

5/20/93

LECTURES ON RADIATIVE TRANSFER

I. GAS ABSORPTION

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EQUATION OF RADIATIVE TRANSFER

$$\mu \frac{dI}{d\tau} = I - S$$

μ = cosine of observer's \angle

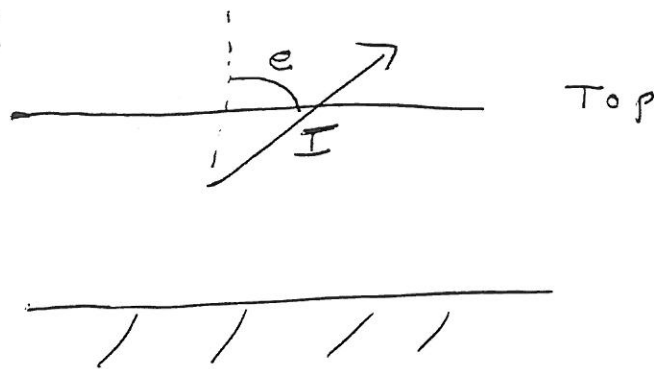
I = Specific Intensity
(energy flux in direction μ)

S = Source Function

τ = Optical depth

(a measure of the probability of light interacting with gases and particles in path of Travel)

e = View \angle



GAS OPACITY

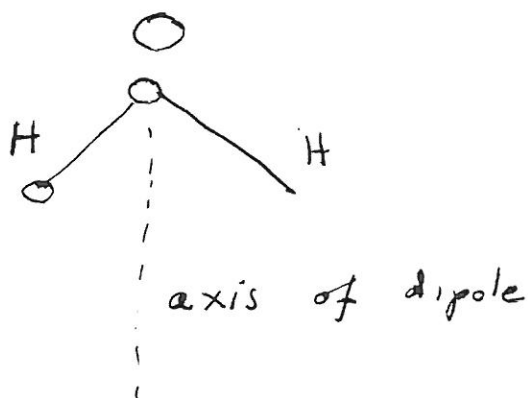


NECESSARY CONDITION FOR
ABSORPTION/EMISSION :

Gas Molecule (Atom) have a
time varying electric (or magnetic)
dipole (or higher order) moment

Example :

H_2O :



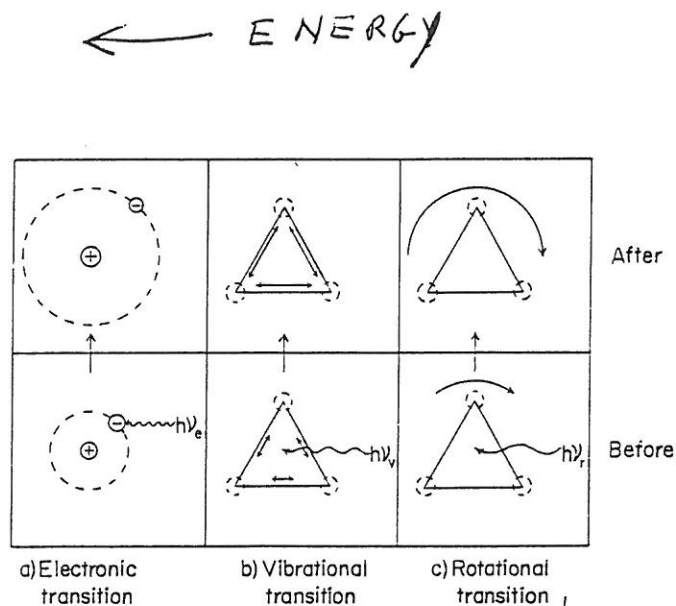
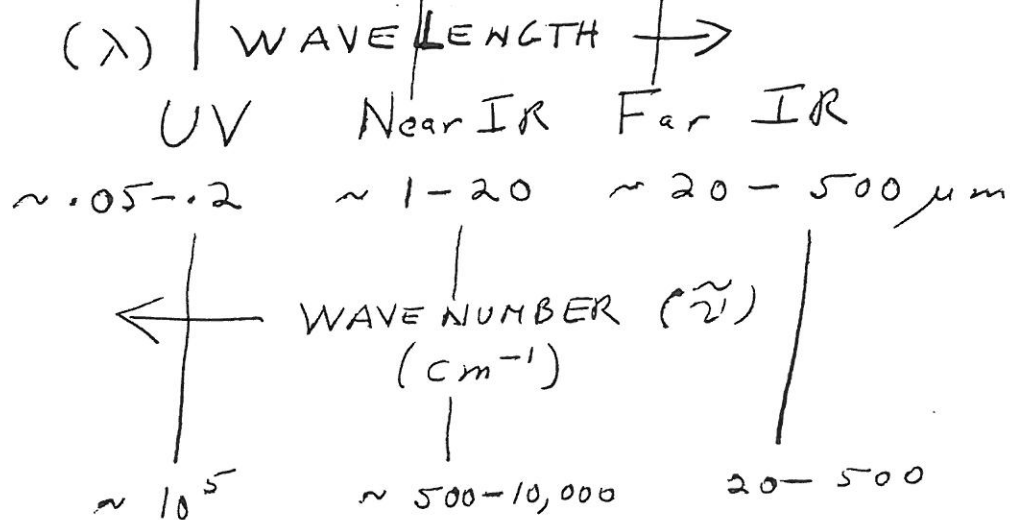


FIG. 8.1. Three kinds of atomic and molecular transitions that can occur upon absorption of a quantum of energy. The arrow lengths are proportional to the energy of vibration and rotation.



$$\tilde{\nu} (\text{cm}^{-1}) = \frac{1}{\lambda (\text{cm})} = \frac{10^4}{\lambda (\mu\text{m})}$$

