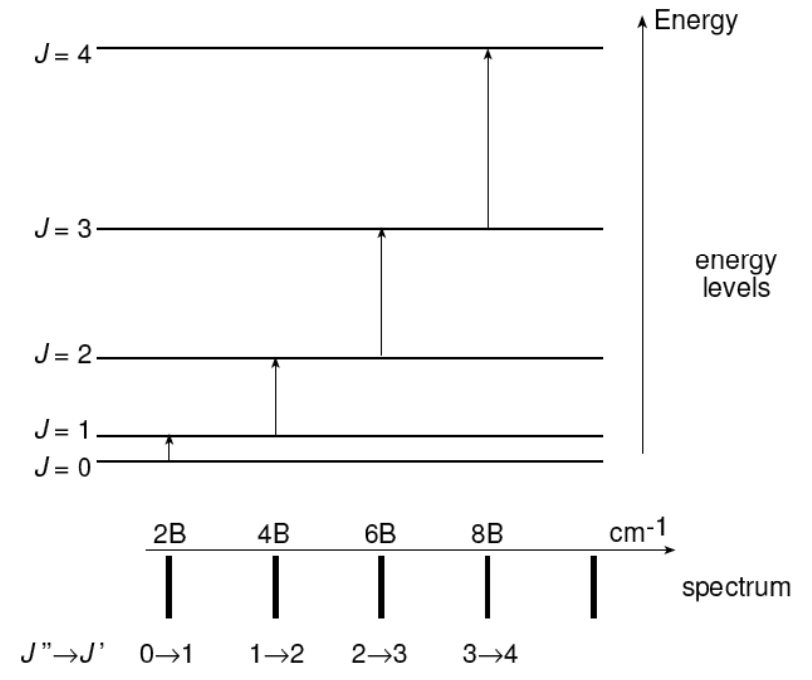
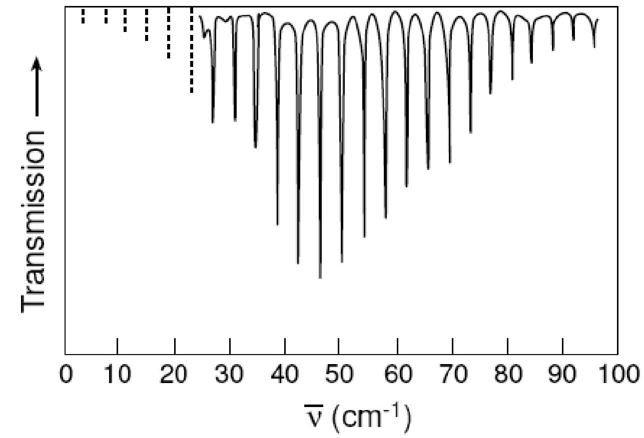
AOSC 621 Lesson 5-6

Absorption Line Intensity and Levels for Vibrational, Rotational and Electronic Absorption

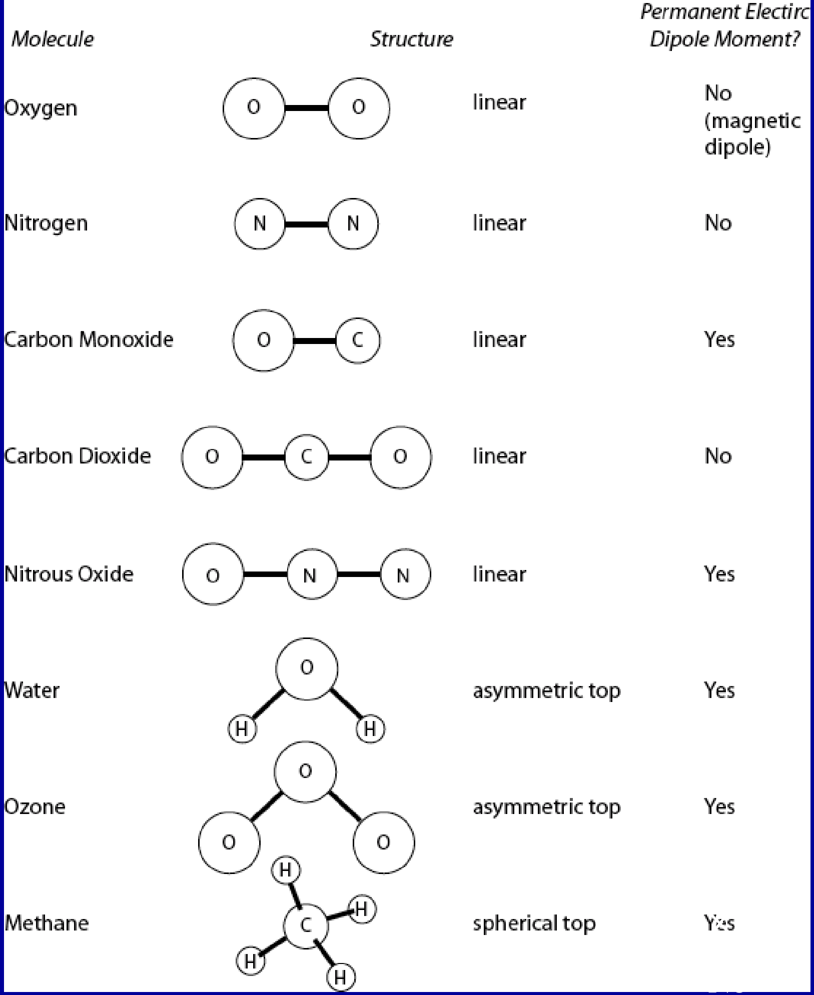
Absorption in molecular lines and bands

- Molecules have three types of energy levels - electronic, vibrational, and rotational
- Transitions between electronic levels occur mainly in the ultraviolet
- Transitions between vibrational levels - visible/near IR
- Transitions between rotational levels - far IR/ mm wave region
- O_2 and N_2 have essentially no absorption in the IR
- 4 most important IR absorbers H_2O, CO_2, O_3, CH_4





The microwave absorption spectrum of CO



Molecule	*Structure*		*Permanent Electirc Dipole Moment?*
Oxygen	O–O	linear	No (magnetic dipole)
Nitrogen	N–N	linear	No
Carbon Monoxide	O–C	linear	Yes
Carbon Dioxide	O–C–O	linear	No
Nitrous Oxide	O–N–N	linear	Yes
Water	H, O, H	asymmetric top	Yes
Ozone	O, O, O	asymmetric top	Yes
Methane	H, C, H, H, H	spherical top	~~Yes~~

Absorption by gaseous species

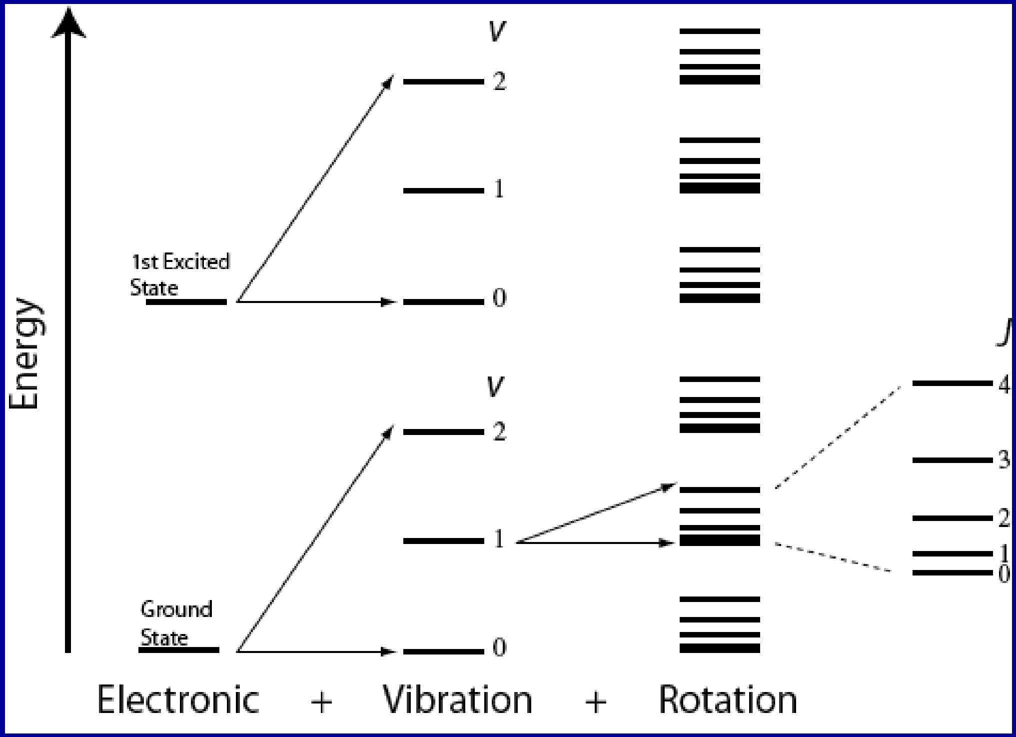
- Particles in the atmosphere are absorbers of radiation.
- Absorption is inherently a quantum process.
- A transition takes place from an initial quantum state to a higher quantum state.
- When the photon energy is close to the energy difference between the lower and the higher states, the process is called resonance. And the absorption is high.
- When the opposite is true the absorption is small.

Generally vibrational transitions occur in conjunction with rotational transitions. Consequently, it is possible to observe both rotational and vibrational transitions in the vibrational spectrum.

The energy of rotational transitions is on the order of 10^{-23} J whereas vibrational transitions have energies on the order of 10^{-20} J. Therefore, highly-resolved vibrational spectra will contain fine structure corresponding to the rotational transitions that occur at the same time as a vibrational transition.

Rotational-vibrational spectra will also show some fine structure due to the presence of different isotopes in the spectrum.

Hierarchy of energy levels



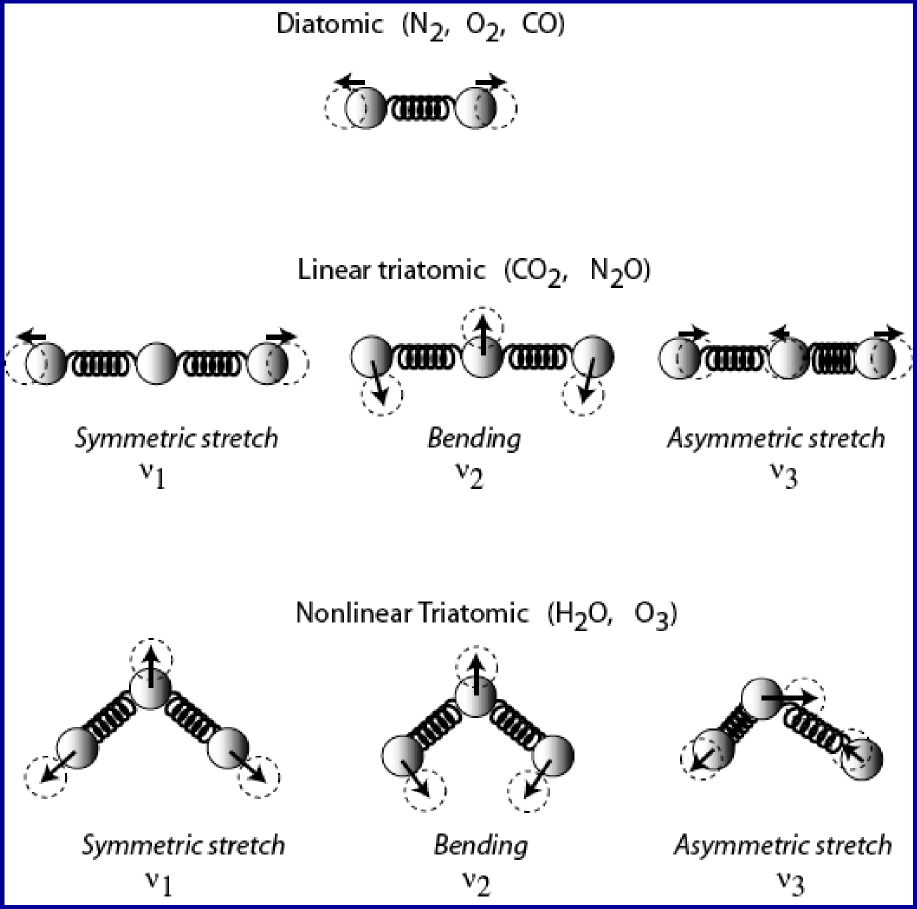
Total excitation energy of molecules:

$$E_{tot}=E_{el}+E_{vib}+E_{rot}$$

Absorption by gaseous species

- This energy selectivity is an outstanding characteristic of absorption. Scattering is generally much less selective and occurs over a much larger region of the spectrum.
- As we shall see later, molecules have a myriad of discrete energy levels and hence have complex absorption spectra.
- One reason for our interest in the spectra of molecules lies in the fact that many molecules have absorption features in the thermal infra-red and these are responsible for the thermal equilibrium of the atmosphere.
- Another is that many molecules absorb strongly on the ultraviolet, where the photons have enough energy to break apart the molecules. The resulting radicals start the chemical processes in both the troposphere and stratosphere.

