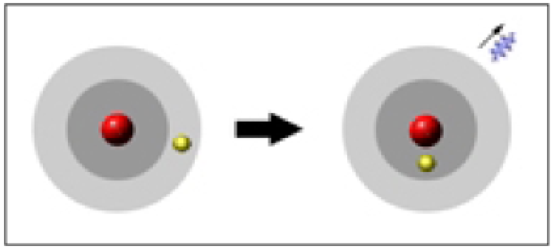


Figure 1.9 Energy level diagram for a hydrogen atom showing the quantum number n for each level and some of the transitions that appear in the spectrum. An infinite number of levels is crowded in between the levels marked $n = 6$ and $n = \infty$.

Absorption

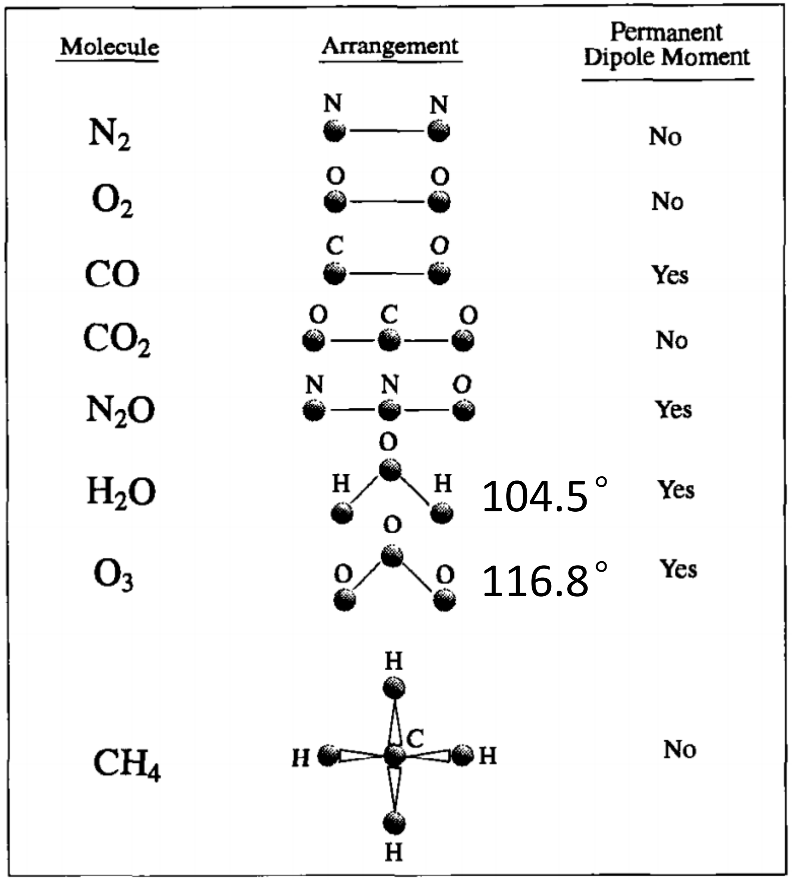


Emission

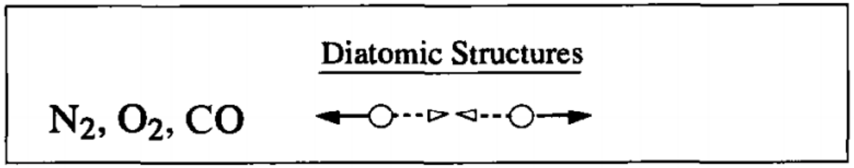


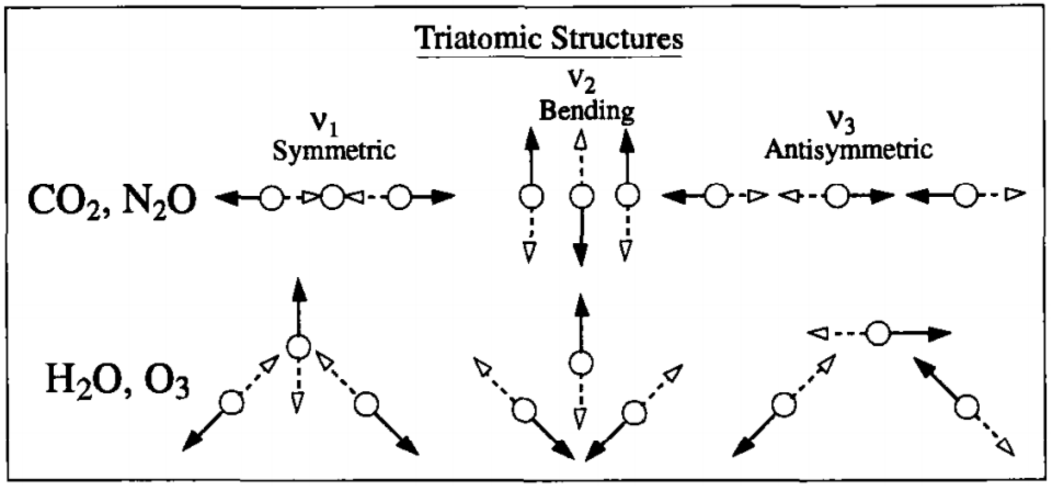
Vibrational Modes of Diatomic and Triatomic Molecules