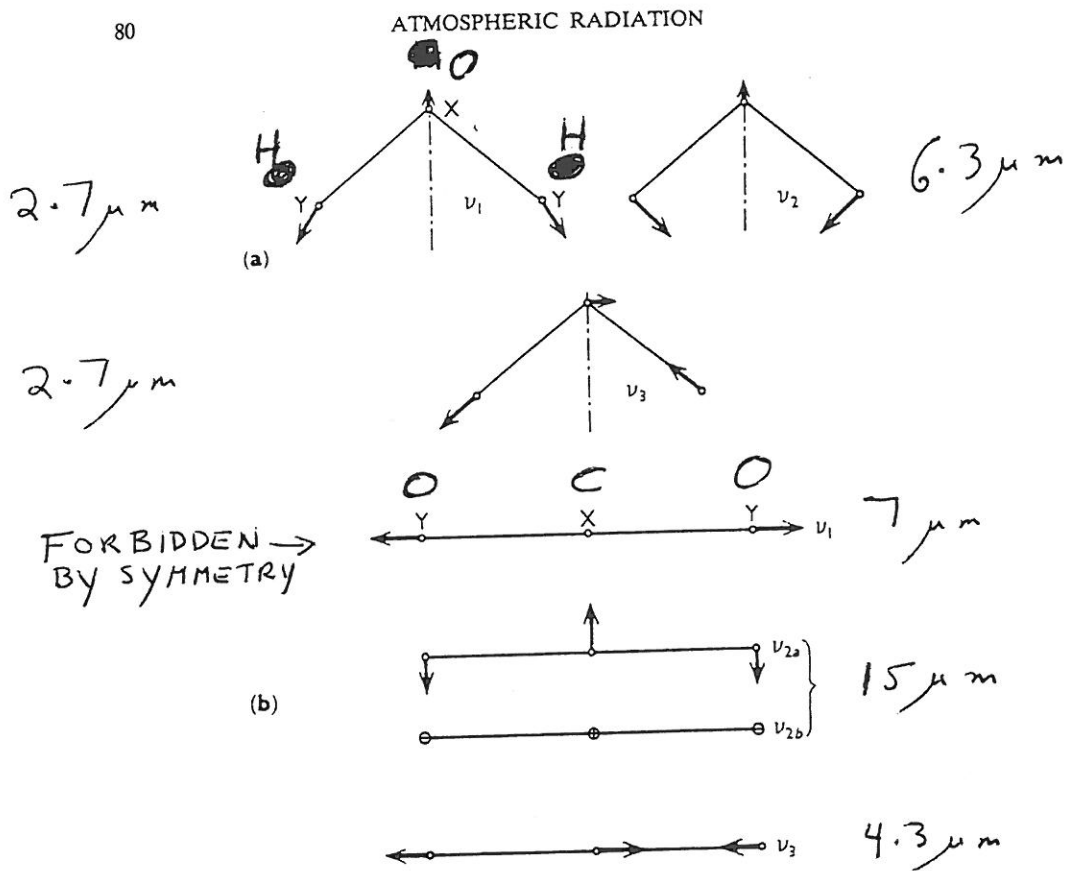


FIG. 3.9. Normal vibrations of a triatomic molecule. (a) H_2O is an example of a nonlinear triatomic molecule. (b) CO_2 is an example of a linear triatomic molecule. After Herzberg (1945).

Number of vibrational modes =
 Total # degree of freedom ($3 \times \# \text{ atoms}$)
 - # Translational modes ($= 3$) \downarrow polyatomic
 - # rotational modes ($2 \text{ or } 3$) \uparrow diatomic

Ex: CO_2 - # vibr modes = $9 - 3 - 3 = 3$

QUANTIZED ENERGY LEVELS

ROTATIONAL

— ENERGY LEVELS DEPEND ON
MOMENTS OF INERTIA, I

$$E_r = h c F(J, K_A, K_C)$$

\swarrow Planck constant \searrow speed of light

$$F(J, K_A, K_C) = B J(J+1) + (A-B) K_A^2 + (C-B) K_C^2$$

$$A, B, C = h / 8 \pi^2 c I_i$$

E_x :

CO_2 - Linear molecule $\rightarrow A = B = C$

CH_4 - spherical top $\rightarrow A = B = C$

NH_3 - symmetric top $\rightarrow A \neq B = C$

H_2O - asymmetric top $\rightarrow A \neq B \neq C$

O_3 - symmetric top

— SELECTION RULES

permitted, dipole

$$\begin{cases} \Delta J = +1 & (\text{rotation only}) \\ \Delta J = -1, 0, 1 & (\text{vibration + rotation}) \end{cases}$$

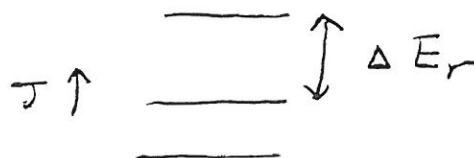
~~LINE LOCATION~~

LINE LOCATIONS:

$$\Delta E_r = hc \tilde{\nu} = hc \Delta F$$

$$\tilde{\nu} \xrightarrow{\quad} = 2 B_J (J+1)$$

(linear ~~or~~ spherical top)



VIBRATIONAL

Energy $E_v = \sum_k hc \tilde{\nu}_k (v_k + 1/2)$

↑ vibrational qt. #

Selection Rules $\Delta v_k = + n_k \leftarrow \text{any integer}$

if $n_k = 1$ for $k = k^*$ & $= 0$ otherwise
fundamental

$n_k > 1$ for $k = k^*$ & $= 0$ otherwise
overtone

$n_k > 0$ for several $k \rightarrow$
combination band

$\Delta J = \pm 1$

LINE LOCATIONS: $\tilde{\nu} = \sum_k \tilde{\nu}_k n_k \pm 2 B_J (J+1)$

$\Delta J = 0 \rightarrow (\text{or } \approx 0)$

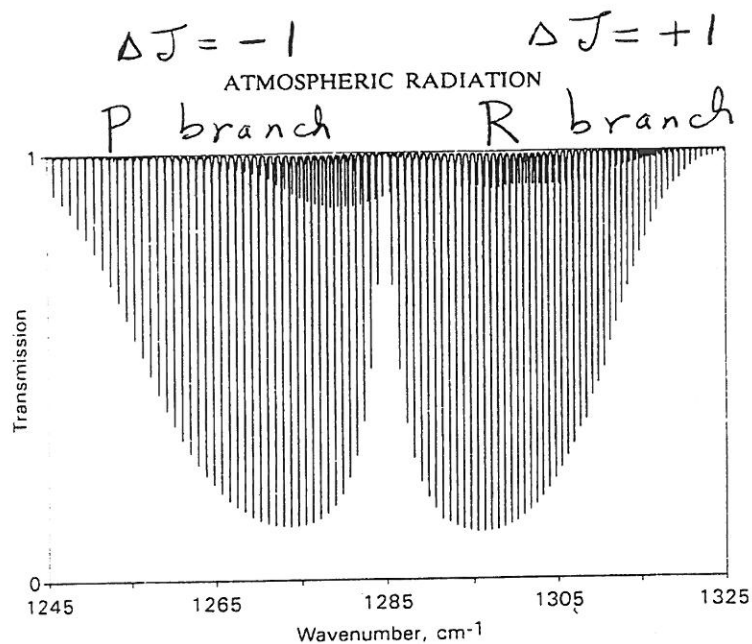


FIG. 3.3. Synthetic spectrum of N_2O near $7.78 \mu m$. Spectral range: $1245-1325 \text{ cm}^{-1}$. Altitude of observation: 15 km. Zenith angle of observation: 30° . Terrestrial concentration $\times 1$.

Figure 3.2a and Fig. 3.2b are both centered on a region in the wing of the strong $3.31 \mu m$ band of methane. Figure 3.2a shows eight groups of lines (*manifolds*) while Fig. 3.2b shows details of one manifold. At the high dispersion of spectrum (b), each line is seen to have a finite width.