Normal modes of vibration

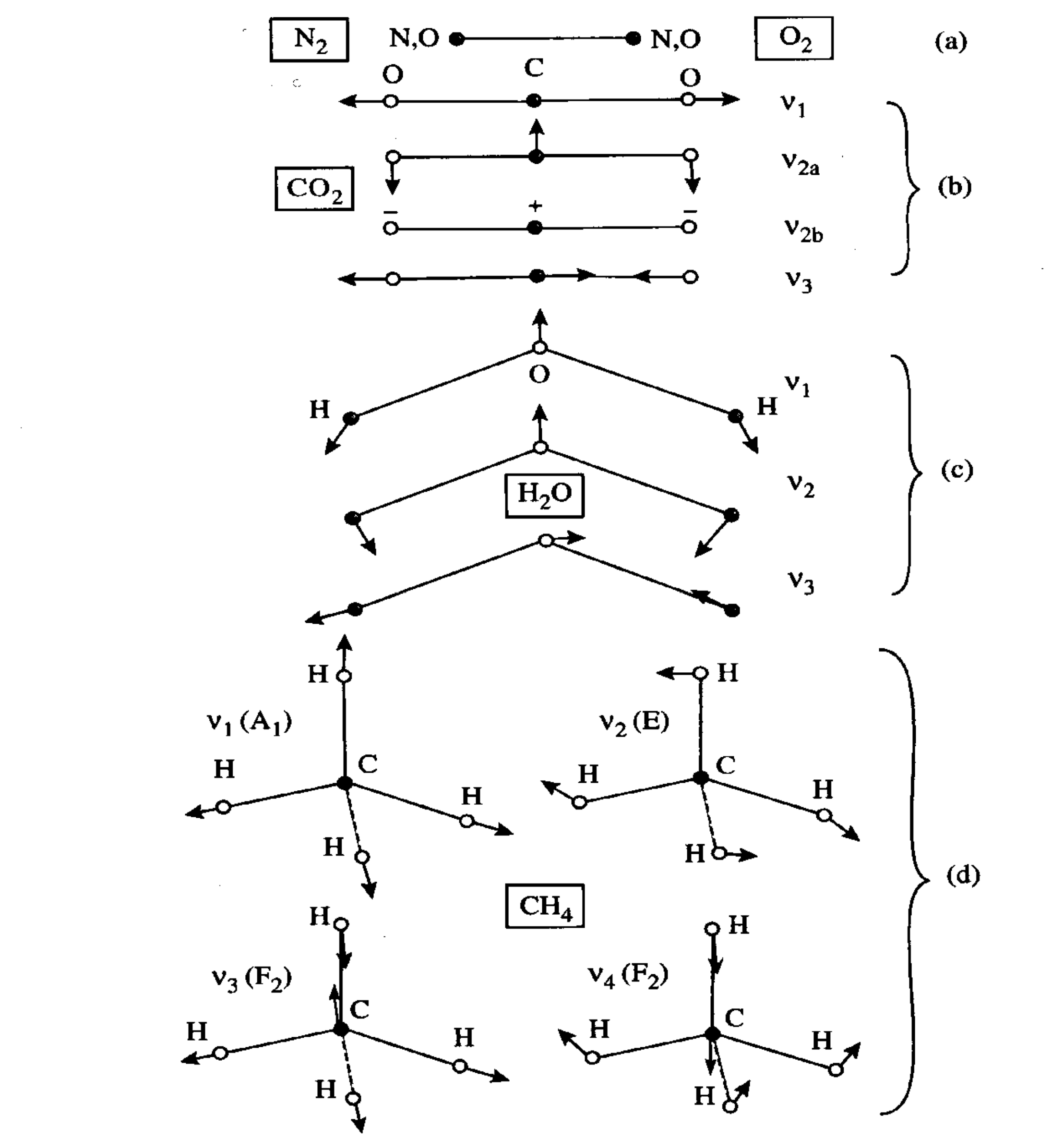


number of atoms

For linear: $3N$-5 modes

In general: $3N$-6 modes

Various forms of molecular vibration

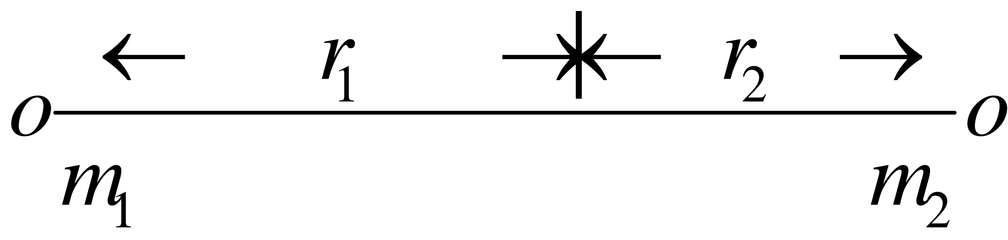


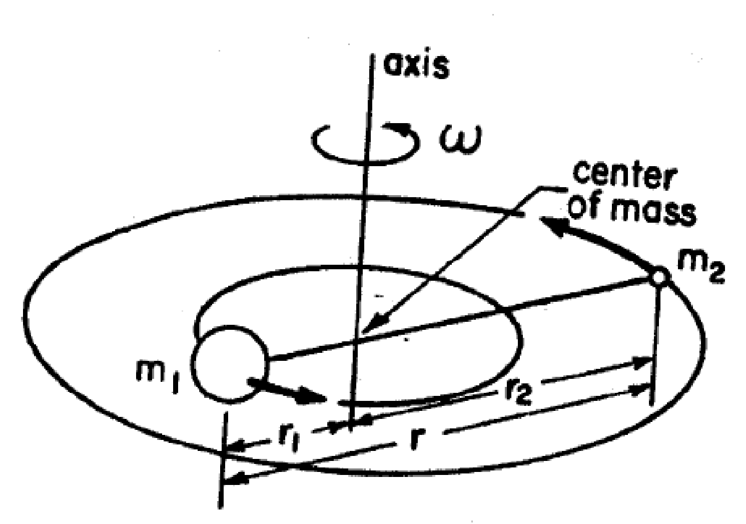
Selection Rules

- Not all vibration excitation in molecules produces radiation.
- To produce radiation one needs to have an oscillating dipole. When the molecule is set into a vibration mode, the combined electric field at the center of mass must also oscillate
- O_2 and N_2, homonuclear molecules , do not possess an oscillating dipole at their center of mass when in the ground state and so do not show vibrational spectra in the IR.

Rotational levels

- Consider a diatomic molecule with different atoms of mass m_1 and m_2, whose distance from the center of mass are r_1 and r_2 respectively



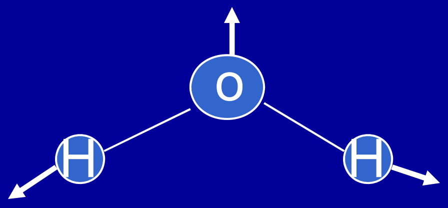


- The moment of inertia of the system about the center of mass is:

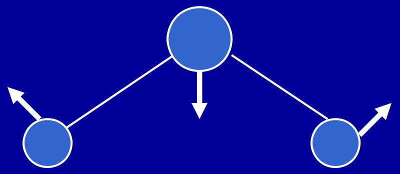
$$I = m_1 r_1^2 + m_2 r_2^2$$

H_2O

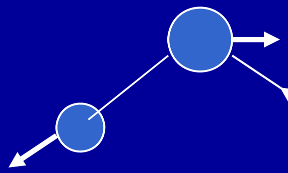
- Most important IR absorber
- Asymmetric top → Nonlinear, triatomic molecule has complex line structure, no simple pattern
- 3 different moments of inertia (I_A, I_B, I_C)
- 3 Vibrational fundamental modes



symmetric stretch
$\lambda_1 = 2.74\ \mu m$



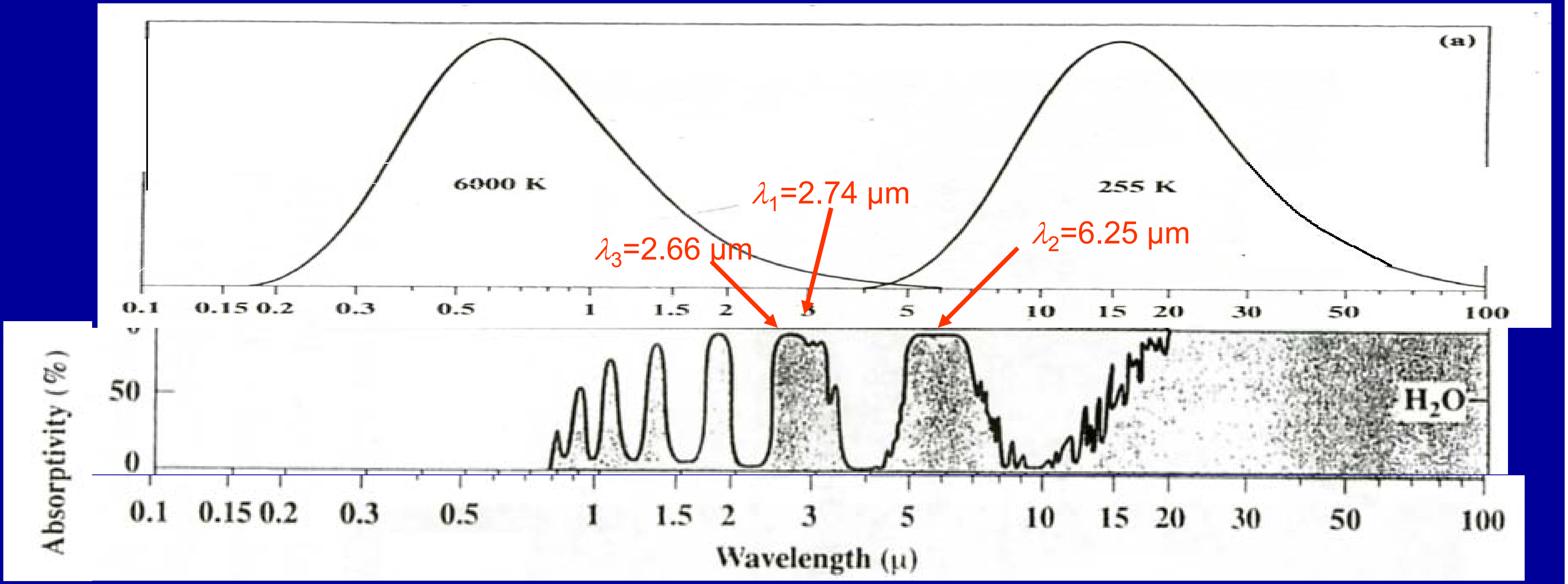
bend
$\lambda_2 = 6.25\ \mu m$



asymmetric stretch
$v_3 = 2.66\ \mu m$

- Higher order vibrational transitions ($\Delta\upsilon > 1$) give weak absorption bands at shorter wavelengths in the shortwave bands
- ^{2}H isotope (0.03% in atm) and ^{18}O (0.2%) adds new (weak) lines to vibrational spectrum
- Overtones and combinations of rotational and vibrational transitions lead to several more weak absorption bands in the NIR

Absorption Spectrum of H_2O

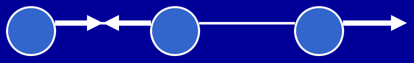


CO_2

- Linear → no permanent dipole moment, no pure rotational spectrum
- Fundamental modes:

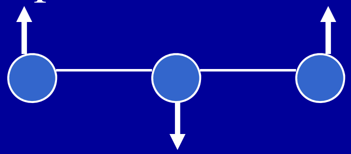
symmetric stretch

λ_1 = 7.5 μm => **IR inactive**



asymmetric stretch

λ_3 = 4.3 μm



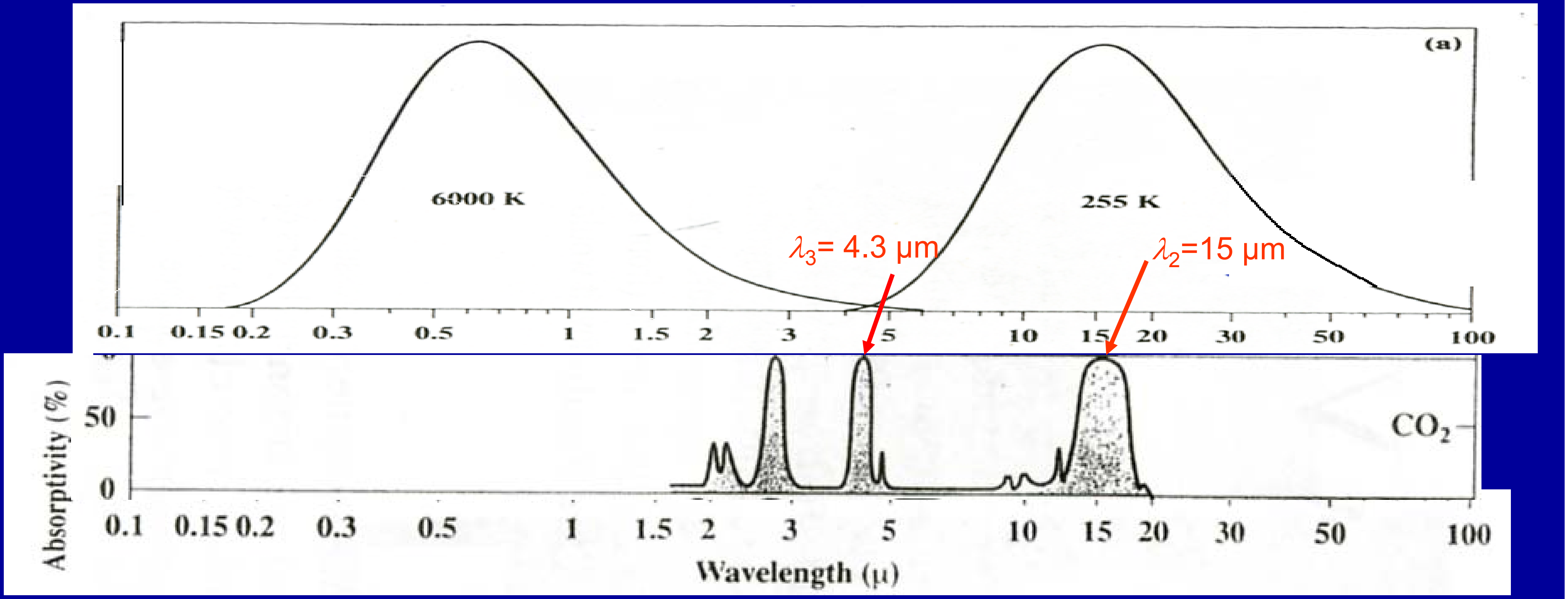
bend

λ_2 = 15 μm

bend λ_2

- λ_1 vibration is a parallel band (dipole moment oscillates parallel to symmetric axis), transition $\otimes J = 0$ is forbidden, greater total intensity than λ_2 fundamental
- λ_2 vibration is perpendicular band
- λ_3 fundamental strongest vibrational band but λ_2 fundamental most effective due to "matching" of vibrational frequencies with terrestrial Planck emission functions
- ^{13}C isotope (1% of C in atm) and $^{17/18}$O isotope (0.2%) cause a weak splitting of rotational and vibrational lines in the CO_2 spectrum