永久偶极矩



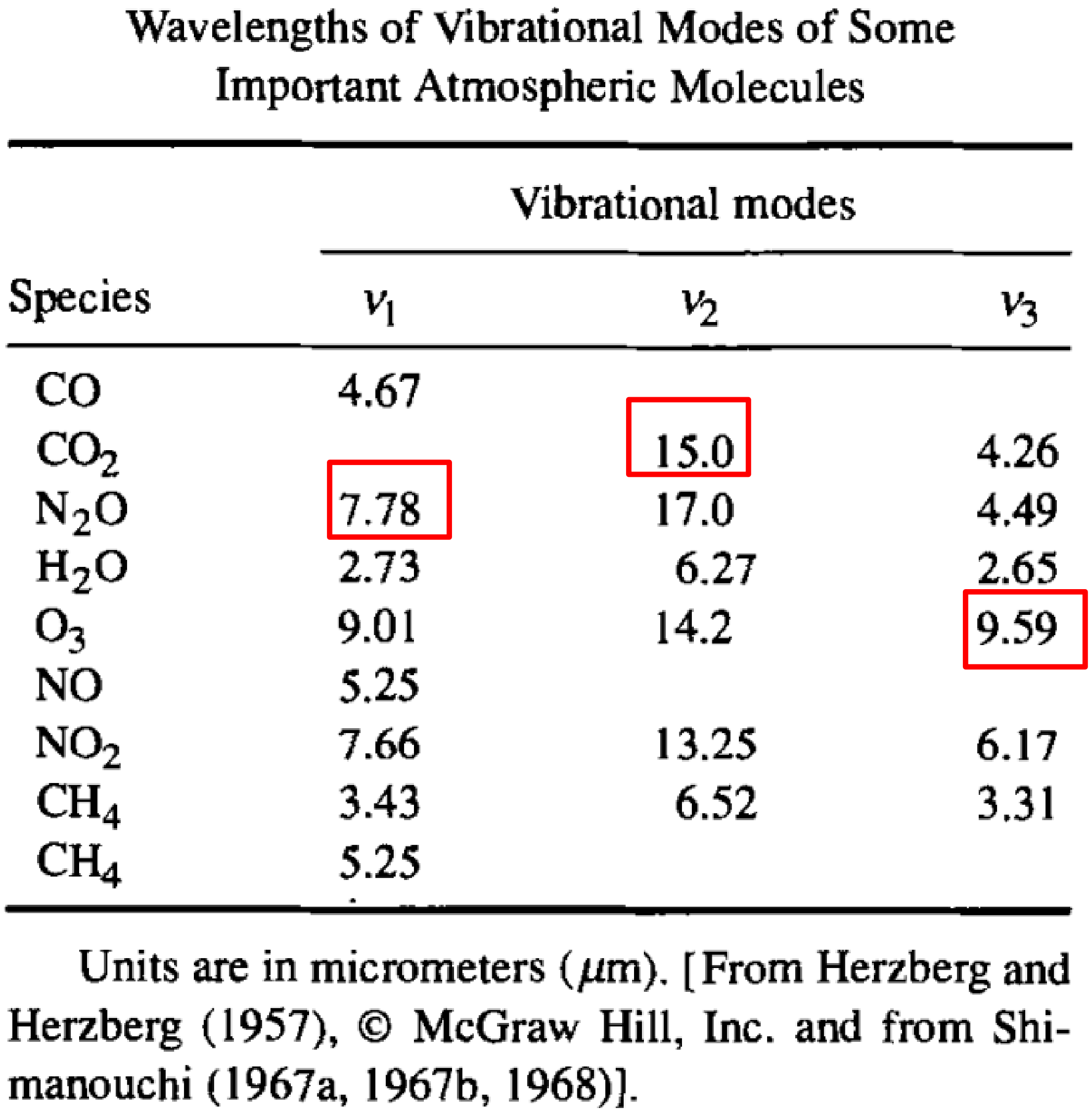
Molecule	Arrangement	Permanent Dipole Moment
N_2	N—N	No
O_2	O—O	No
CO	C—O	Yes
CO_2	O—C—O	No
N_2O	N—N—O	Yes
H_2O	H O H 104.5°	Yes
O_3	O O O 116.8°	Yes
CH_4	H H C H H	No





- Normal modes of vibration: 3N-6 or 3N-5 (for 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