Figure 3.3 shows the central region of the strongest band of nitrous

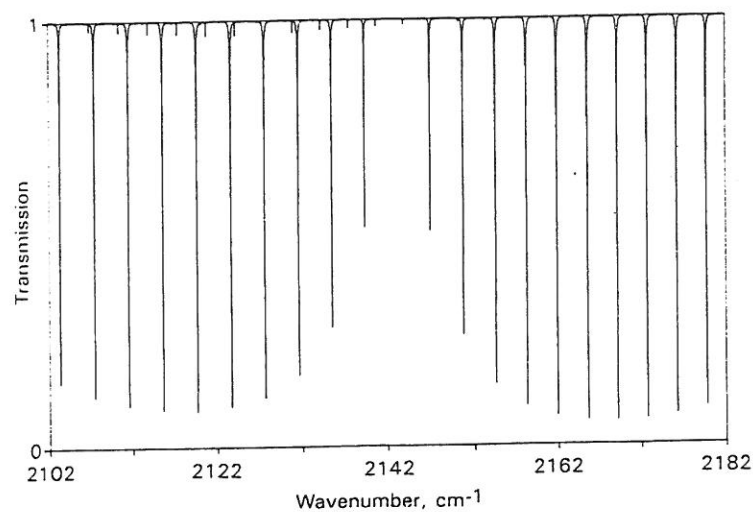


FIG. 3.4. Synthetic spectrum of CO near $4.67 \mu m$. Spectral range: $2102-2182 \text{ cm}^{-1}$. Altitude of observation: 10 km. Zenith angle of observation: 30° . Terrestrial concentration $\times 1$.

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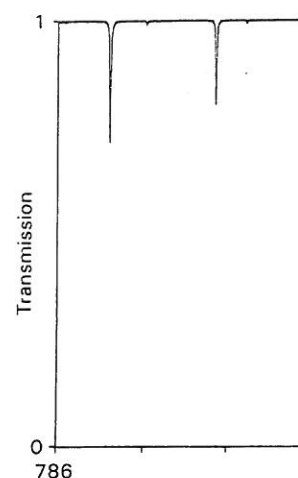


FIG. 3.5. Synthetic spectrum of CO near $7.78 \mu m$. Altitude of observation: 15 km. Zenith angle of observation: 30° . Terrestrial concentration $\times 10$.

oxide. The two very regular groups of lines on the left and the right, respectively, are caused by a missing line at the center of the band is superimposed (an *upper* center. Mixed in here, and also

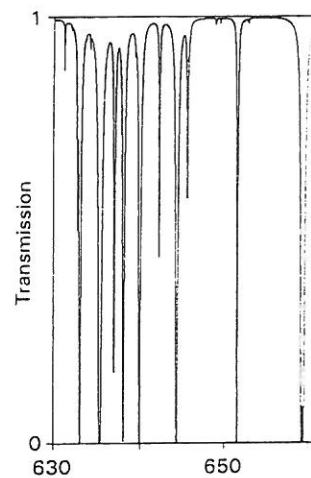
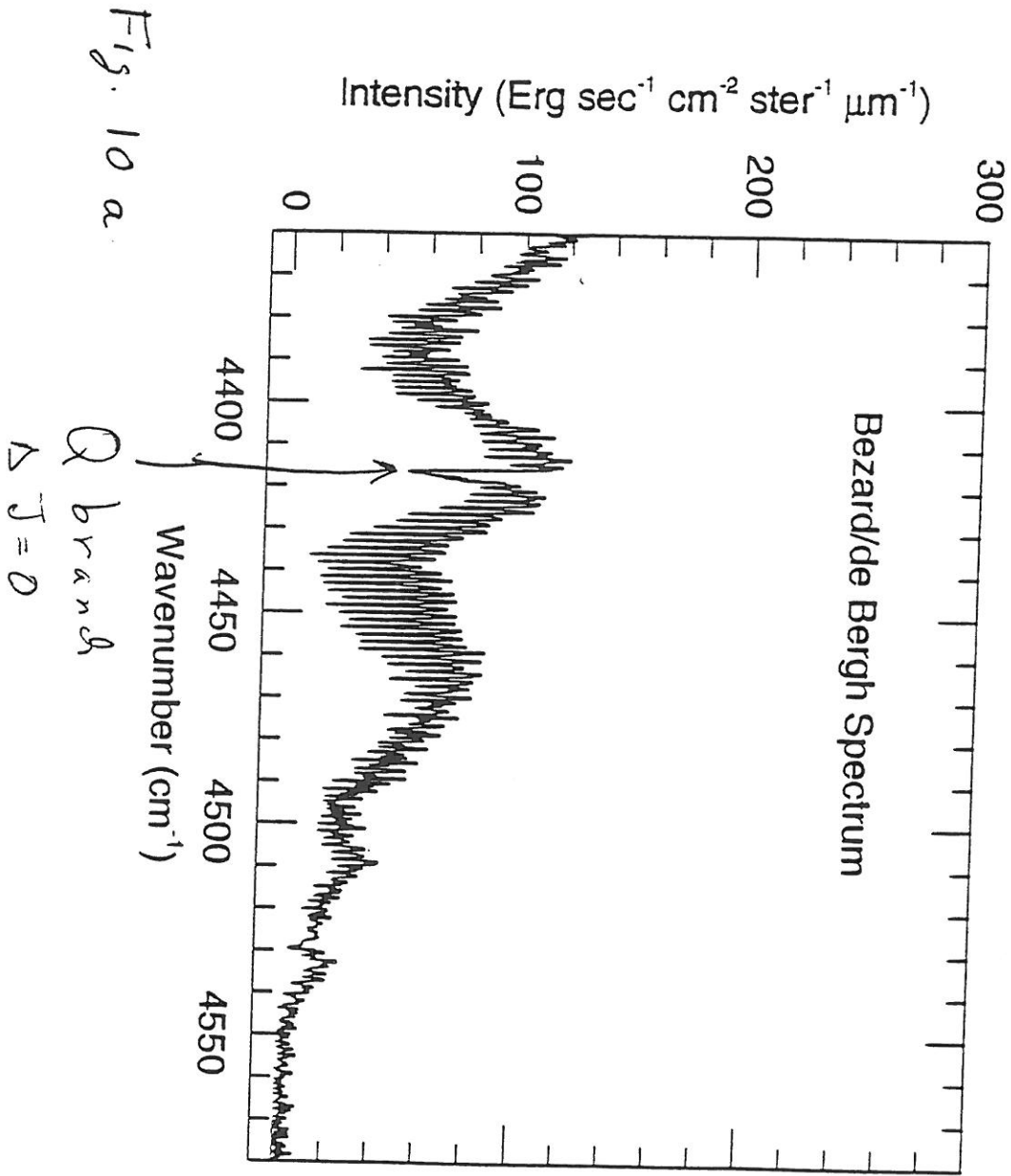
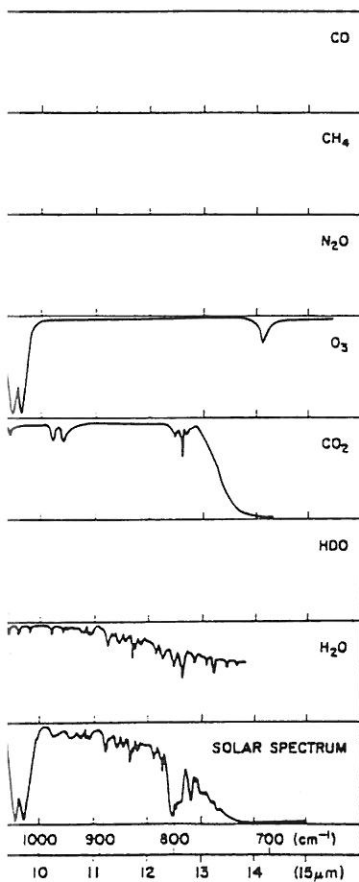