IR Absorption Spectrum of CO_2



CO_2

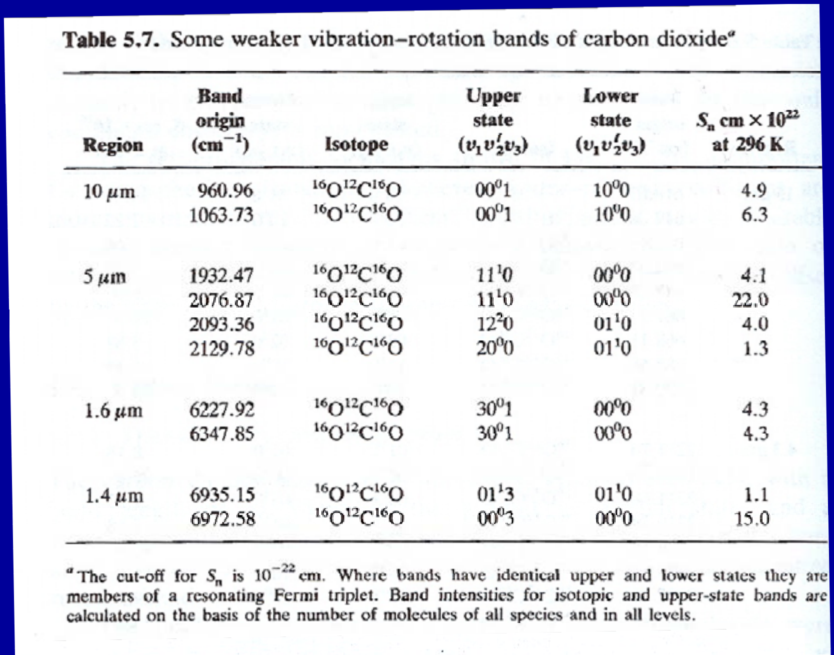
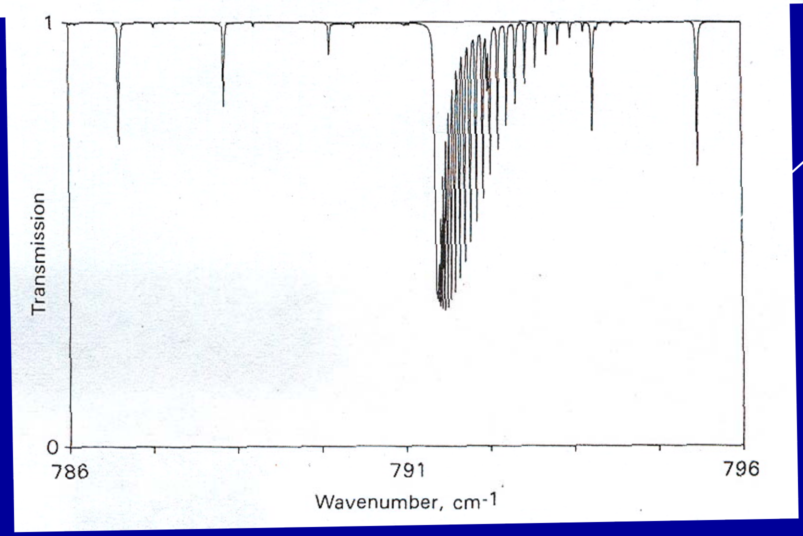


Table 5.7. Some weaker vibration–rotation bands of carbon dioxide[a]

Region	Band origin (cm^{-1})	Isotope	Upper state ($v_1v_2^lv_3$)	Lower state ($v_1v_2^lv_3$)	S_n cm × 10^{22} at 296 K
10 μm	960.96	$^{16}O^{12}C^{16}O$	00^01	10^00	4.9
	1063.73	$^{16}O^{12}C^{16}O$	00^01	10^00	6.3
5 μm	1932.47	$^{16}O^{12}C^{16}O$	11^10	00^00	4.1
	2076.87	$^{16}O^{12}C^{16}O$	11^10	00^00	22.0
	2093.36	$^{16}O^{12}C^{16}O$	12^20	01^10	4.0
	2129.78	$^{16}O^{12}C^{16}O$	20^00	01^10	1.3
1.6 μm	6227.92	$^{16}O^{12}C^{16}O$	30^01	00^00	4.3
	6347.85	$^{16}O^{12}C^{16}O$	30^01	00^00	4.3
1.4 μm	6935.15	$^{16}O^{12}C^{16}O$	01^13	01^10	1.1
	6972.58	$^{16}O^{12}C^{16}O$	00^03	00^00	15.0

[a] The cut-off for S_n is 10^{-22} cm. Where bands have identical upper and lower states they are members of a resonating Fermi triplet. Band intensities for isotopic and upper-state bands are calculated on the basis of the number of molecules of all species and in all levels.



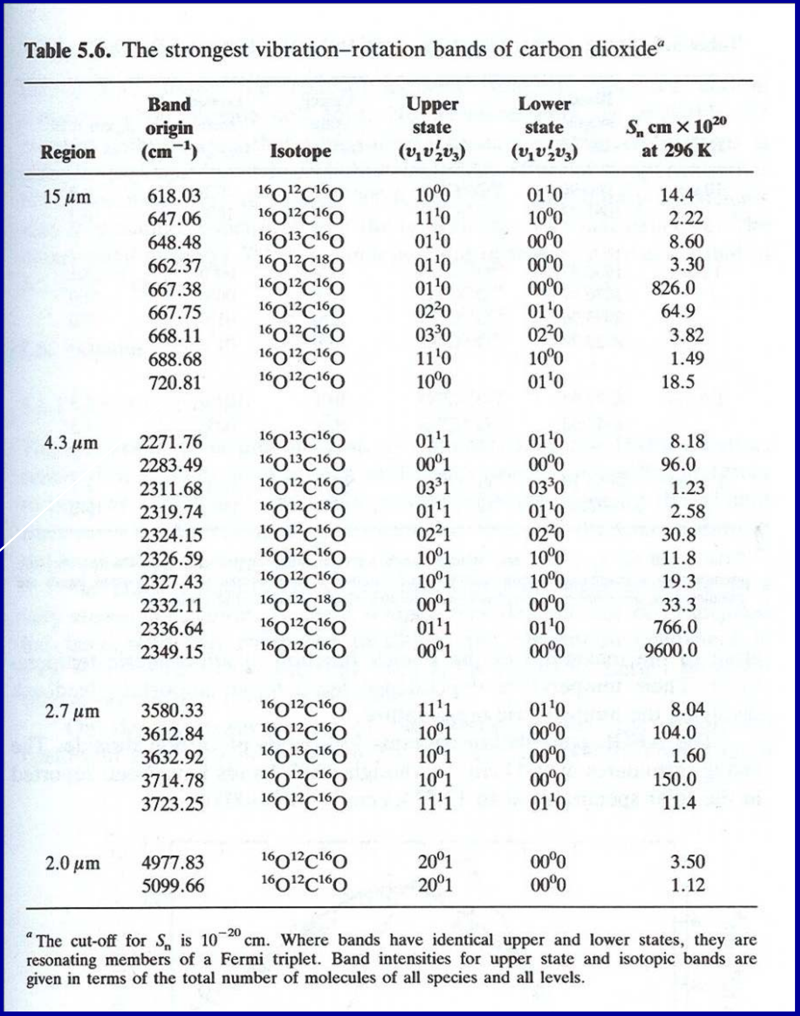


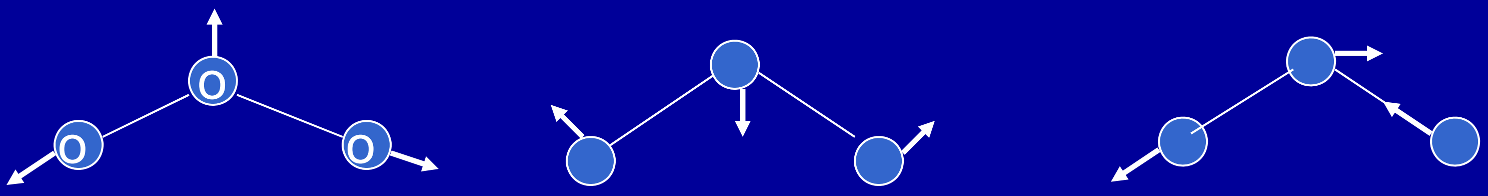
Table 5.6. The strongest vibration–rotation bands of carbon dioxide[a]

Region	Band origin (cm^{-1})	Isotope	Upper state ($v_1v_2^lv_3$)	Lower state ($v_1v_2^lv_3$)	S_n cm × 10^{20} at 296 K
15 μm	618.03	$^{16}O^{12}C^{16}O$	10^00	01^10	14.4
	647.06	$^{16}O^{12}C^{16}O$	11^10	10^00	2.22
	648.48	$^{16}O^{13}C^{16}O$	01^10	00^00	8.60
	662.37	$^{16}O^{12}C^{18}O$	01^10	00^00	3.30
	667.38	$^{16}O^{12}C^{16}O$	01^10	00^00	826.0
	667.75	$^{16}O^{12}C^{16}O$	02^20	01^10	64.9
	668.11	$^{16}O^{12}C^{16}O$	03^30	02^20	3.82
	688.68	$^{16}O^{12}C^{16}O$	11^10	10^00	1.49
	720.81	$^{16}O^{12}C^{16}O$	10^00	01^10	18.5
4.3 μm	2271.76	$^{16}O^{13}C^{16}O$	01^11	01^10	8.18
	2283.49	$^{16}O^{13}C^{16}O$	00^01	00^00	96.0
	2311.68	$^{16}O^{12}C^{16}O$	03^31	03^30	1.23
	2319.74	$^{16}O^{12}C^{18}O$	01^11	01^10	2.58
	2324.15	$^{16}O^{12}C^{16}O$	02^21	02^20	30.8
	2326.59	$^{16}O^{12}C^{16}O$	10^01	10^00	11.8
	2327.43	$^{16}O^{12}C^{16}O$	10^01	10^00	19.3
	2332.11	$^{16}O^{12}C^{18}O$	00^01	00^00	33.3
	2336.64	$^{16}O^{12}C^{16}O$	01^11	01^10	766.0
	2349.15	$^{16}O^{12}C^{16}O$	00^01	00^00	9600.0
2.7 μm	3580.33	$^{16}O^{12}C^{16}O$	11^11	01^10	8.04
	3612.84	$^{16}O^{12}C^{16}O$	10^01	00^00	104.0
	3632.92	$^{16}O^{13}C^{16}O$	10^01	00^00	1.60
	3714.78	$^{16}O^{12}C^{16}O$	10^01	00^00	150.0
	3723.25	$^{16}O^{12}C^{16}O$	11^11	01^10	11.4
2.0 μm	4977.83	$^{16}O^{12}C^{16}O$	20^01	00^00	3.50
	5099.66	$^{16}O^{12}C^{16}O$	20^01	00^00	1.12

[a] The cut-off for S_n is 10^{-20} cm. Where bands have identical upper and lower states, they are resonating members of a Fermi triplet. Band intensities for upper state and isotopic bands are given in terms of the total number of molecules of all species and all levels.

O_3

- Ozone is primarily present in the stratosphere aside from anthropogenic ozone pollution which exists in the troposphere
- Asymmetric top → similar absorption spectrum to H_2O due to similar configuration (nonlinear, triatomic)
- Strong rotational spectrum of random spaced lines
- Fundamental vibrational modes



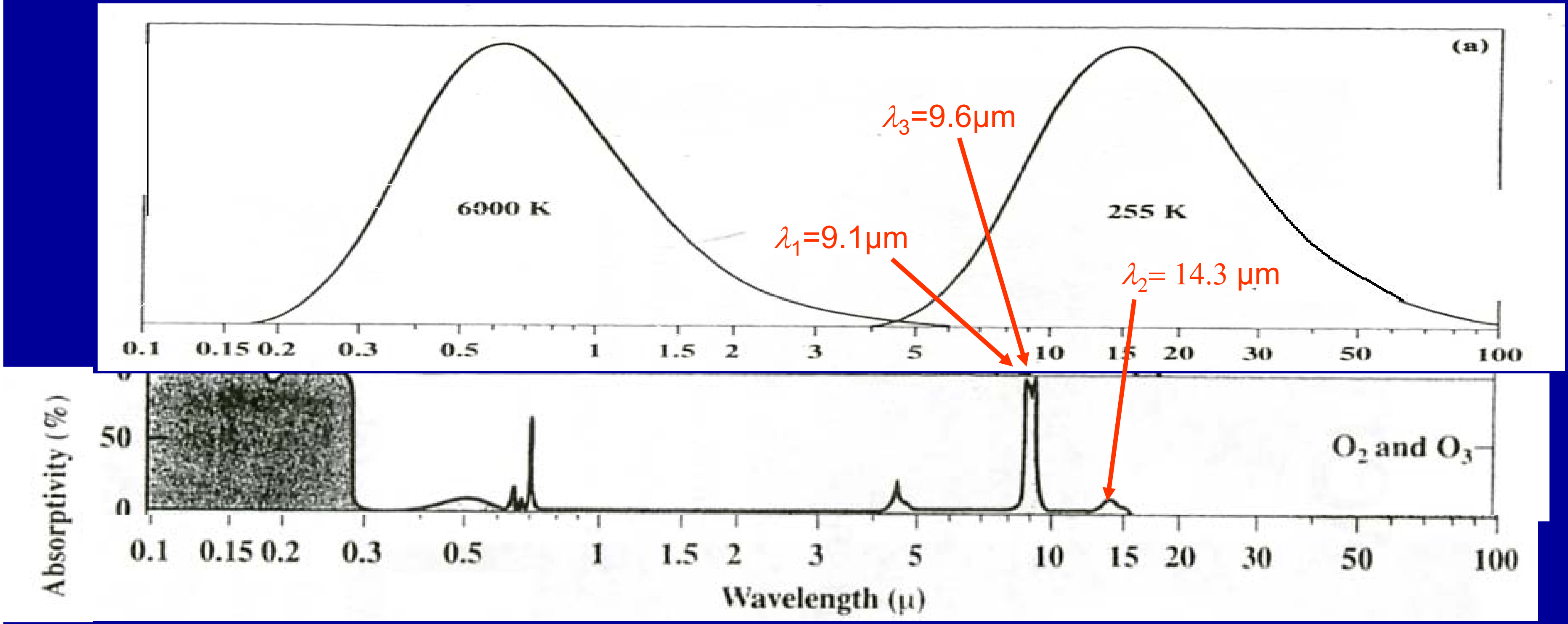
symmetric stretch
$\lambda_1 = 9.1\ \mu m$

bend
$\lambda_2 = 14.3\ \mu m$

asymmetric stretch
$\lambda_3 = 9.6\ \mu m$

  - 14.3 μm band masked by CO_2 15 μm band
  - Strong λ_3 band and moderately strong λ_1 band are close in frequency, often seen as one band at 9.6 μm
  - 9.6 μm band sits in middle of 8-12 μm H_2O window and near peak of terrestrial Planck function
  - Strong 4.7 μm band but near edge of Planck functions