Some Vibration Modes

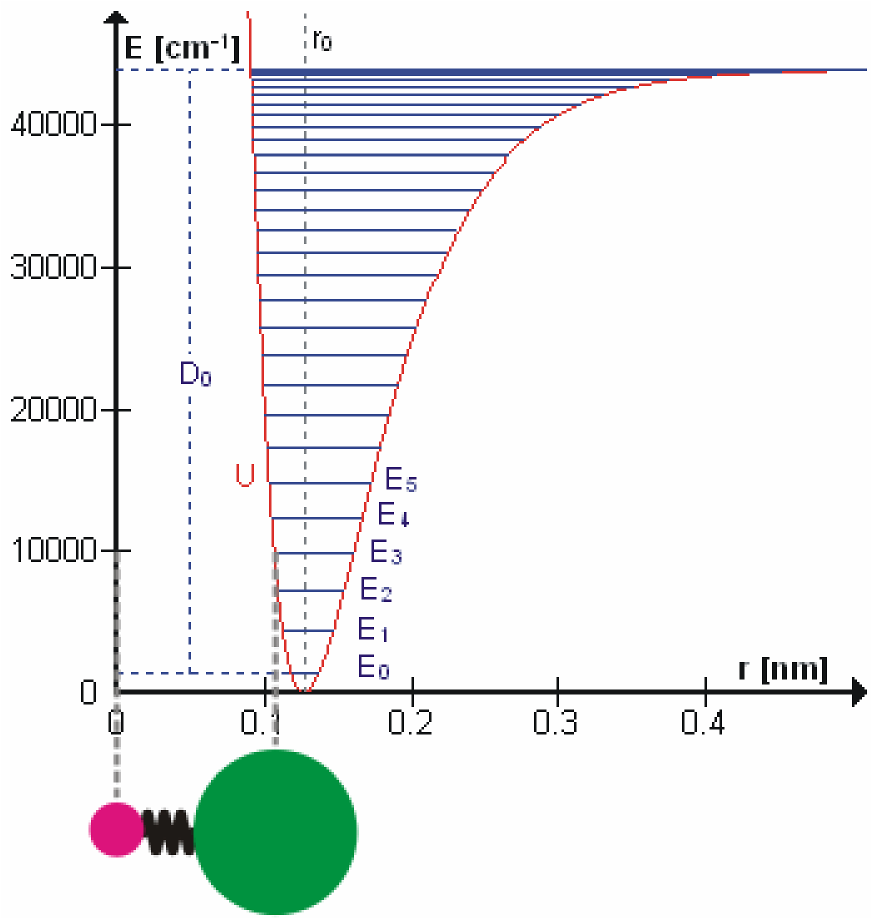


Wavelengths of Vibrational Modes of Some Important Atmospheric Molecules

	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：在哪个波长吸收？

- 吸收伴随着分子或原子内部能级的跃迁，因此，吸收波长（即吸收线的位置）与分子或原子内部的能级结构有关
- 气体分子“可以跃迁”的动能分为三部分：

$$E = E_e + E_v + E_r$$

原子外层电子围绕原子核运动的能量 E_e

原子在平衡位置上振动的能量 E_v

分子转动的能量 E_r

吸收系数、吸收截面

- 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**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掉了
- 单位体积中有 N个分子，**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，从运动的物体上所接收的波其频率与静止物体所接收波的频率有一个差别，称为多普勒频偏，导致多普勒增宽。

火车由远及近声音的变化？

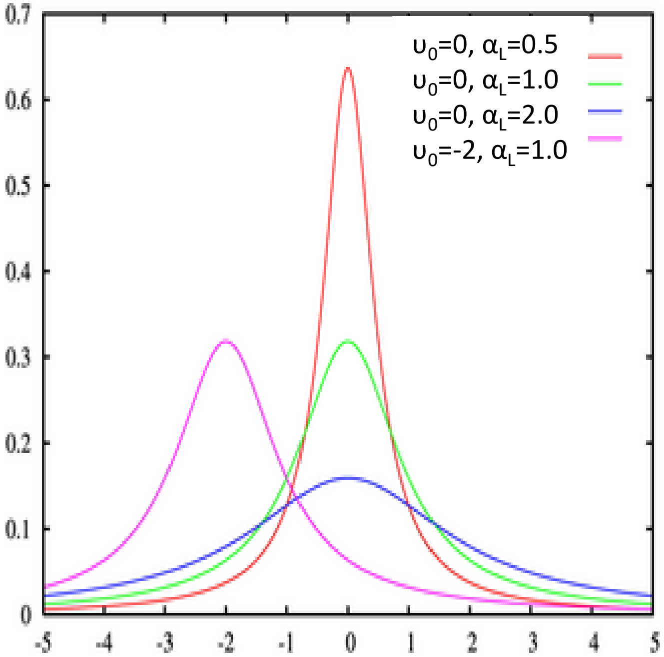
压力增宽（Lorentz增宽）

- **压力增宽可以用Lorentz公式来表示：**

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

- **S 是谱线的强度，即吸收线增宽后的总面积**

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



- $\upsilon_0 = (E_U - E_L)/hc$ **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：**

  吸收线在 $\upsilon=\upsilon_0$ 处的强度为$k_{\upsilon 0}=S/(\pi\alpha_L)$, 而在 $\upsilon=\upsilon_0\pm\alpha_L$ 处，$k_{\upsilon 0}=1/2k_{\upsilon 0}=S/(2\pi\alpha_L)$

- **吸收线半宽度与分子碰撞频率成正比，因此与气压成正比，与$T^{1/2}$成反比：**

$$\alpha(P,T)=\alpha_0\frac{P}{P_0}\left(\frac{T_0}{T}\right)^{1/2}$$

- **大气中温度变化在200K 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 Lorentz 半宽度大约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，从运动的物体上所接收的波其频率与静止物体所接收波的频率有一个差别，称为多普勒频偏。

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

- 多普勒增宽：

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

$\alpha_D = \sqrt{2}$ 标准差

α_D 是多普勒谱宽，与气压无关，而与$T^{1/2}$成正比

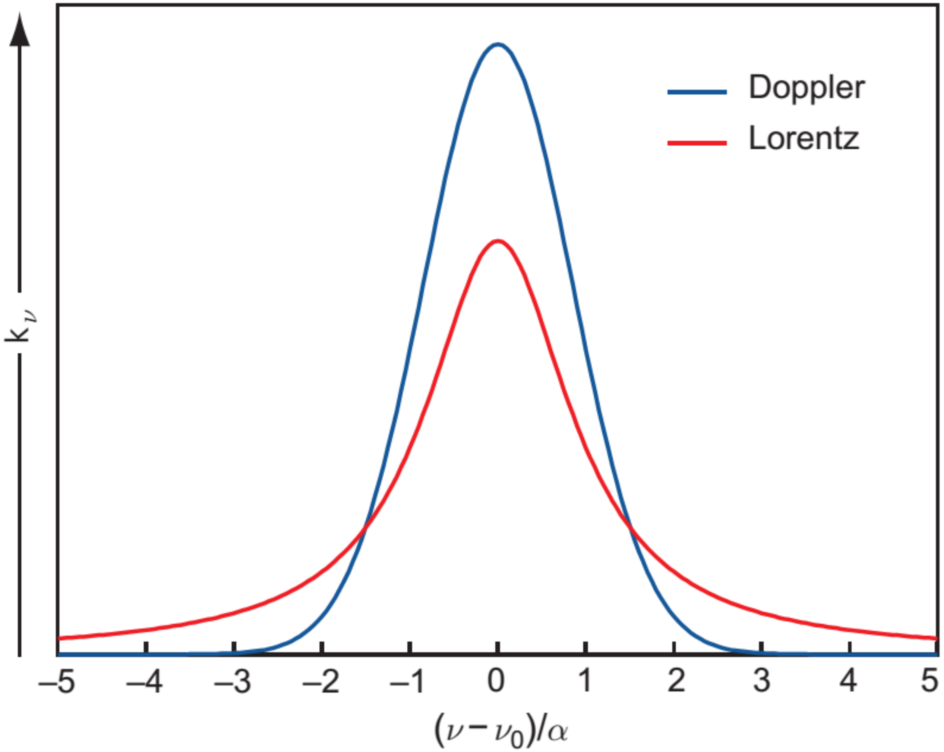
Maxwellian distribution:

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

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

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， $\alpha_L >> \alpha_D$
- ✓ 但到某一高度， $\alpha_L = \alpha_D$
- ✓ 再高，多普勒增宽就变得重要了



标准状态下的α_L和α_D，以及$\alpha_L = \alpha_D$ 时的气压

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 pH(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： Lorentz + Doppler

同时考虑Lorentz和Doppler增宽所产生的卷积效果：

$$V(\upsilon|\sigma,\gamma) = \int_{-\infty}^{\infty} D(\upsilon'|\sigma)\cdot L(\upsilon-\upsilon'|\gamma)\cdot d\upsilon'$$

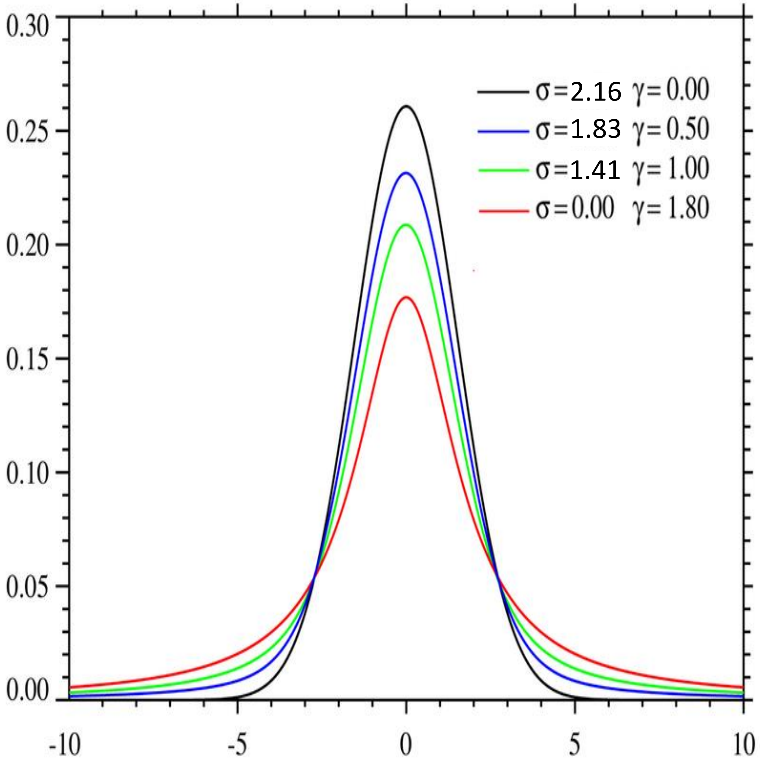
✓ $D(\upsilon'|\sigma)$: Centered Doppler profile:

$$D(\upsilon'|\sigma) = \frac{e^{-\upsilon'^2/\sigma^2}}{\sigma\sqrt{\pi}}$$

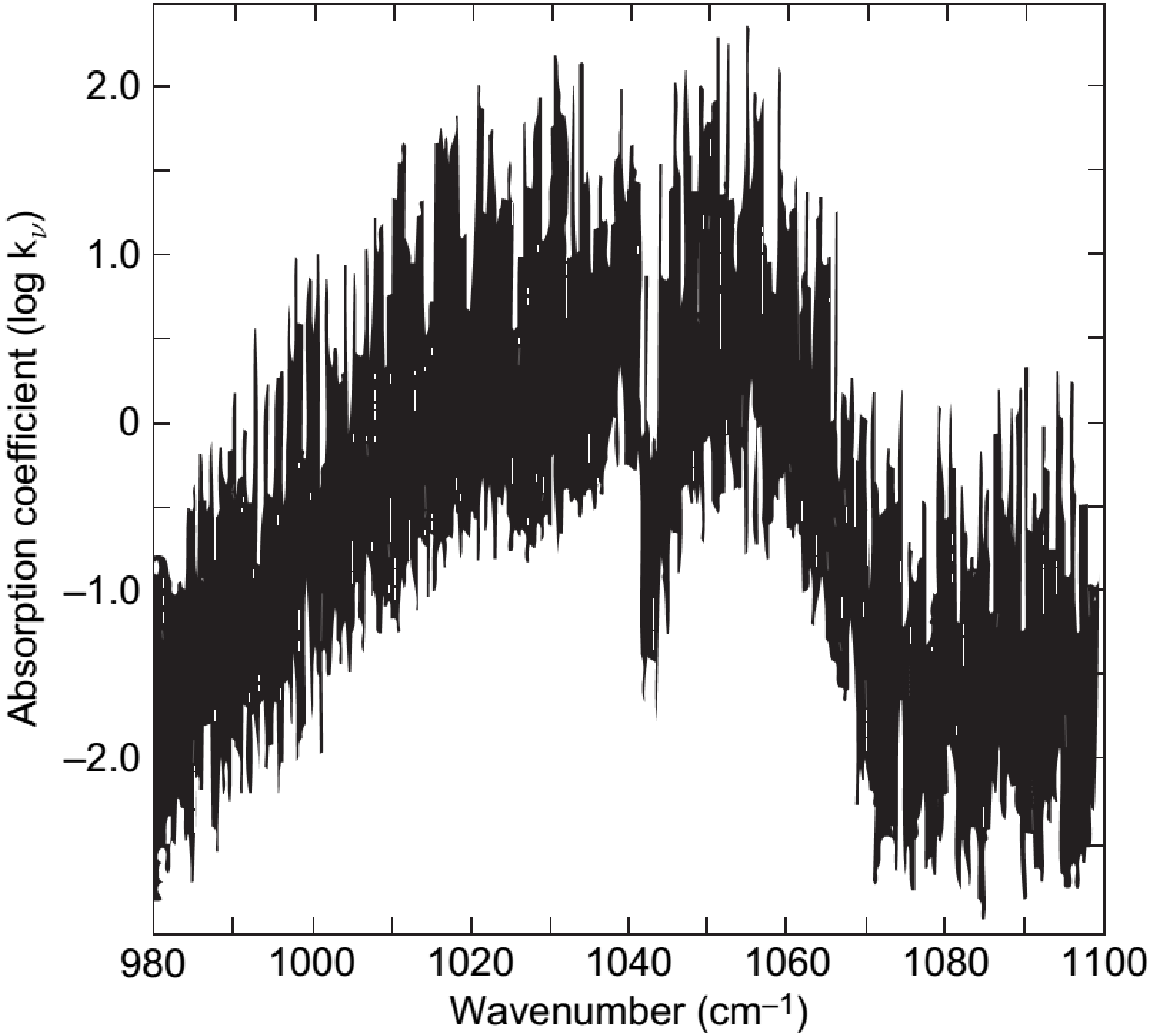
$\sigma = \sqrt{2}$ 标准差

✓ $L(\upsilon-\upsilon'|\gamma)$: Lorentzian profile:

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



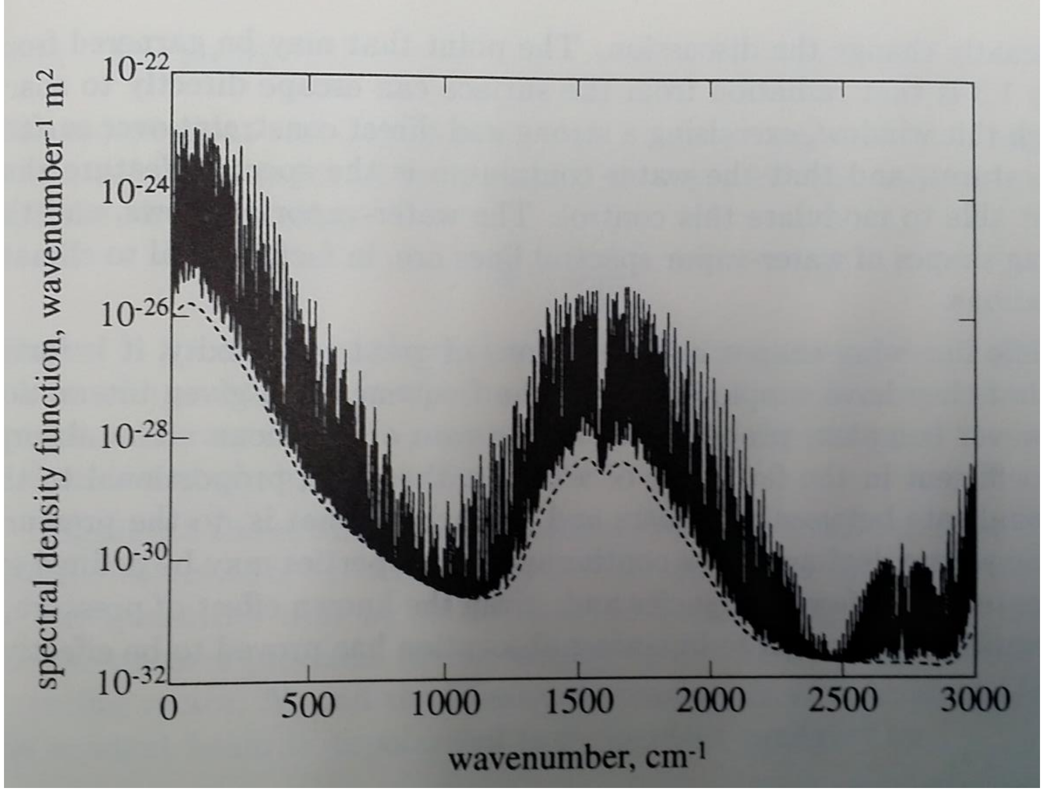
High-res Absorption at the 1000 cm^{-1} Line



Line Wings

The tail of the shape profile may be very important!