FIG. 3.6. Synthetic spectrum of H_2O near $6.3 \mu m$. Altitude of observation: 0 km. Zenith angle of observation: 30° . Terrestrial concentration $\times 0.03$.





atmosphere. The top six panels are
ies. The bottom panel is a simulated
(1965).

ore complex theoretically but
s shown in Fig. 3.1. Data for
ical calculations are discussed

the form of discrete bands of
nd of water vapor, stretching
all involve a change in the
tering widths of the bands are
e rotational energy, and the
n bands.

otation bands at much higher
.2, 3.3, 3.4, 3.5, 3.6, and 3.7.

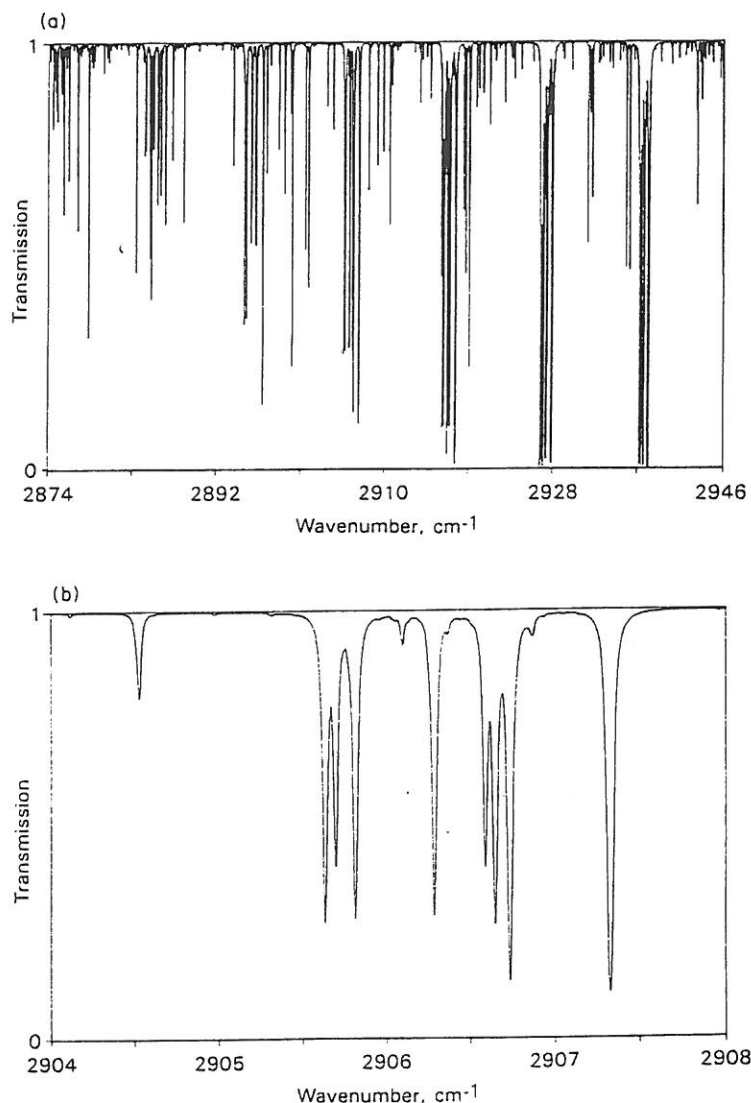
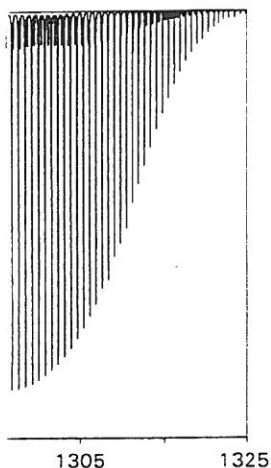


FIG. 3.2. Synthetic spectrum of CH_4 near $3.44 \mu\text{m}$. Spectral range: (a) $2874\text{--}2946 \text{ cm}^{-1}$; (b) $2904\text{--}2908 \text{ cm}^{-1}$. Level of observation: 10 km. Zenith angle of observation: 30° . Terrestrial concentration $\times 1$.

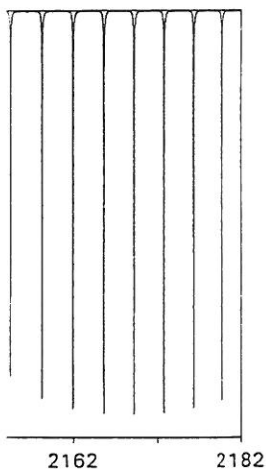
Each has been constructed by a computer for a single atmospheric constituent. The absorption path reaches from outside the atmosphere down to the level of observation at the given zenith angle of observation. Terrestrial gas concentrations are employed or a given multiple of them, if this makes for a clearer illustration.