IR Absorption Spectrum of O_3



O_3

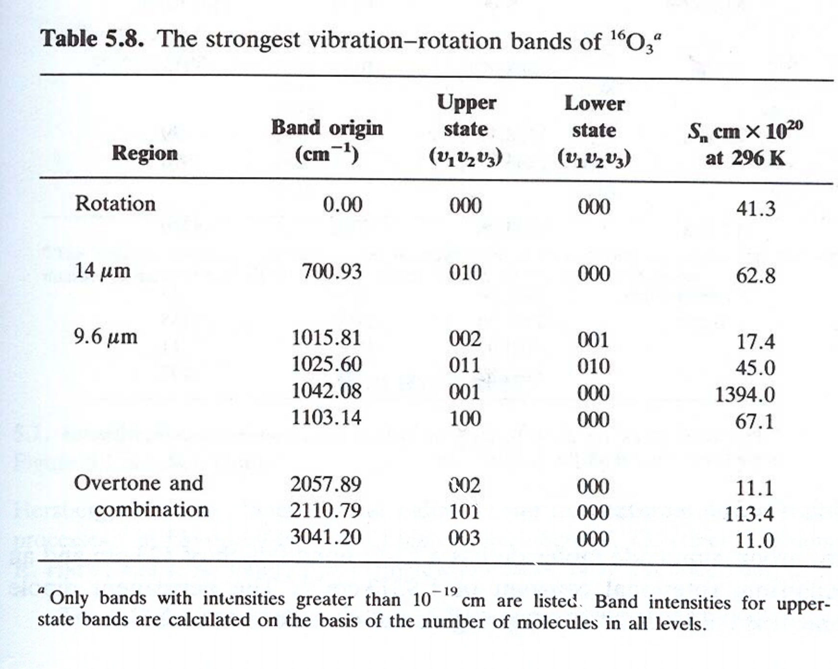
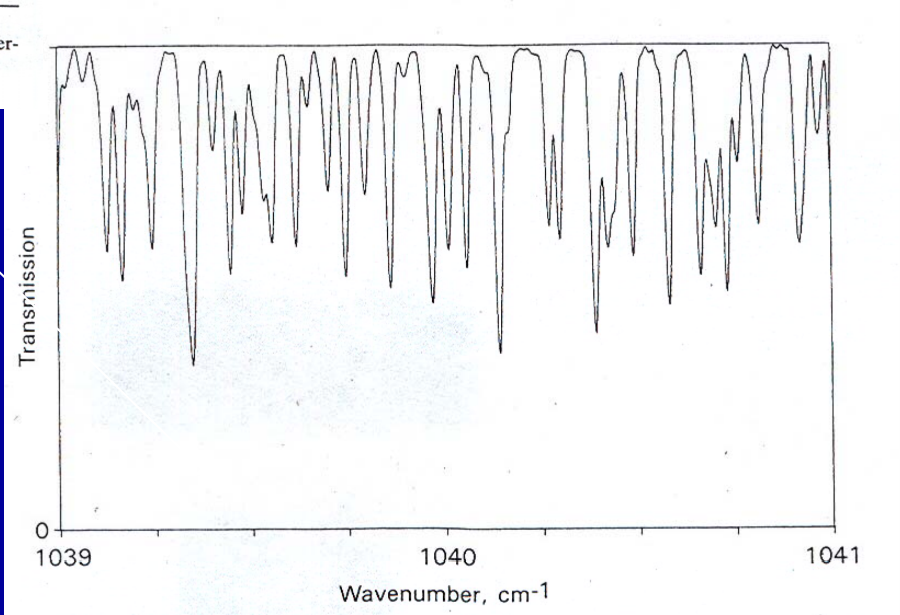


Table 5.8. The strongest vibration–rotation bands of $^{16}O_3$[a]

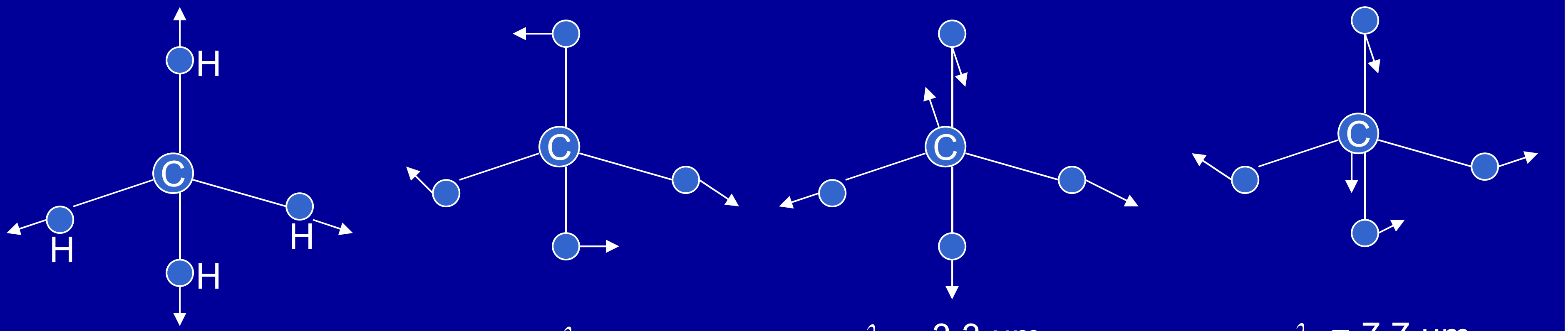
Region	Band origin (cm^{-1})	Upper state ($v_1v_2v_3$)	Lower state ($v_1v_2v_3$)	S_n cm × 10^{20} at 296 K
Rotation	0.00	000	000	41.3
14 μm	700.93	010	000	62.8
9.6 μm	1015.81	002	001	17.4
	1025.60	011	010	45.0
	1042.08	001	000	1394.0
	1103.14	100	000	67.1
Overtone and combination	2057.89	002	000	11.1
	2110.79	101	000	113.4
	3041.20	003	000	11.0

[a] Only bands with intensities greater than 10^{-19} cm are listed. Band intensities for upper-state bands are calculated on the basis of the number of molecules in all levels.



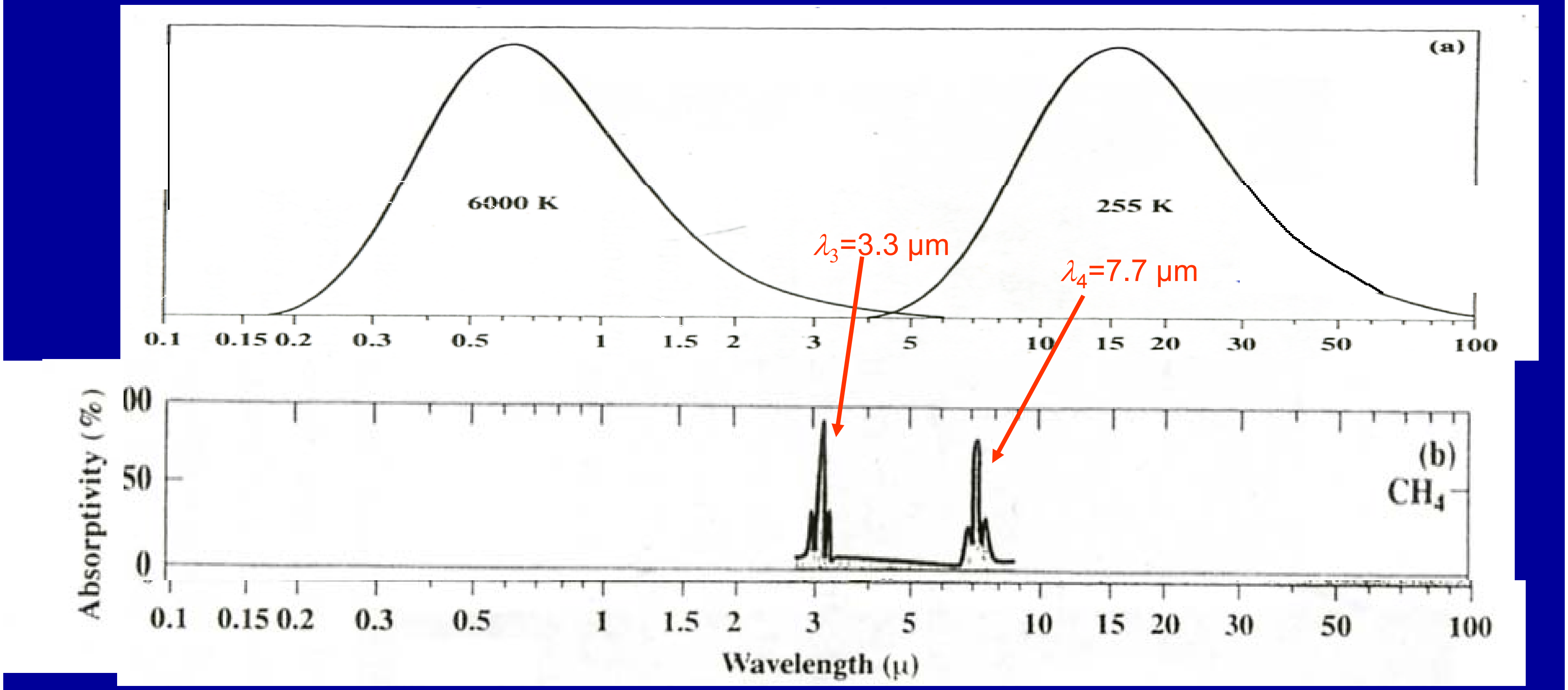
CH_4

- Spherical top
- 5 atoms, 3(5) – 6 = 9 fundamental modes of vibration
- Due to symmetry of molecule, 5 modes are degenerate, only v_3 and v_4 fundamentals are IR active
- No permanent dipole moment => No pure rotational spectrum
- Fundamental modes



λ_1 λ_2 λ_3 = 3.3 μm λ_4 = 7.7 μm

IR Absorption Spectrum of CH_4



CH_4

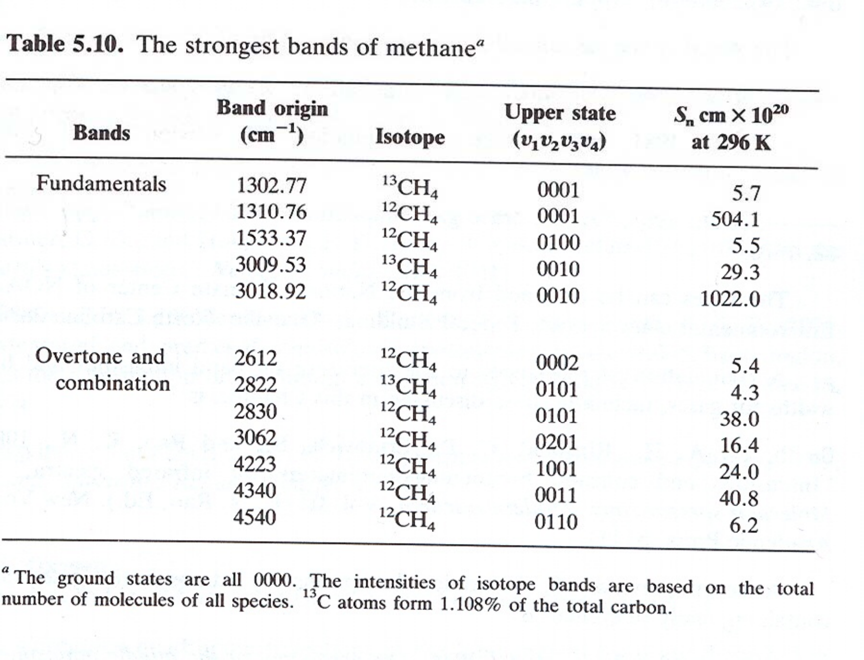
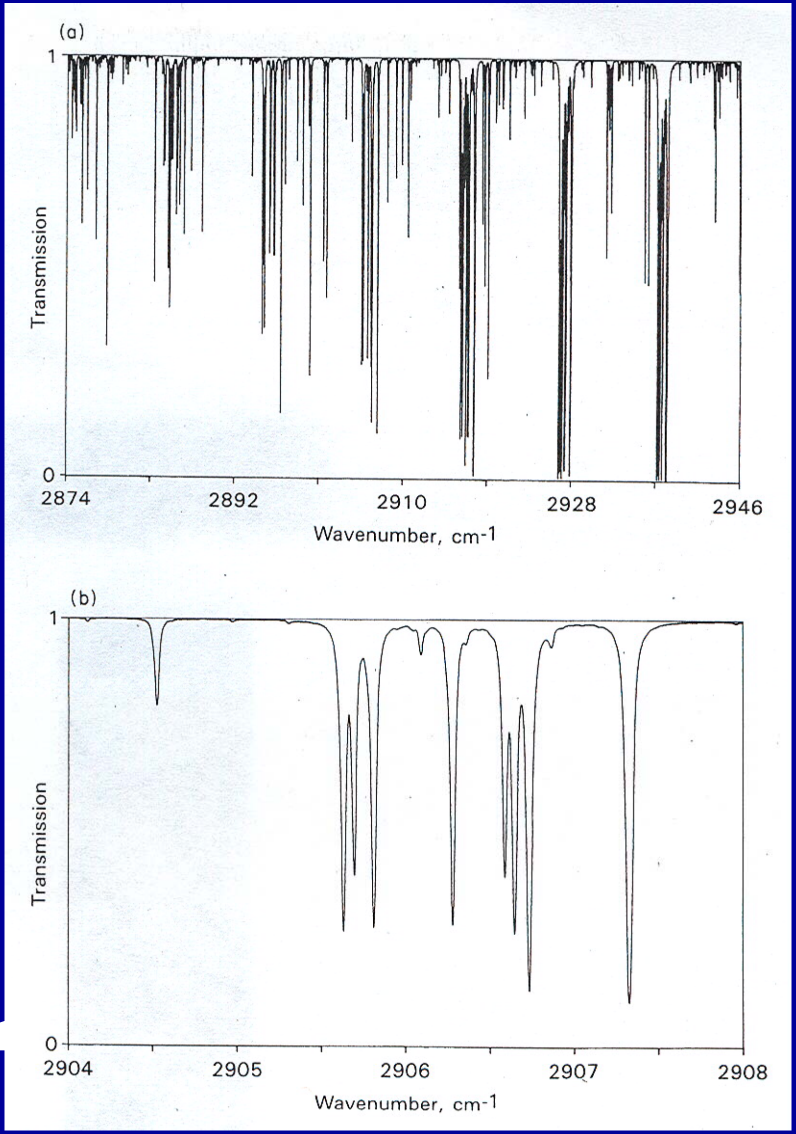