Absorption of H_2O

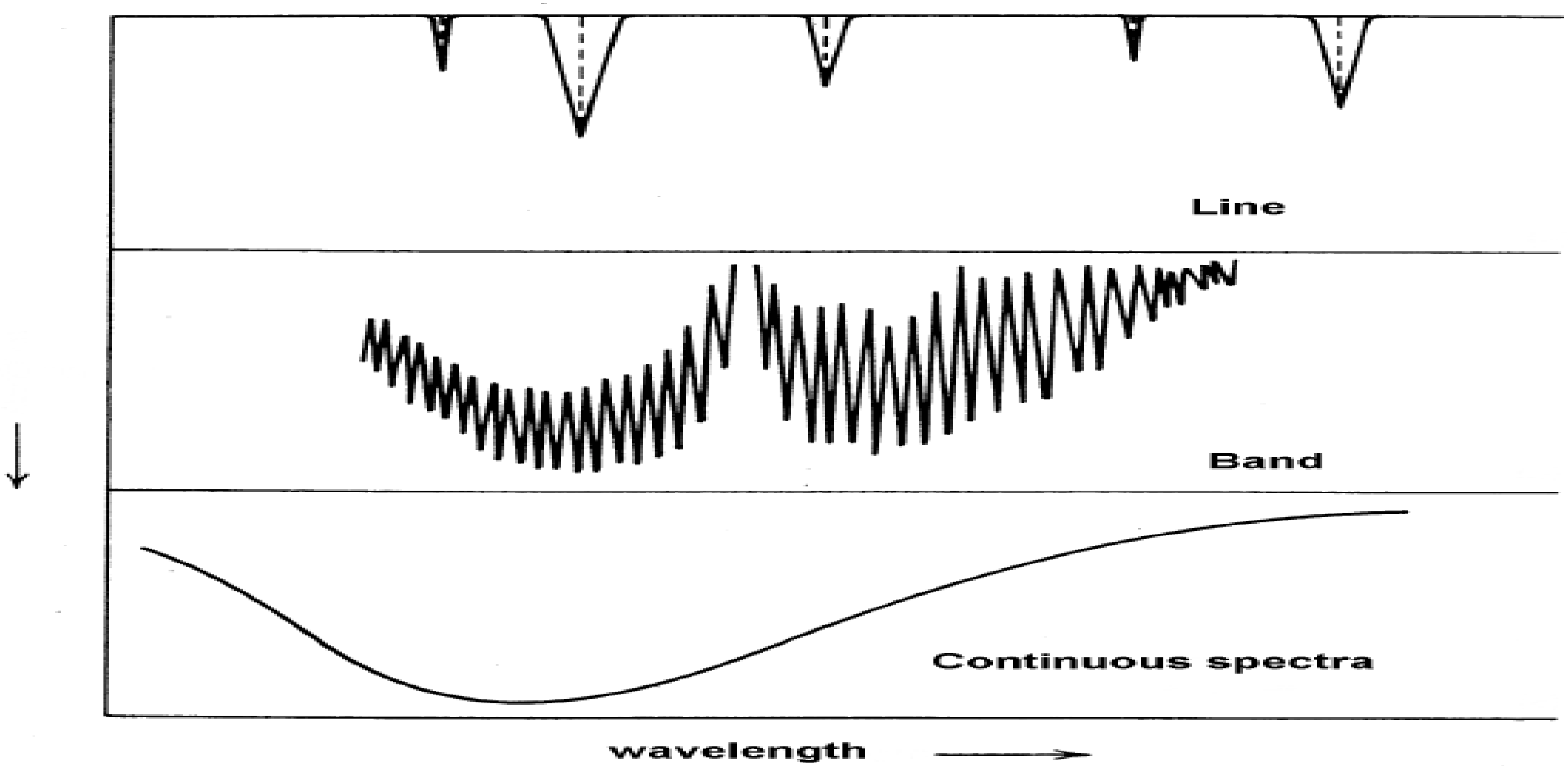


Line contributions
Continuum contributions

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



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.

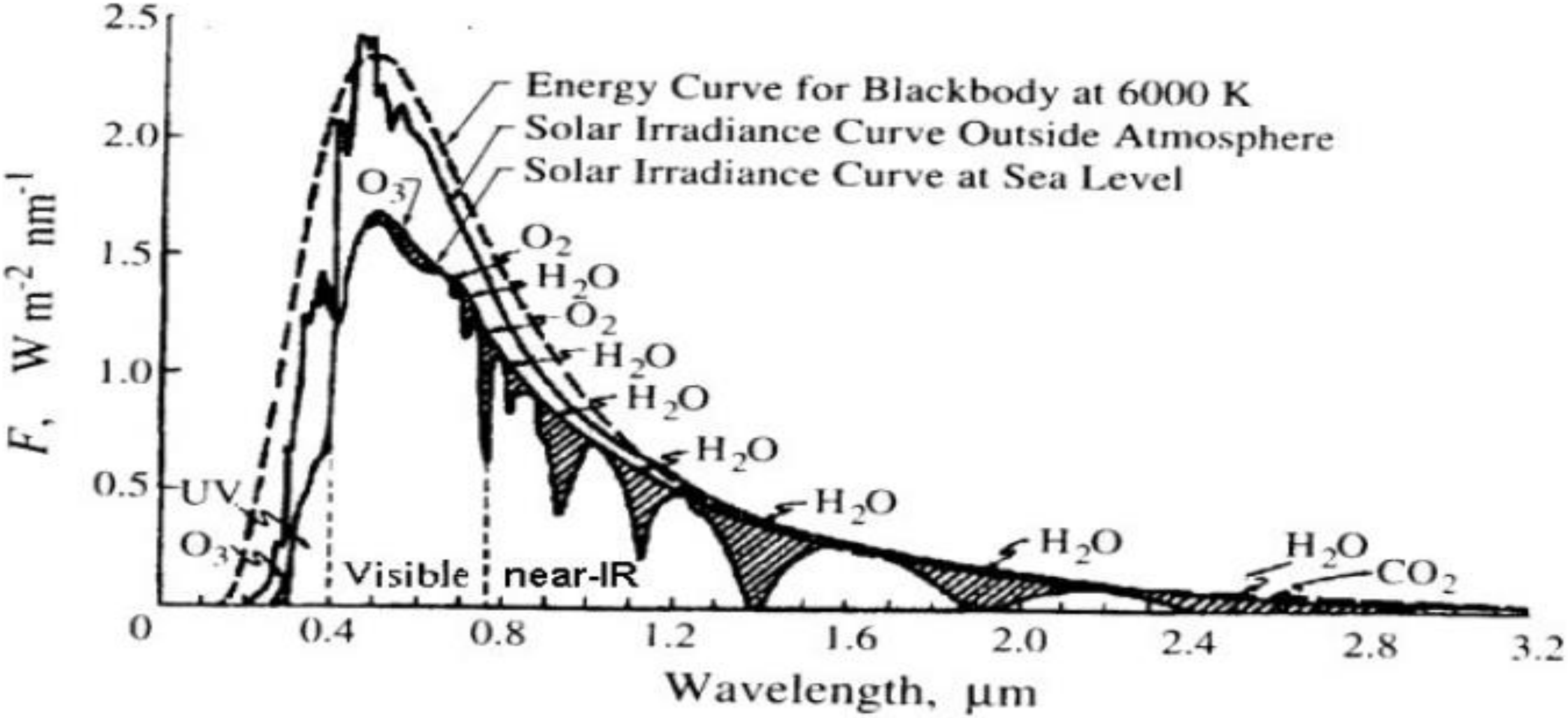


Figure 7.4 Solar spectral irradiance (flux) at the top of the atmosphere and at the surface.