TION



Spectral range: 1245–1325 cm^{-1} .
Altitude of observation: 30°. Terrestrial concentration

ferred on a region in the wing
are 3.2a shows eight groups
tails of one manifold. At the
seen to have a finite width.
the strongest band of nitrous



Spectral range: 2102–2182 cm^{-1} .
Altitude of observation: 30°. Terrestrial concentration

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VIBRATION-ROTATION SPECTRA OF GASEOUS MOLECULES

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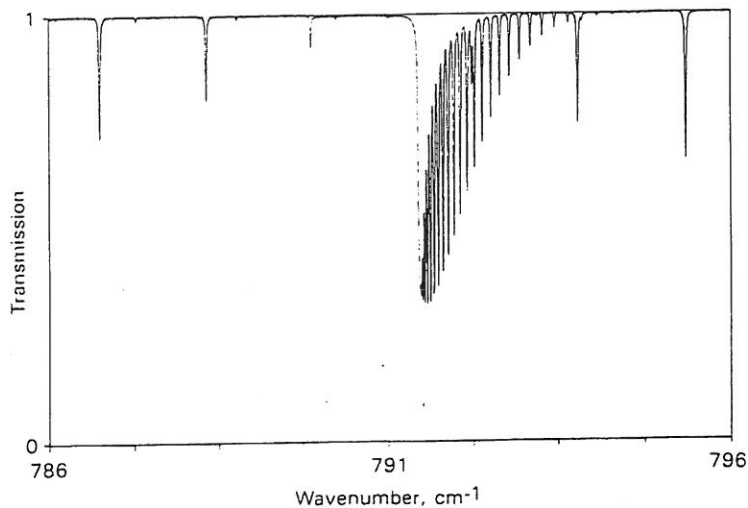


FIG. 3.5. Synthetic spectrum of CO_2 near 12.64 μm . Spectral range: 786–796 cm^{-1} .
Altitude of observation: 15 km. Zenith angle of observation: 30°. Terrestrial concentration $\times 10$.

oxide. The two very regular groups of lines are the *P*- and *R*-branches (to the left and the right, respectively) and they are separated by a gap caused by a missing line at the center of the band. A second, weaker band is superimposed (an *upper state band*) with a slightly different band center. Mixed in here, and also in most of the other spectra shown in this

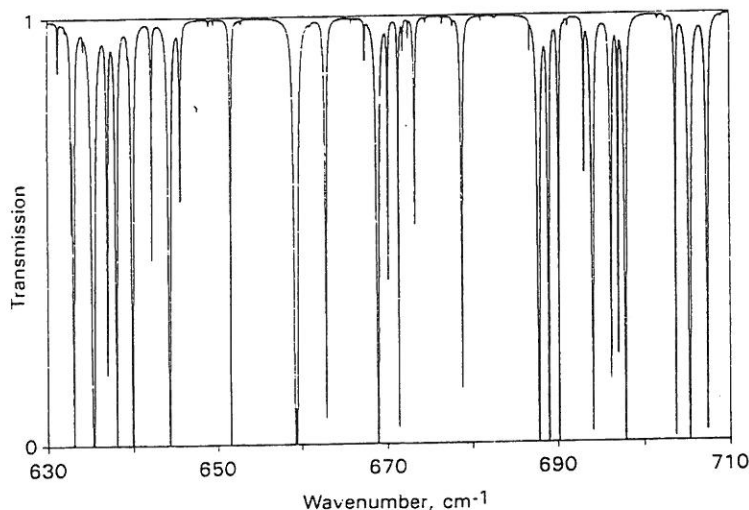


FIG. 3.6. Synthetic spectrum of H_2O near 14.9 μm . Spectral range: 630–710 cm^{-1} .
Altitude of observation: 0 km. Zenith angle of observation: 30°. Terrestrial concentration $\times 0.03$.

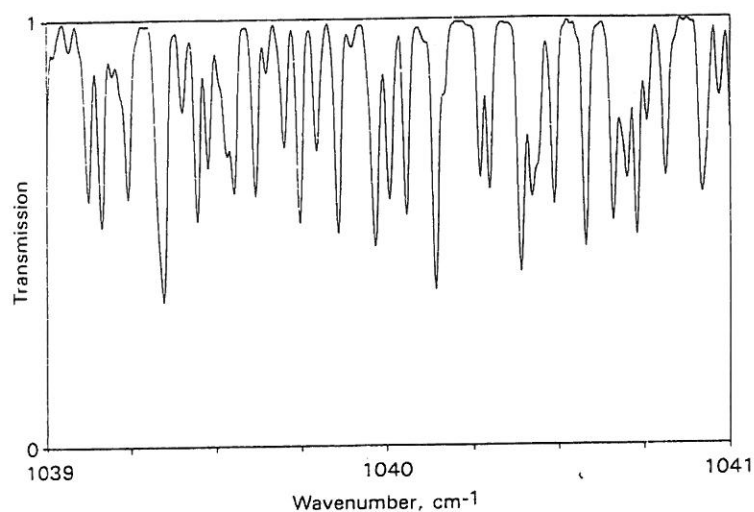


FIG. 3.7. Synthetic spectrum of O_3 near $9.61 \mu m$. Spectral range: $1039\text{--}1041 \text{ cm}^{-1}$. Altitude of observation: 30 km. Zenith angle of observation: 30° . Terrestrial concentration $\times 1$. Unlike most of the other synthetic spectra shown in this chapter, individual rotation lines are not resolved.

chapter, are weaker isotopic lines. In this spectrum, a few of the weak lines are from $^{14}N^{15}N^{16}O$.

Carbon monoxide, like nitrous oxide, is a linear molecule and the center of the $4.67 \mu m$ band shows a simple band structure (Fig. 3.4) similar to that in Fig. 3.3. The lines are more widely spaced than for nitrous oxide because the carbon monoxide molecule has a smaller moment of inertia. Again there is a gap in the band center (characteristic of a *parallel band*); a weak band of $^{13}C^{16}O$ is superimposed.

A high-resolution spectrum of a *perpendicular band* of a linear molecule is shown in Fig. 3.5. This is a weak band on the wing of the $15 \mu m$ band of carbon dioxide. It is the result of a transition involving two vibrational levels in close resonance (*Fermi resonance*), a circumstance that can greatly complicate the interpretation of a molecular spectrum. The P- and R-branches of this band are represented by the five, widely spaced, isolated lines. The gap between the bands is now filled with a partially resolved *Q-branch* near 790 cm^{-1} . Some weak isotopic lines of $^{16}O^{12}C^{17}O$ and $^{16}O^{12}C^{18}O$ are also present.

Figures 3.3, 3.4, and 3.5 illustrate arrays of lines containing some obvious order, but a glance at most regions of the atmospheric spectrum is more suggestive of a completely disordered situation. Figure 3.6 shows a region in the wing of the water vapor rotation band (this region is usually dominated by a very strong carbon dioxide band but the computer permits us to isolate species). The spectrum appears to be completely disordered, both as regards line positions and line intensities.

Figure 3.7 shows a section of the synthetic spectrum with a spectral resolution. The altitude above this level and the pressure (see § 3.3.1); nevertheless, the lines are not resolved. Each feature in the spectrum is a rotation line.