Table 5.10. The strongest bands of methane[a]

Bands	Band origin (cm^{-1})	Isotope	Upper state ($v_1v_2v_3v_4$)	S_n cm × 10^{20} at 296 K
Fundamentals	1302.77	$^{13}CH_4$	0001	5.7
	1310.76	$^{12}CH_4$	0001	504.1
	1533.37	$^{12}CH_4$	0100	5.5
	3009.53	$^{13}CH_4$	0010	29.3
	3018.92	$^{12}CH_4$	0010	1022.0
Overtone and combination	2612	$^{12}CH_4$	0002	5.4
	2822	$^{13}CH_4$	0101	4.3
	2830	$^{12}CH_4$	0101	38.0
	3062	$^{12}CH_4$	0201	16.4
	4223	$^{12}CH_4$	1001	24.0
	4340	$^{12}CH_4$	0011	40.8
	4540	$^{12}CH_4$	0110	6.2

[a] The ground states are all 0000. The intensities of isotope bands are based on the total number of molecules of all species. ^{13}C atoms form 1.108% of the total carbon.

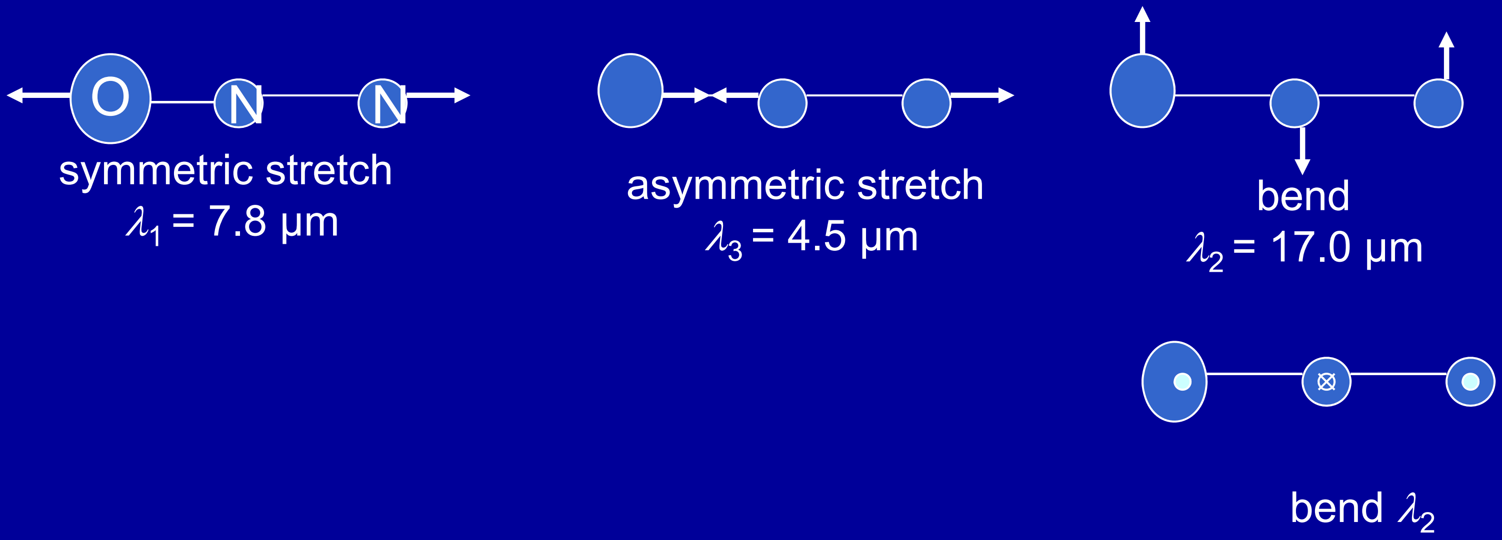


~3.4 μ

N_2O

- Linear, asymmetric molecule (has permanent dipole moment)
- Has rotational spectrum and 3 fundamentals
- Absorption band at 7.8 µm broadens and strengthens methane's 7.6 µm band.
- 4.5 µm band less significant because at edge of Planck function.

- Fundamental modes:



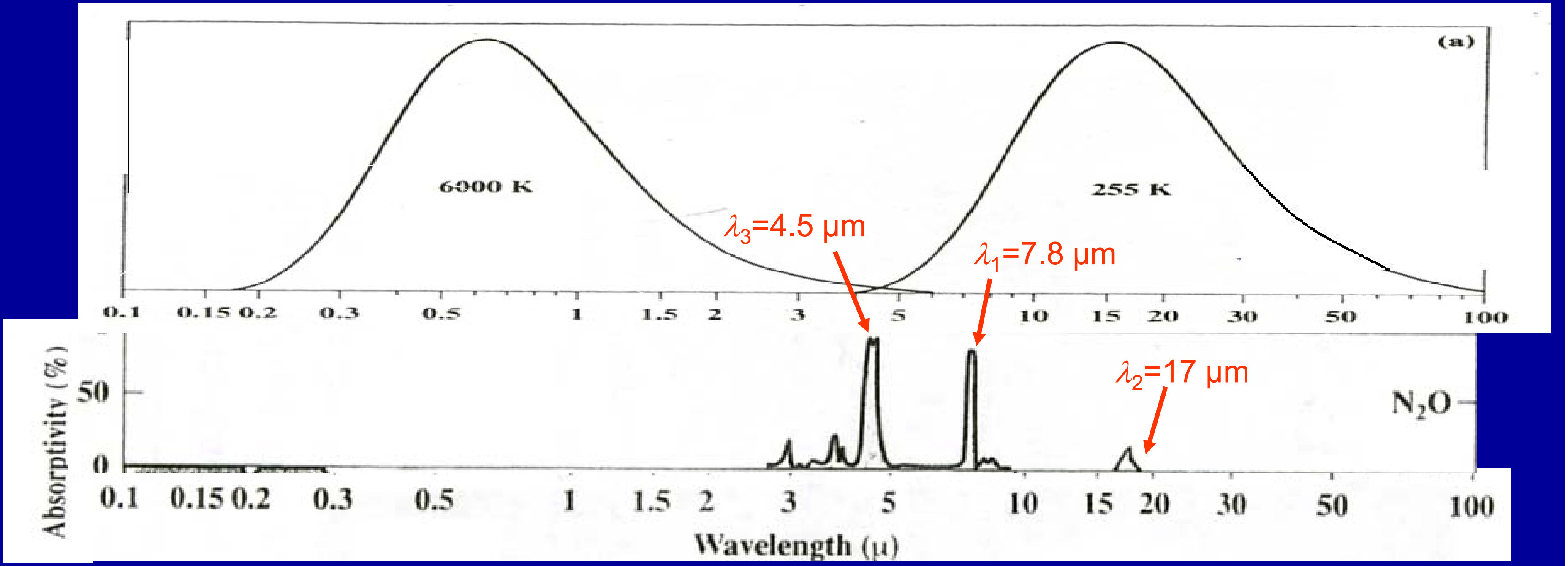
symmetric stretch
λ_1 = 7.8 µm

asymmetric stretch
λ_3 = 4.5 µm

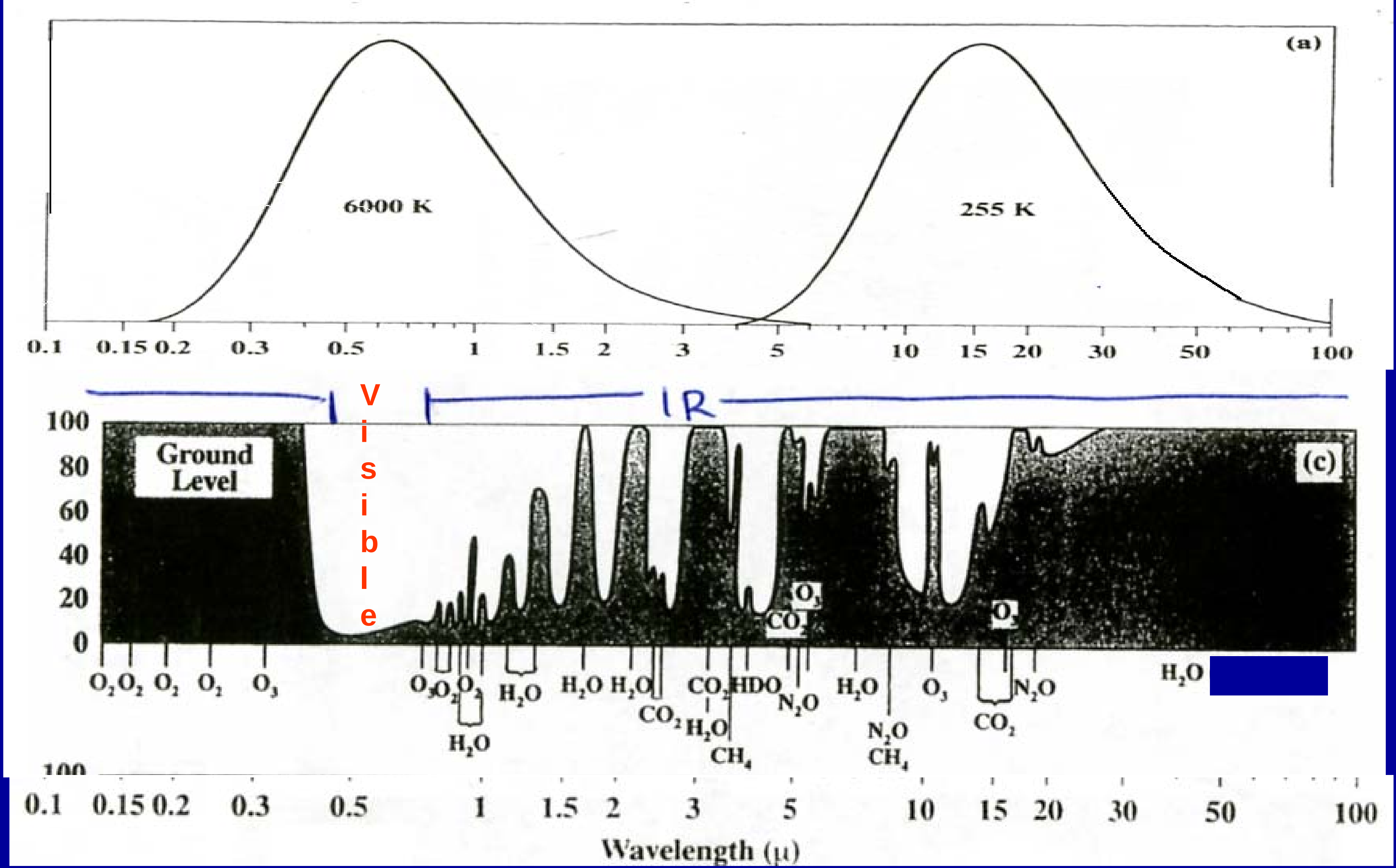
bend
λ_2 = 17.0 µm

bend λ_2

IR Absorption Spectrum of N_2O



Total IR Absorption Spectrum of the Atmosphere



[redacted]

Vibrational levels

- Consider a diatomic molecule. The two atoms are bound together by a force, and can oscillate along the axis of the molecule.
- The force between the two atoms is given by

$$F = -k.x = m\frac{d^2x}{dt^2}$$

- The solution of which is

$$x = x_0 \sin(2\pi\nu_0 t + \phi)$$

Vibrational levels

- ν_0 is known as the vibrational frequency

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

- theoretically ν_0 can assume all values
- However in quantum mechanics these values must be discrete

$$E_v = h\nu_0(v + 1/2)$$

- v is the vibrational quantum number

Rotational levels

- The classical expression for energy of rotation is

$$E_r = \frac{I\omega^2}{2} = \frac{L^2}{2I} \quad \textit{where } L = \textit{angular momentum}$$

$$L^2 \rightarrow \left(\frac{h}{2\pi}\right)^2 J(J+1)$$

- where *J* is the rotational quantum number

$$E(J) = \frac{1}{2I}\left(\frac{h}{2\pi}\right)^2 J(J+1) = h\,c\,B_v J(J+1)$$

$$B_v = \frac{h}{8\,\pi^2 c\,I} \quad \text{the rotational constant}$$

Vibrating Rotator

- If there were no interaction between the rotation and vibration, then the total energy of a quantum state would be the sum of the two energies. But there is, and we get

$$\frac{E(v,J)}{hc} = \omega_0(v+1/2) - \omega_0 x_e (v+1/2)^2$$
$$+ B_v J(J+1) + D_v J^2 (J+1)^2$$