Absorption of UV Radiation (by O_2 and O_3)

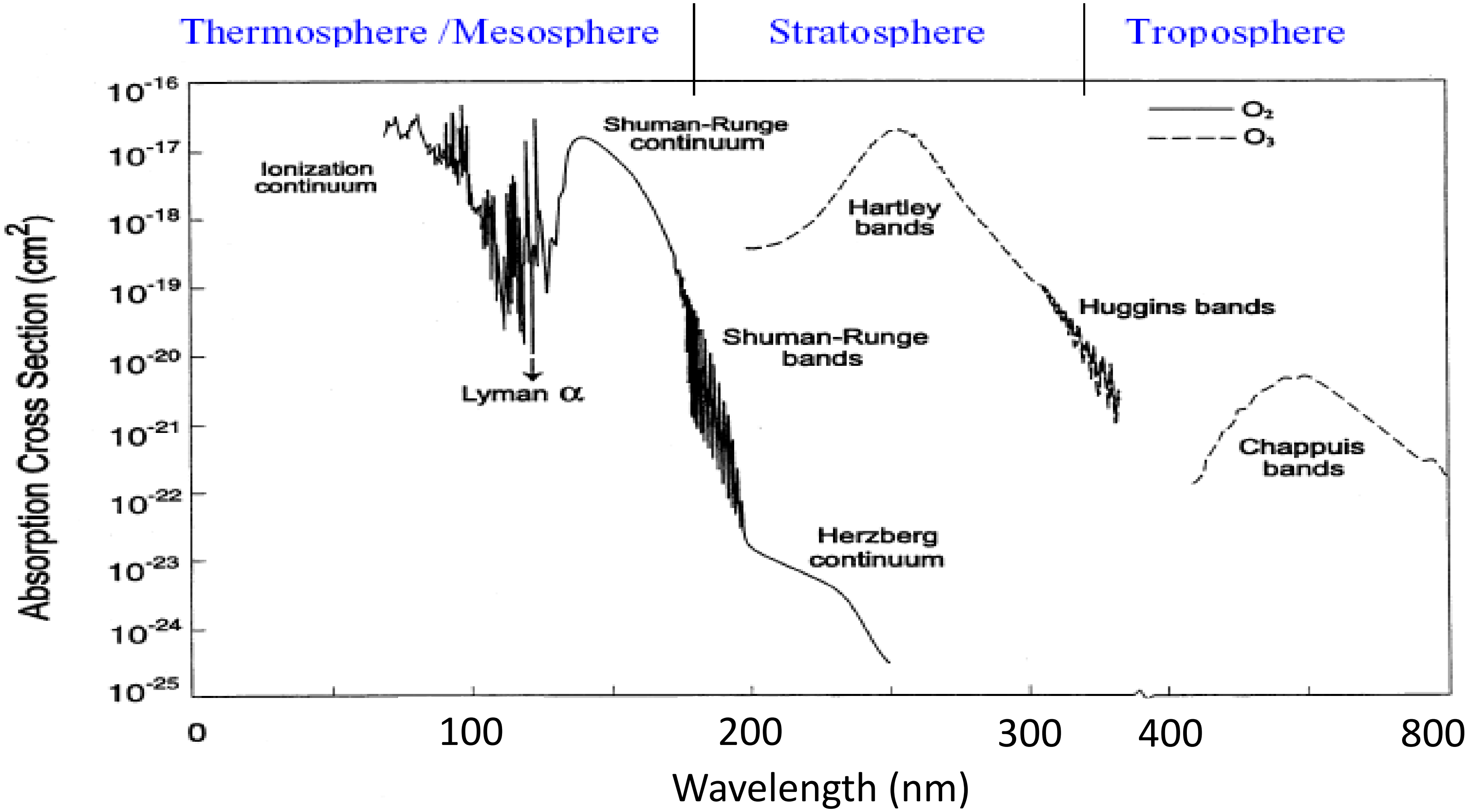


Figure 7.5 Spectral absorption cross-sections of O_2 and O_3

Absorption of Infrared Radiation

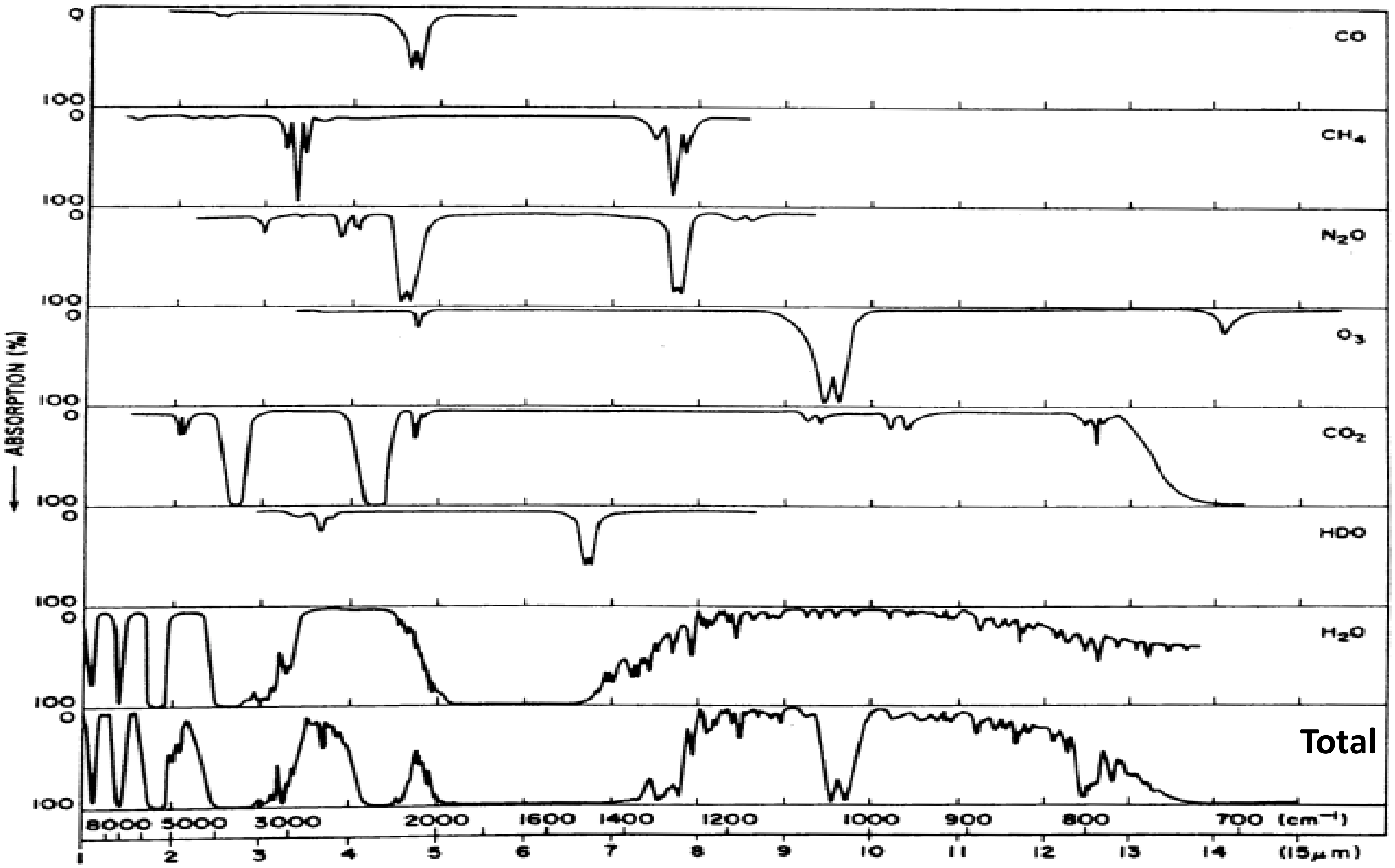


Figure 7.3 Low-resolution IR absorption spectra of the major atmospheric gases.

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，其对热辐射的吸收率的变化？