3.2. Vibration-rotation spectra

3.2.1. The Hamiltonian for a diatomic molecule

The quantum-mechanical treatment of a diatomic molecule involves replacing variables by operators. The energy E , of a system, consisting, in this case, of the two atoms that make up a molecule. The equation is

We may separate the independent terms,

H

(q represents the particle coordinates and s states of the molecule from

This equation has discrete energy levels, ψ_n . Transitions between levels involve absorption and emission of photons (from

Provided that the time-dependent perturbation theory is used, the probability that a stationary state ψ_n will transition to a stationary state ψ_m is

It is common practice to treat the vibrational energy, electronic energy, nuclear spin interactions, and energy levels. The total energy, the wave functions, and emitted or absorbed radiation are

2 CLASSES OF GAS ABSORPTION

- PERMITTED

- ISOLATED MOLECULE (ATOM) HAS
TIME VARYING ELECTRIC (MAGNETIC)
MOMENT
- SHARP SPECTRAL FEATURES
- GOOD ABSORBER AT LOW AND
HIGH PRESSURES

- PRESSURE INDUCED

- REQUIRES A PAIR OF
"COLLIDING" MOLECULES —
ONE INDUCES AN ELECTRIC (MAGNETIC)
MOMENT IN THE OTHER
- BROAD SPECTRAL FEATURES
- IMPORTANT ~~ONLY~~ ONLY AT
HIGH PRESSURES

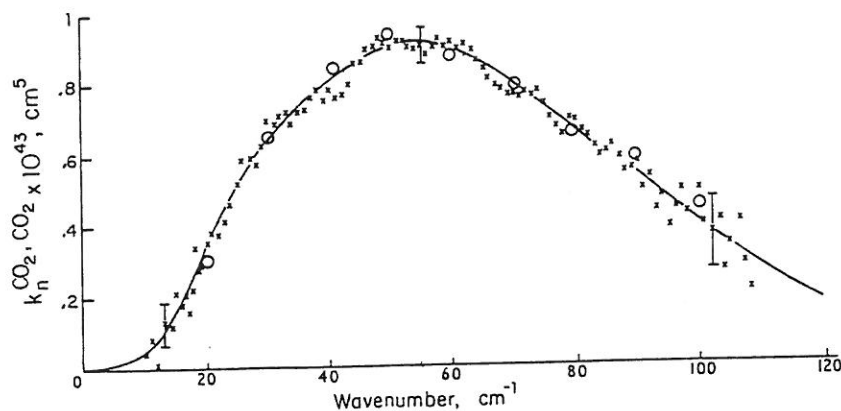


FIG. 5.10. The collision-induced rotation band of pure carbon dioxide at 293 K. The spectral resolution is 1.0 cm^{-1} . The circles and crosses are two independent sets of measurements. The vertical bars are error estimates. After Herries (1970).

CO₂ vs H₂O

CO₂ - NO PERMANENT DIPOLE MOMENT
 → NO PERMITTED PURE ROTATIONAL TRANSITIONS

H₂O - PERMANENT DIPOLE MOMENT
 → PERMITTED ROTATIONAL TRANSITIONS

CONTINUUM OPACITY

- BROAD ABSORPTION FEATURES
- SOURCE :
 - PRESSURE INDUCED TRANSITIONS
 - FAR WINGS OF LINES
 - DIMERS
- ABSORPTION COEFFICIENT, $\alpha_{\tilde{\nu}}$

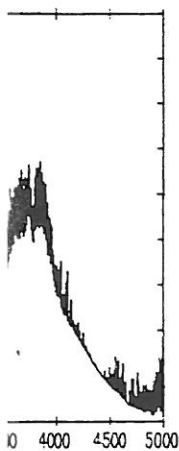
$$\alpha_{\tilde{\nu}} = D_{\tilde{\nu}}(\tilde{\nu}) F(T) P_b n_a$$

P_b = ~~pressure~~ partial pressure of broadener

n_a = number density of absorber

$$\tau_{\tilde{\nu}} = \alpha_{\tilde{\nu}} L$$

\uparrow path length
~~path~~



vapor at 1 bar and 296 K. The
by a "radiation term,"

numbers) for $\nu/c > 500 \text{ cm}^{-1}$.

on coefficients, although
al coefficients with linear
ne thing. To attribute the
s is equivalent to saying
positioned close to band
and there are reasonable
he observed continuum

a theoretical line shape.
um; the fine structure by
lines; but, in fact, both
on line positions and line
a occur at all frequencies.
bsorption is stronger than
l, but only the 1000 cm^{-1}

ption coefficients for the
ese are for water-water
coefficients for water-
he much larger concentra-
water-nitrogen collisions
view corresponds to that

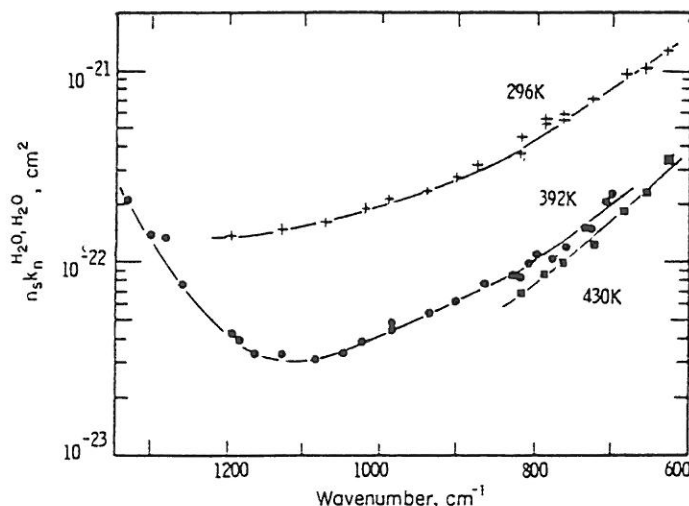


FIG. 5.8. Binary absorption coefficients for water-water collisions in the 1000 cm^{-1} window. n_s is Loschmidt's number. After Burch and Gryvnak (1980).

of some field investigators, based on studies of the correlation between atmospheric absorption and water vapor pressure. The term *e-type absorption* (from the meteorological symbol for water vapor pressure) is often used to describe the self-broadening nature of this phenomenon.

The increase of absorption with decreasing temperature shown in Fig. 5.8 has been cited as a reason to favor dimer theories of the continuum, but this temperature variation is also consistent with far wing line shapes, given appropriate interaction potentials.