- The wavenumber of a spectral line is given by the difference of the term values of the two states

Energy levels of a vibrating rotator

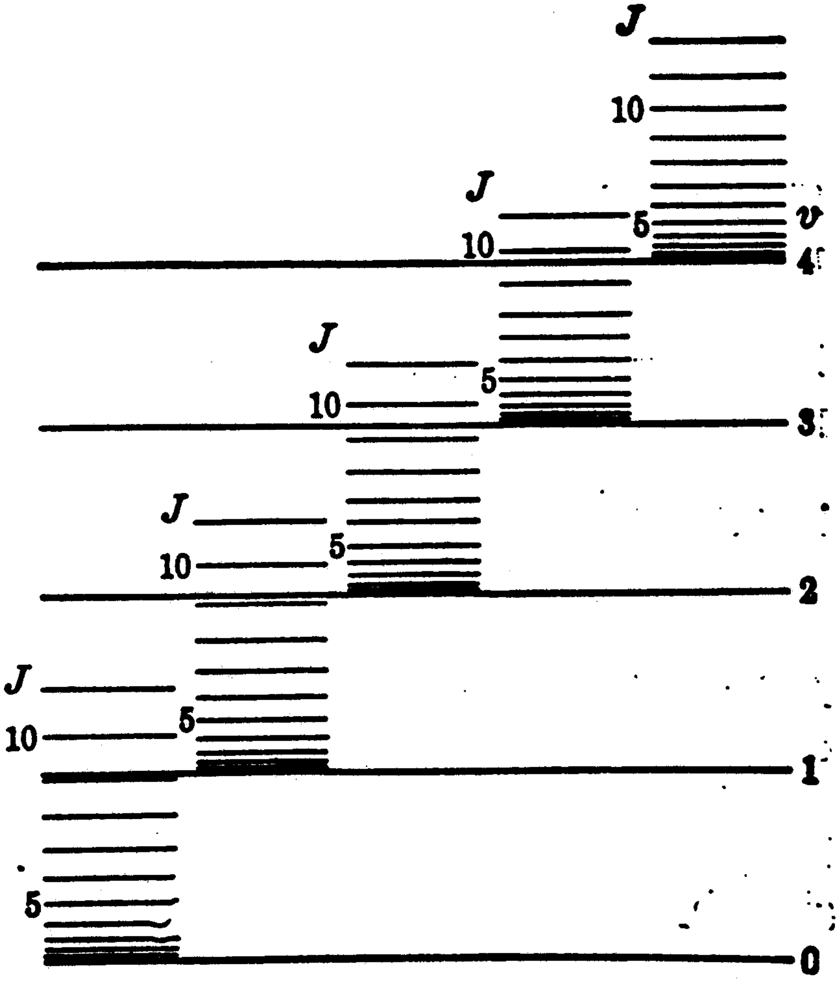


Fig. 53. Energy Levels of the Vibrating Rotator. For each of the first five vibrational levels, a number of rotational levels are drawn (short horizontal lines).

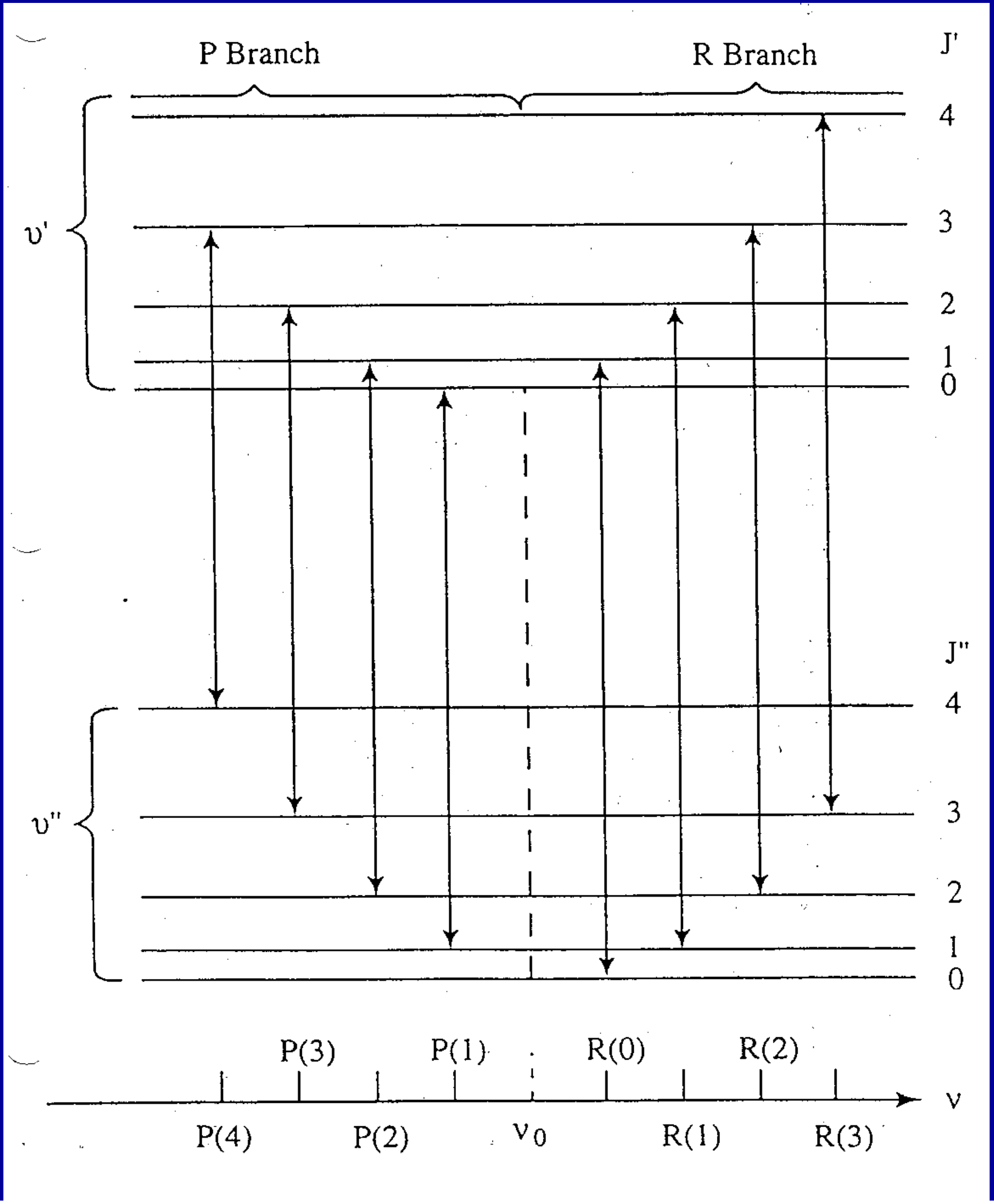
Transition rules

- Not all transitions are allowed - selection rules, e.g. in rotational transitions changes in J are restricted to 0, and ±1

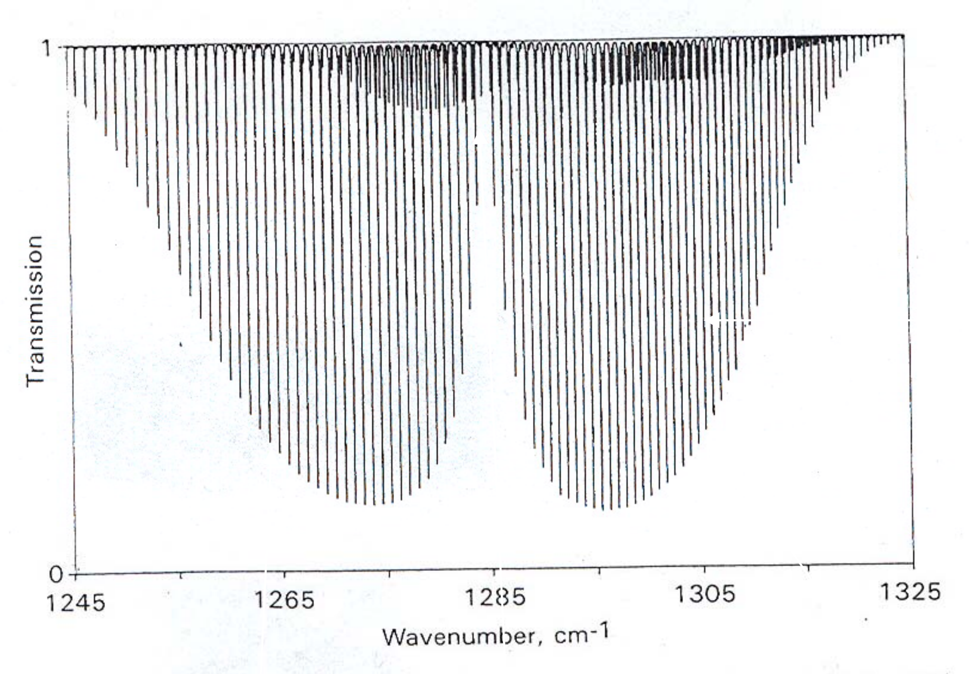
•The complete set of rotational transitions between two vibrational levels is known as a ‘band’

•A band normally consists of three separate sequences; if ΔJ=0 we have the Q branch, ΔJ=1 the R branch, ΔJ=-1 the P branch

Selection rules



N_2O



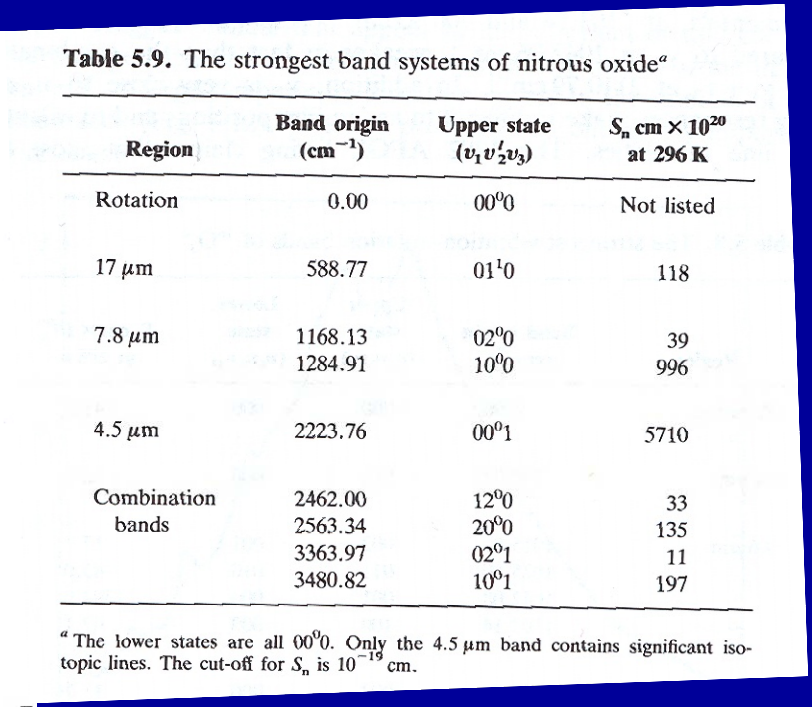


Table 5.9. The strongest band systems of nitrous oxide[a]

Region	Band origin (cm^{-1})	Upper state ($v_1 v_2^l v_3$)	S_n cm × 10^{20} at 296 K
Rotation	0.00	00^00	Not listed
17 μm	588.77	01^10	118
7.8 μm	1168.13	02^00	39
	1284.91	10^00	996
4.5 μm	2223.76	00^01	5710
Combination bands	2462.00	12^00	33
	2563.34	20^00	135
	3363.97	02^01	11
	3480.82	10^01	197

[a] The lower states are all 00^00. Only the 4.5 μm band contains significant isotopic lines. The cut-off for S_n is 10^{-19} cm.

P
branch

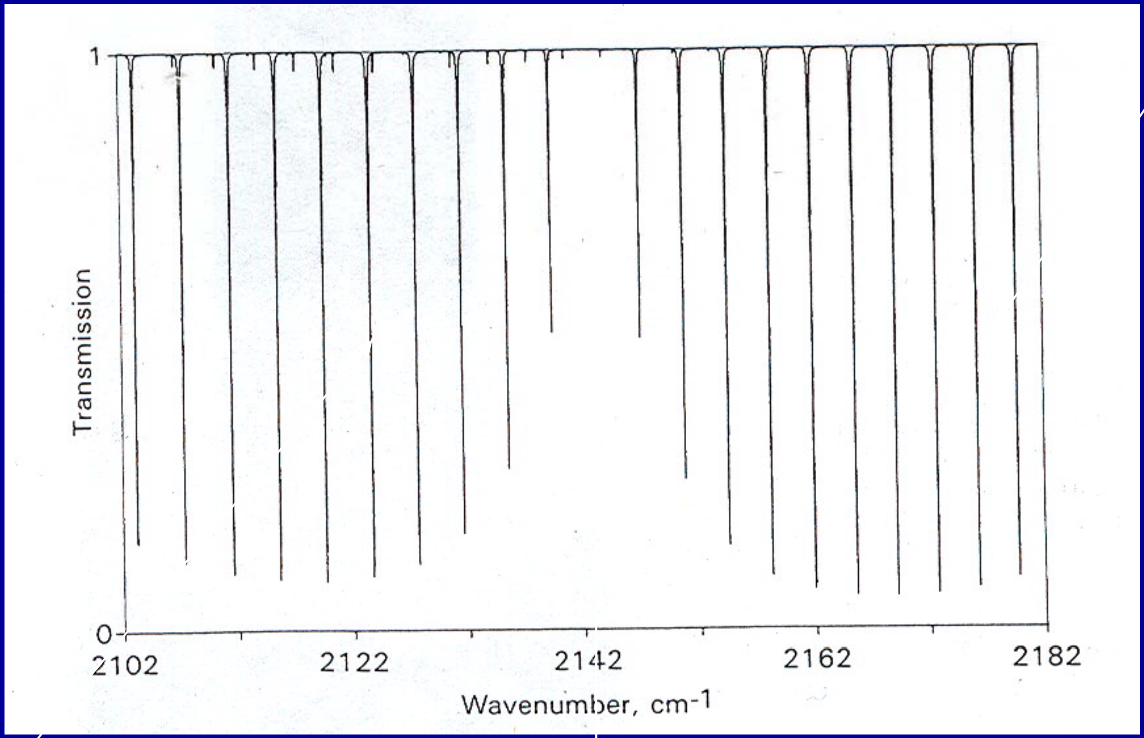
No Q
branch

R
branch

CO

- •Linear diatomic, simple spectrum
- •Vibration-rotation band at ~4.67 μm

R branch



P branch

No Q branch

Line strengths

- The line strength is for an isolated line, S. In the case of a vibration-rotation band we define a band strength
- To determine the line strength of a individual transition we need to determine the population of the lowest level for each vibration/rotation level. As the electronic levels have a large energy difference, nearly all molecules are in the so-called ‘ground’ state.