- 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：

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

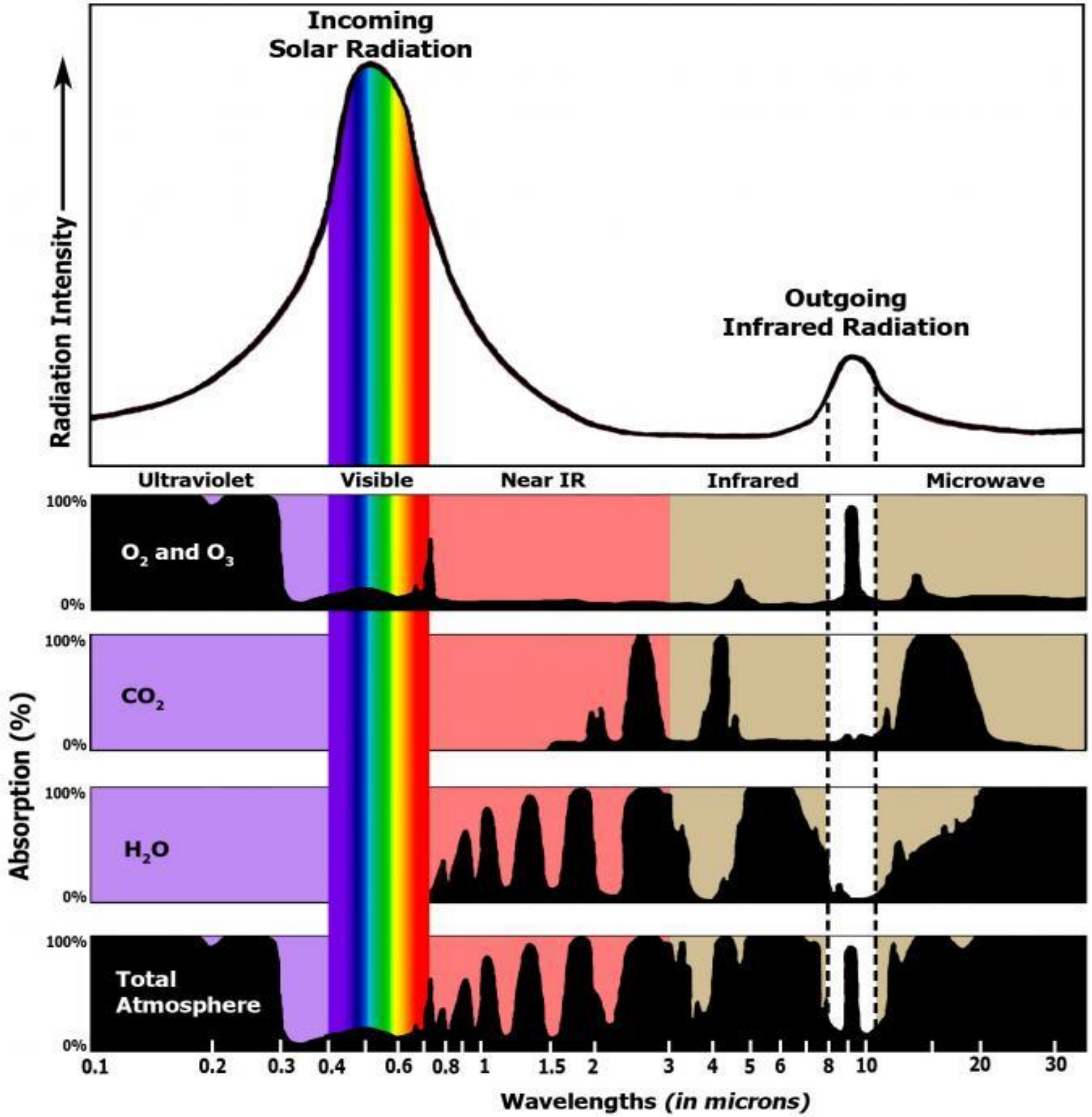
$$\times\exp\left[\frac{1.434\,E_L\,(T-296)}{296\,T}\right]$$

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

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**