Figure 5.9 shows binary absorption coefficients in the 2600 cm^{-1}

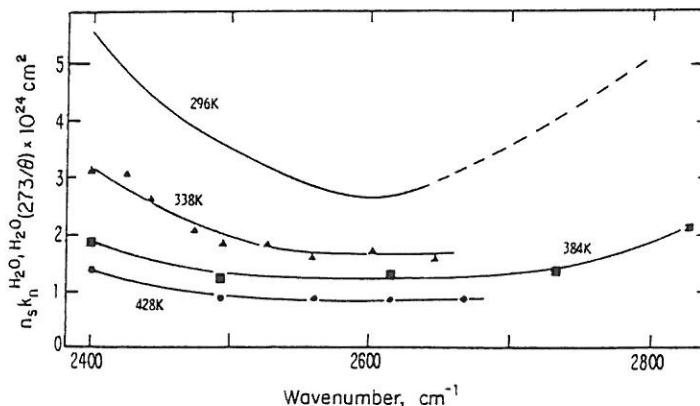


FIG. 5.9. Binary absorption coefficients for water-water collisions in the 2500 cm^{-1} window. n_s is Loschmidt's number. The data for 296 K are extrapolated. After Burch and Gryvnak (1980).

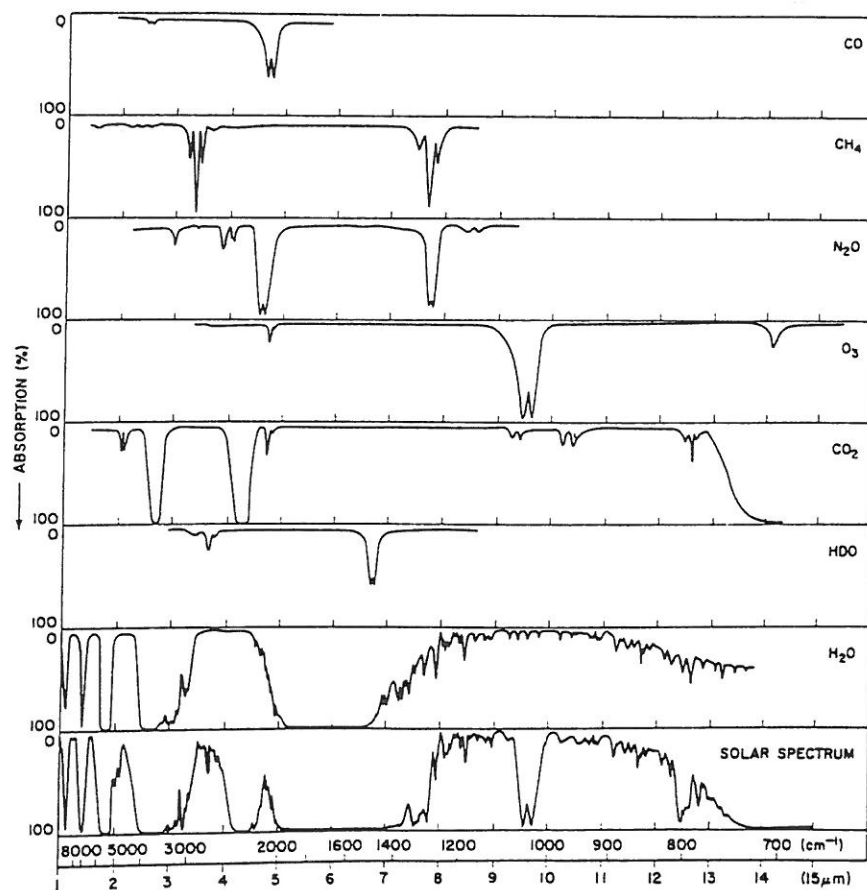


FIG. 3.1. Low-resolution absorption spectrum of the atmosphere. The top six panels are the absorption spectra of important atmospheric species. The bottom panel is a simulated absorption spectrum of the atmosphere. After Valley (1965).

be treated in this chapter since they are more complex theoretically but easier to handle empirically than the bands shown in Fig. 3.1. Data for electronic bands that are suitable for empirical calculations are discussed in Chapter 5.

The absorptions shown in Fig. 3.1 take the form of discrete bands of differing widths. Apart from the rotation band of water vapor, stretching from $16\mu\text{m}$ to the microwave spectrum, all involve a change in the vibrational energy of the molecule. The differing widths of the bands are the result of simultaneous changes in the rotational energy, and the features are referred to as *vibration-rotation bands*.

The structures of selected vibration-rotation bands at much higher spectral resolution are illustrated by Figs. 3.2, 3.3, 3.4, 3.5, 3.6, and 3.7.

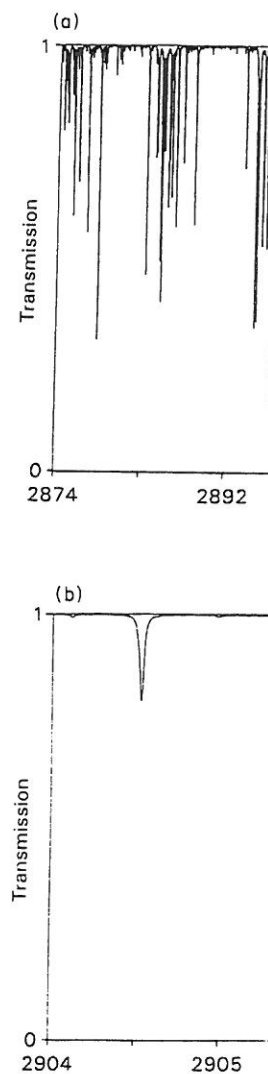


FIG. 3.2. Synthetic spectrum of (a) $2874\text{--}2892\text{ cm}^{-1}$. Level of c Terrestrial concentration $\times 1$.

Each has been constructed from the synthetic spectrum of the constituent. The absorption is shown down to the level of observation. The level of terrestrial gas concentration is shown if this makes for a clearer illustration.

LINE STRENGTH

$$S_L = S_L^0 \quad W \quad F_R \quad F_V$$

\uparrow constant \uparrow weight (degeneracy factor)

F_R = fraction of molecules in INITIAL rotational energy level, J

F_V = fraction of molecules in initial vibrational state

$$W = \frac{(J+1)}{(2J+1)} \quad \text{for } J \rightarrow J+1 \text{ linear molecule}$$

molecules in the (v, J) level is the product of the fractions in the v level and the J level separately. From (2.45), (3.16), and (3.24)

$$F_{vJ} = \frac{n(v)}{n} = Q_v^{-1} \exp\left(\frac{-v h \nu}{k \theta}\right), \quad (3.26)$$

where

$$Q_v = \sum_{v=0}^{\infty} \exp\left(\frac{-v h \nu}{k \theta}\right) = \left[1 - \exp\left(\frac{-h \nu}{k \theta}\right)\right]^{-1} \quad (3.27)$$

is the vibrational partition function, and

$$F_R = \frac{n(J)}{n} = Q_r^{-1} (2J + 1) \exp\left[\frac{-B h c J(J + 1)}{k \theta}\right], \quad (3.28)$$

where Q_r is the rotational partition function. Under normal atmospheric conditions, $B h c / k \theta \ll 1$ and

$$Q_r = k \theta / h c B. \quad (3.29)$$

Equations (3.16) and (3.18) are plotted as continuous functions of v or J in Figs. 3.13 and 3.14, and Table 3.2 gives populations of certain lowest excited vibrational states at two temperatures. The iodine molecule, illustrated in Fig. 3.13, has an unusually low vibrational frequency.