Line strengths

- The population of the vibrational levels is governed by the Boltzmann distribution

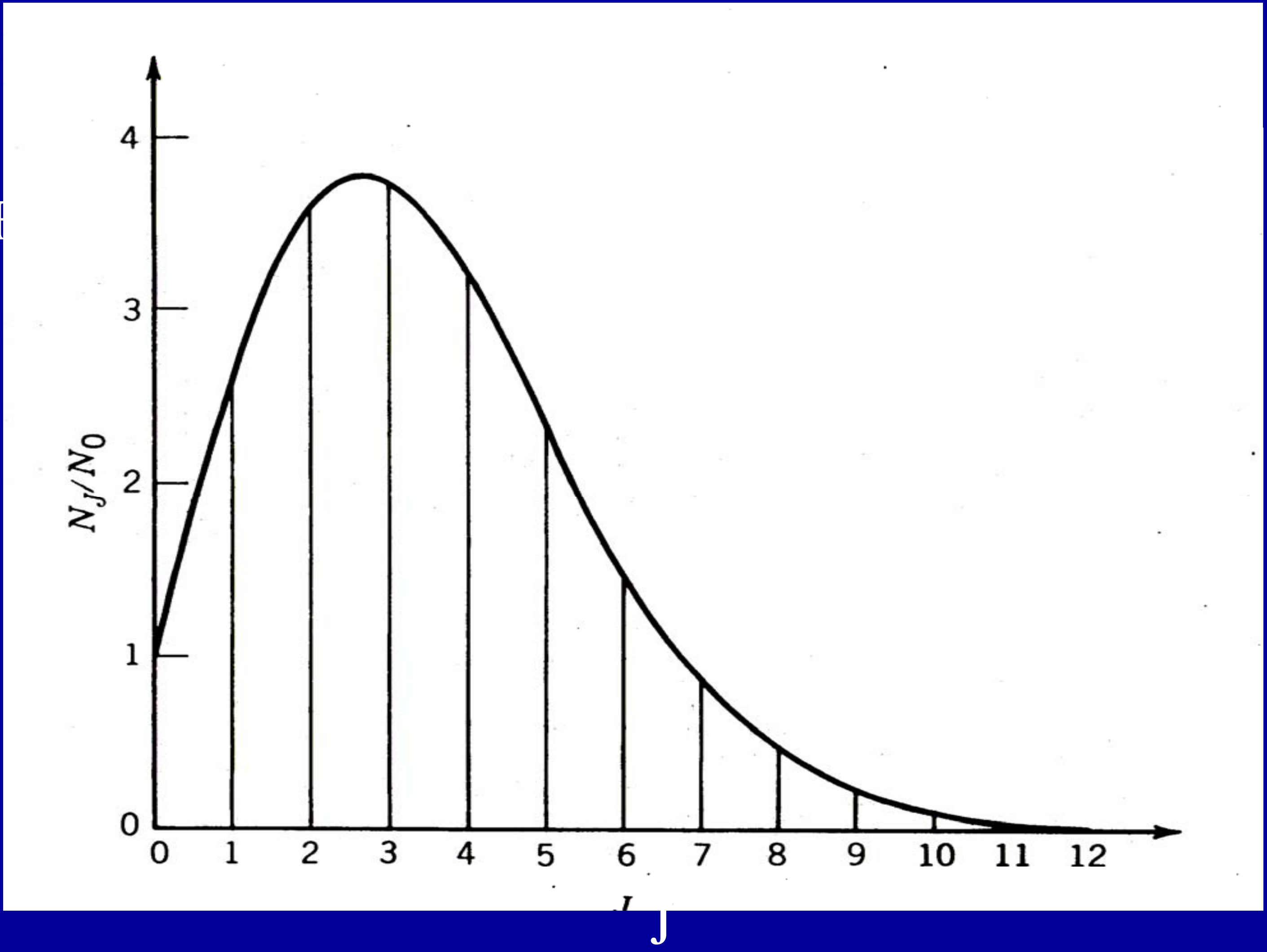
$$N(v) = N_0 \exp\left(-\frac{G(v)}{k_B T}\right)$$

where N_0 is the total number of molecules per cm^3

- For each rotational number *J* there are *(2J+1)* levels.

$$N(J) = N_0 \frac{hcB_v}{k_B T}(2J+1)\exp-\frac{E(J)}{k_B T}$$

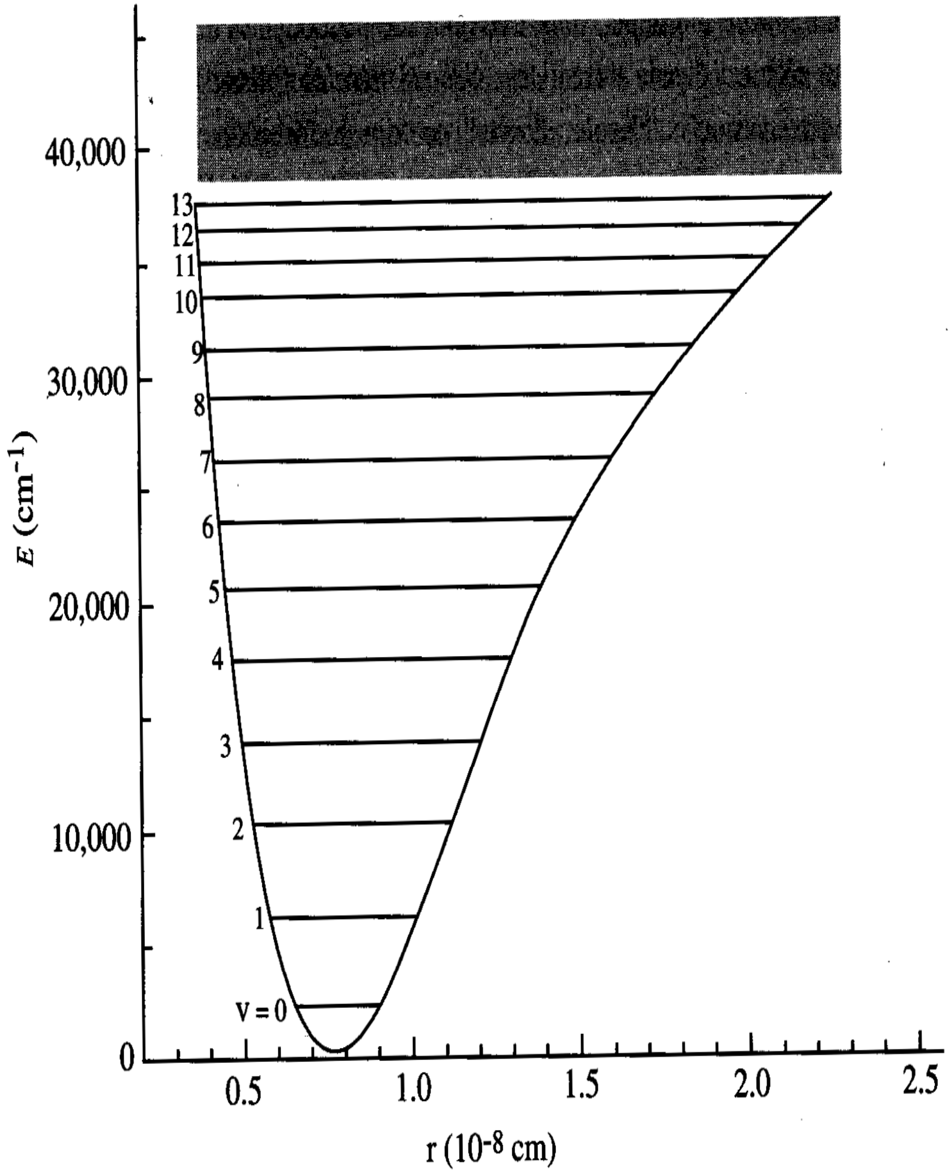
Relative populations of rotational levels



Electronic levels

- In molecules we have two opposing forces - the repelling force of the nuclei, and the binding force of the electrons.
- If the orbit of the electrons change then the binding force will change, i.e. the net potential energy of the molecule will change.
- This means that the inter-atomic distance will change
- Different electronic levels will have different rotational and vibrational constants

Potential energy diagram for a typical diatomic molecule



- The x axis is the inter-nuclear separation r, and the y axis is the potential energy.

- As the two atoms come together the electrons of each overlap and produce a binding force which stabilizes the molecule.

- Hence the ‘potential well’.

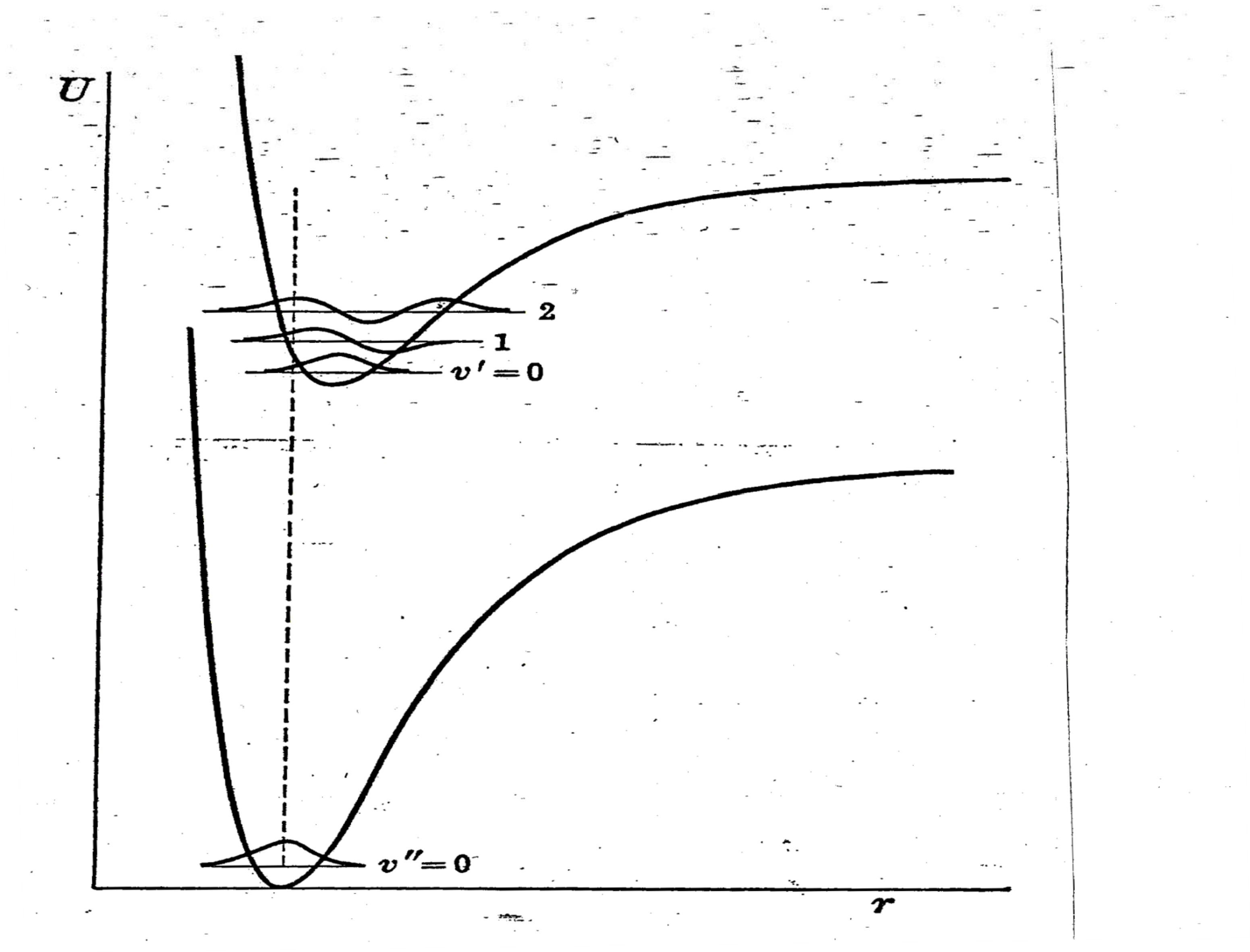
- The shaded area represents energies for which the molecule can be broken apart. When this occurs the molecule is not restricted to absorbing discrete energies as any additional energy can be taken away by the atoms as kinetic energy which is not quantized.

- The shaded area is referred to as a dissociation continuum.

Franck-Condon principle

- The time for a transition is extremely small, and in this time the atoms within a molecule can be assumed not to move.
- Franck and Condon therefore postulated that on a potential energy diagram the most likely transitions would be vertical transitions

Franck-Condon principle



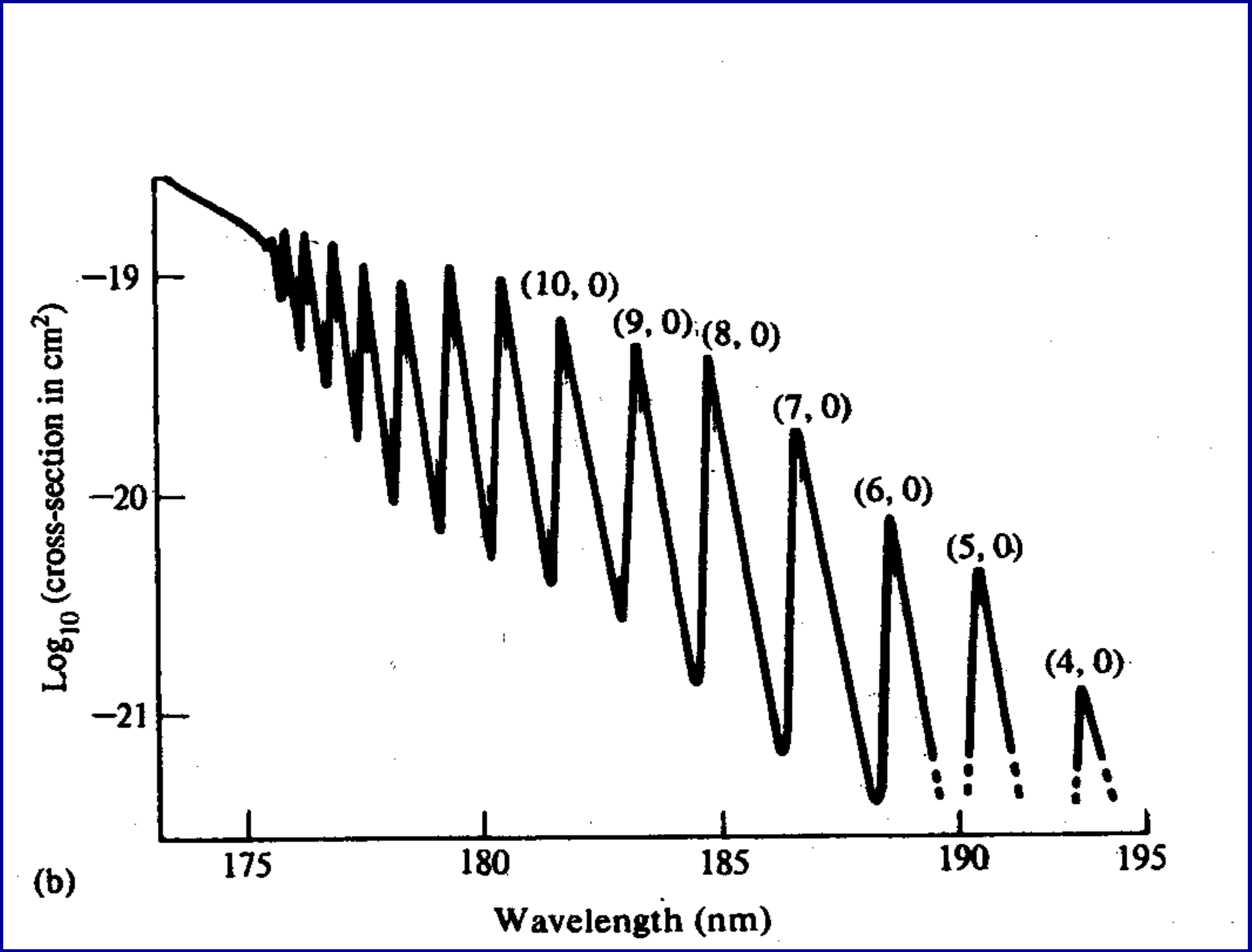
Photodissociation

- The fragmentation of a chemical species following the absorption of light is most important in atmospheric chemistry
- Optical dissociation occurs from the electronic state to which absorption takes place
- Absorption leading to dissociation gives rise to a continuum, as additional energy can be taken away by the fragments as kinetic energy, which is not quantized.
- The atomic products can be in an excited state.

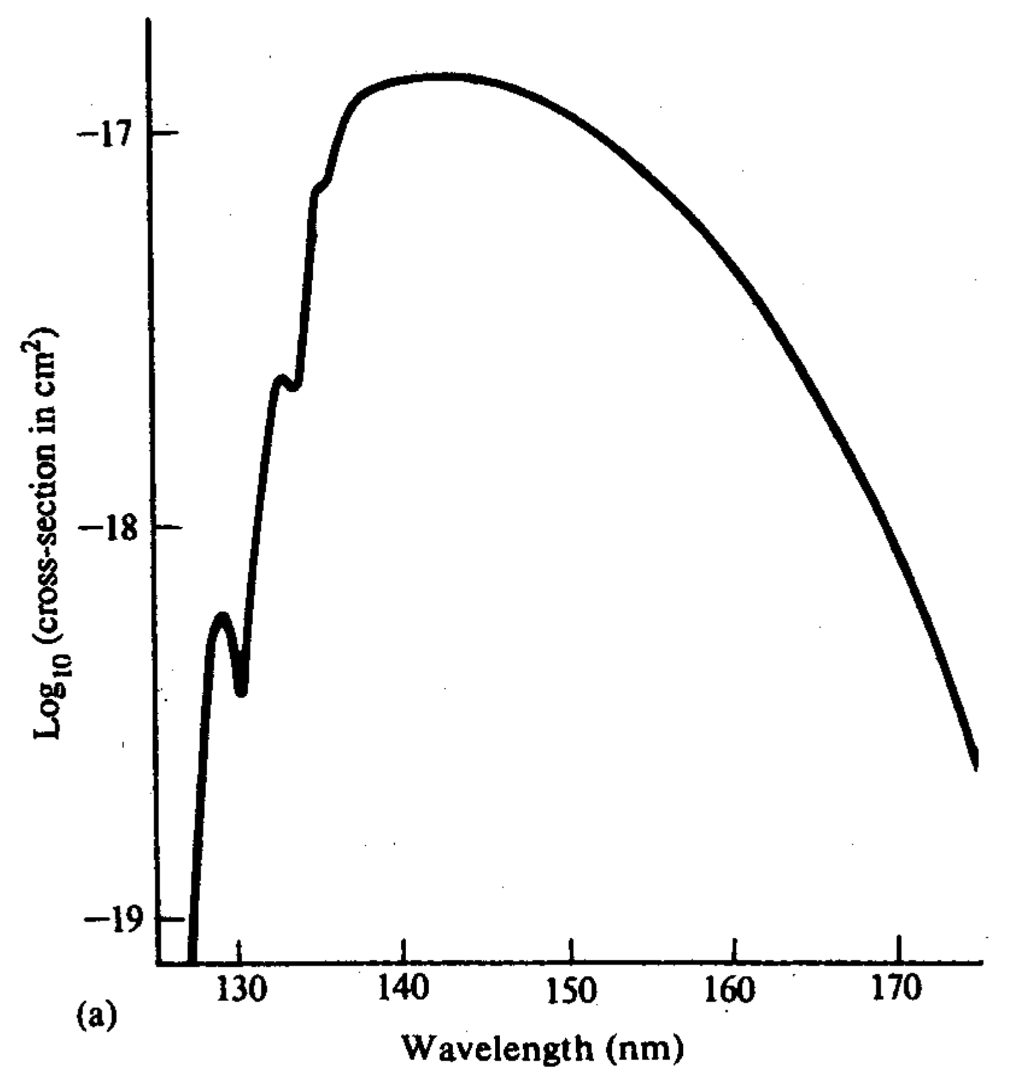
Photodissociation

- Two main mechanisms are recognized for dissociation, optical dissociation and pre-dissociation. These processes will be illustrated in the O_2 molecule.
- Optical dissociation occurs within the electronic state to which the dissociation first occurs. The absorption spectrum leading to dissociation is a continuum.
- At some longer wavelength the spectrum shows vibrational bands. The bands get closer together as the limit is approached – the restoring force for the vibration gets weaker.

Discrete absorption in molecular oxygen, (Schumann-Runge bands)



Absorption continuum in molecular oxygen (Schumann-Runge continuum)



The three line broadening mechanisms

Recall that:

$\alpha_n(\nu) = S\,\Phi(\nu)$ absorption cross section

$[m^2] = [m^2 s^{-1}][Hz^{-1}]$

$\alpha_m(\nu) = S\,\Phi(\nu)$ mass absorption coefficient

$$\int_0^\infty \Phi(\nu)\,d\nu = 1$$

$[m^2 kg^{-1}] = [m^2 s^{-1} kg^{-1}][Hz^{-1}]$

and by definition:

Why do absorption have lines shapes that are not δ-functions?

- Broadening due to Heizenberg's Uncertainty Principle (natural broadening)
- Broadening due to collisions (pressure broadening)
- Broadening due to Doppler effects

Natural broadening

- The line width (full width at half maximum) of the Lorentz profile is the damping parameter, γ.
- For an isolated molecule the damping parameter can be interpreted as the inverse of the lifetime of the excited quantum state.
- If absorption line is dampened solely by the natural lifetime of the state this is natural broadening

$$\Delta E \Delta t \approx \frac{h}{2\pi} \qquad \Delta t \approx \frac{h}{2\pi . h \Delta \nu} \approx \frac{1}{2\pi \Delta \nu}$$

- This is consistent with the Heisenberg Uncertainty Principle

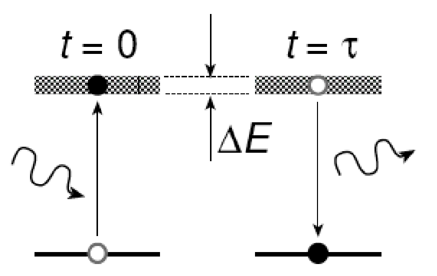
Heisenberg uncertainty principle

- **Heisenberg uncertainty principle** states that certain pairs of physical properties, such as position and momentum of an electron or any other particle, cannot be simultaneously known to arbitrarily high precision.

- That is, a system cannot be *defined* to have simultaneously singular values of these pairs of quantities. A minimum exists for the product of the uncertainties in these properties that is equal to or greater than one half of the reduced Planck constant ($\hbar = h/2\pi$).

Natural line width

Excited molecule decays spontaneously. Upper state has finite lifetime $t_R \equiv \Delta t$



Heizenberg's Uncertainty Principle:

$\Delta E \Delta t \approx h/2\pi \Rightarrow \Delta \nu \Delta t \approx 1/2\pi \Rightarrow \Delta t \equiv t_R \approx (2\pi \Delta \nu)^{-1}$, so $\Delta \nu \approx 1/2\pi t_R \equiv \alpha_N$ (natural line width)

Recall that:

Electronic transitions: $t_R \approx 10^{-8}$ s $\Rightarrow \alpha_N \approx 5\text{x}10^{-4}$ cm^{-1}

Vibrational transitions: $t_R \approx 0.1$ s $\Rightarrow \alpha_N \approx 5\text{x}10^{-11}$ cm^{-1}

Rotational transitions: $t_R \approx$ 1-10 s $\Rightarrow \alpha_N \approx 10^{-12}$ cm^{-1}

Pressure broadening

- For an isolated molecule the typical natural lifetime is about 10^{-8} s, 5×10^{-4} cm^{-1} line width
- However as the pressure increases the distance between molecules becomes shorter. We can view the outcome in two ways
- (1) Collisions between molecules can shorten the lifetime, and hence the line width becomes larger.
- (2) As the molecules get closer their potential fields overlap and this can change the ‘natural line width’.
- Because the molecules interact with each other, molecule collisions reduce the lifetime of the upper state, and thus broaden the line.

Pressure broadening

- Clearly the line width will depend on the number of collisions per second,i.e. on the number density of the molecules (Pressure) and the relative speed of the molecules (the square root of the temperature)

$$\alpha_L \approx \alpha_L(STP)\frac{n\mathrm{v}_{rel}}{n_L\mathrm{v}_{rel}(STP)} = \alpha_L(STP)\frac{n\sqrt{T}}{n_L\sqrt{T_0}}$$

Doppler broadening

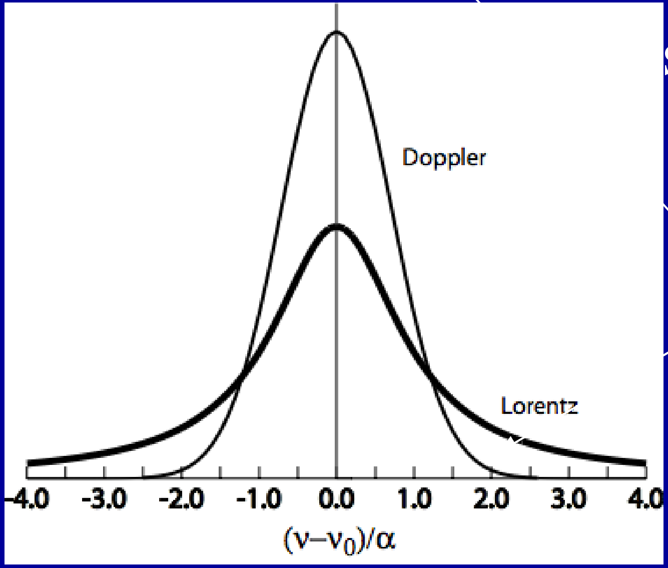
- Second major source of line broadening
- Molecules are in motion when they absorb. This causes a change in the frequency of the incoming radiation as seen in the molecules frame of reference
- Let the velocity be v, and the incoming frequency be ν, then

$$\nu' = \nu + \frac{\mathrm{v}\cos\theta}{\lambda} = \nu + \frac{\nu\,\mathrm{v}\cos\theta}{c} = \nu\left(1 + \frac{\mathrm{v}}{c}\cos\theta\right)$$

Doppler broadening

- Line broadening due to the random motion of atmospheric molecules
- Doppler effect: The frequency of emitted light is higher if the emitter (molecule) approaches the detector, lower if it moves away from the detector.
- For a Maxwell-Boltzmann distribution of molecular velocities it can be shown that the line broadening due to the Doppler effect shape:

$$\Phi_D(\nu) = \frac{1}{\sqrt{\pi}\alpha_D}\exp\left[-\frac{(\nu-\nu_0)^2}{\alpha_D^2}\right]$$



where the Doppler 1/e-(half) width (independent of pressure!) is

$$\alpha_D \equiv \nu_0 \upsilon_0/c \; [\upsilon_0=(2k_B T/m)^{1/2}]$$

Note how the Doppler profile falls faster than the Lorentz profile in the vicinity of the line wings.

$$\int_0^\infty \Phi_D(\nu)\,d\nu = 1$$

Properly normalized

$\sqrt{\ln 2}$

and the line half-width at half