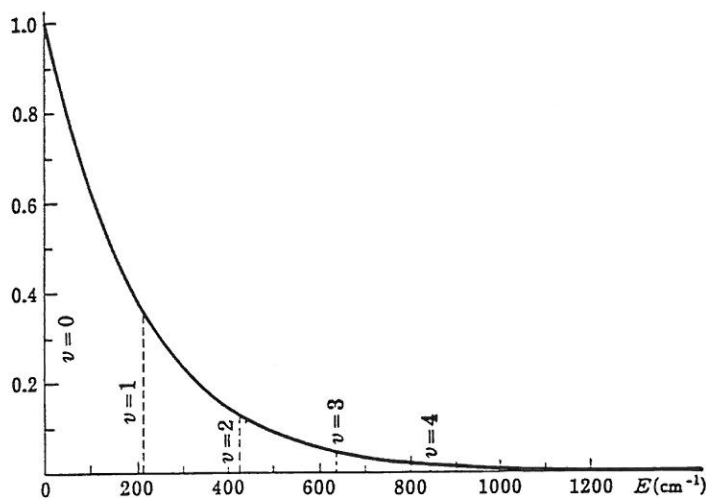


FIG. 3.13. Thermal distribution of vibrational levels. The data correspond to the iodine molecule, with $\nu_1 = 213.2 \text{ cm}^{-1}$, and for a temperature of 300 K. After Herzberg (1950).

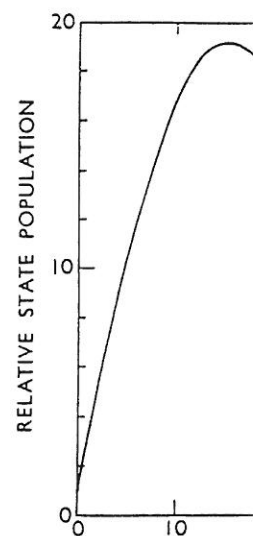


FIG. 3.14. Thermal distribution the same for all J . $B = 0.418 \text{ cm}^{-1}$

For most molecules at at first vibrational level is v . The rotational states h approximately equal to

We have not consi

Table 3.2. Rati
vibrational states

| Gas | ν_1 (cm^{-1}) |
|-----------------|---------------------------------|
| H ₂ | 4160. |
| HCl | 2885. |
| N ₂ | 2330. |
| CO | 2143. |
| O ₂ | 1556. |
| Cl ₂ | 556. |
| I ₂ | 213. |

Source: After Herzbo

of the fractions in the v level
(6), and (3.24)

$$\frac{h\nu}{k\theta}, \quad (3.26)$$

$$\exp\left(\frac{-h\nu}{k\theta}\right)^{-1} \quad (3.27)$$

$$\frac{hcJ(J+1)}{k\theta}, \quad (3.28)$$

. Under normal atmospheric

$$(3.29)$$

as continuous functions of v
gives populations of certain
temperatures. The iodine mole-
ly low vibrational frequency.

1000 1200 $E(\text{cm}^{-1})$

The data correspond to the iodine
of 300 K. After Herzberg (1950).

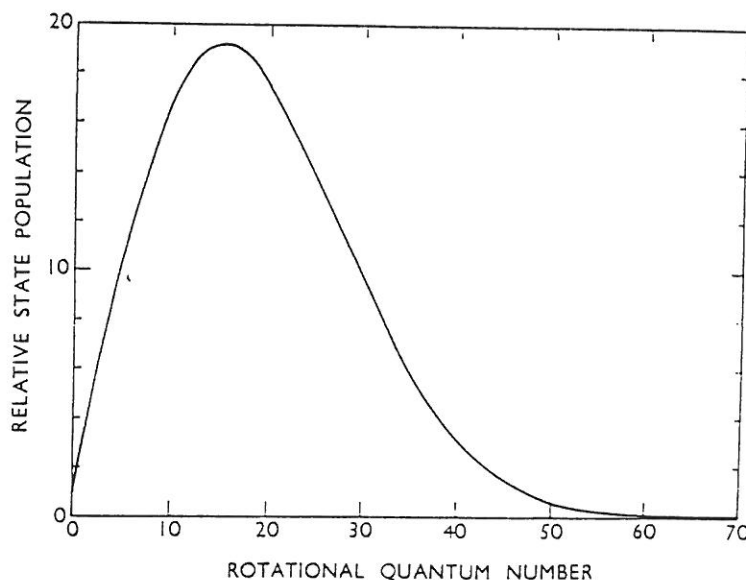


FIG. 3.14. Thermal distribution of rotational levels. The nuclear weights are assumed to be the same for all J . $B = 0.418 \text{ cm}^{-1}$ (nitrous oxide) and the temperature is 300 K.

For most molecules at atmospheric temperatures, the population of the first vibrational level is very small and varies rapidly with temperature. The rotational states have a maximum population for a J value approximately equal to

$$J_{\max} = \left(\frac{k\theta}{hcB}\right)^{1/2} - \frac{1}{2}. \quad (3.30)$$

We have not considered nuclear spins up to this point. They

Table 3.2. Ratio of the populations of the lowest two vibrational states for some molecules at 300 K and 1000 K

| Gas | ν_1 (cm^{-1}) | $\exp(-h\nu_1/k\theta)$ | |
|-----------------|---------------------------------|-------------------------|-----------------------|
| | | 300 K | 1000 K |
| H ₂ | 4160.2 | 2.16×10^{-9} | 2.51×10^{-3} |
| HCl | 2885.9 | 9.77×10^{-7} | 1.57×10^{-2} |
| N ₂ | 2330.7 | 1.40×10^{-5} | 3.50×10^{-2} |
| CO | 2143.2 | 3.43×10^{-5} | 4.58×10^{-2} |
| O ₂ | 1556.4 | 5.74×10^{-4} | 1.07×10^{-1} |
| Cl ₂ | 556.9 | 6.92×10^{-2} | 4.49×10^{-1} |
| I ₂ | 213.2 | 3.60×10^{-1} | 7.63×10^{-1} |

Source: After Herzberg (1950).

LINE SHAPE

— Monochromatic absorption coefficient

$$k_{\tilde{\nu}} = \int_L f(\tilde{\nu} - \tilde{\nu}_0)$$

\uparrow line intensity \uparrow line shape \uparrow line center

— Reasons for finite line extent

— Uncertainty Principle

Lorentz Line Shape $\rightarrow f(\tilde{\nu} - \tilde{\nu}_0) = \frac{\alpha}{\pi [(\tilde{\nu} - \tilde{\nu}_0)^2 + \alpha^2]}$

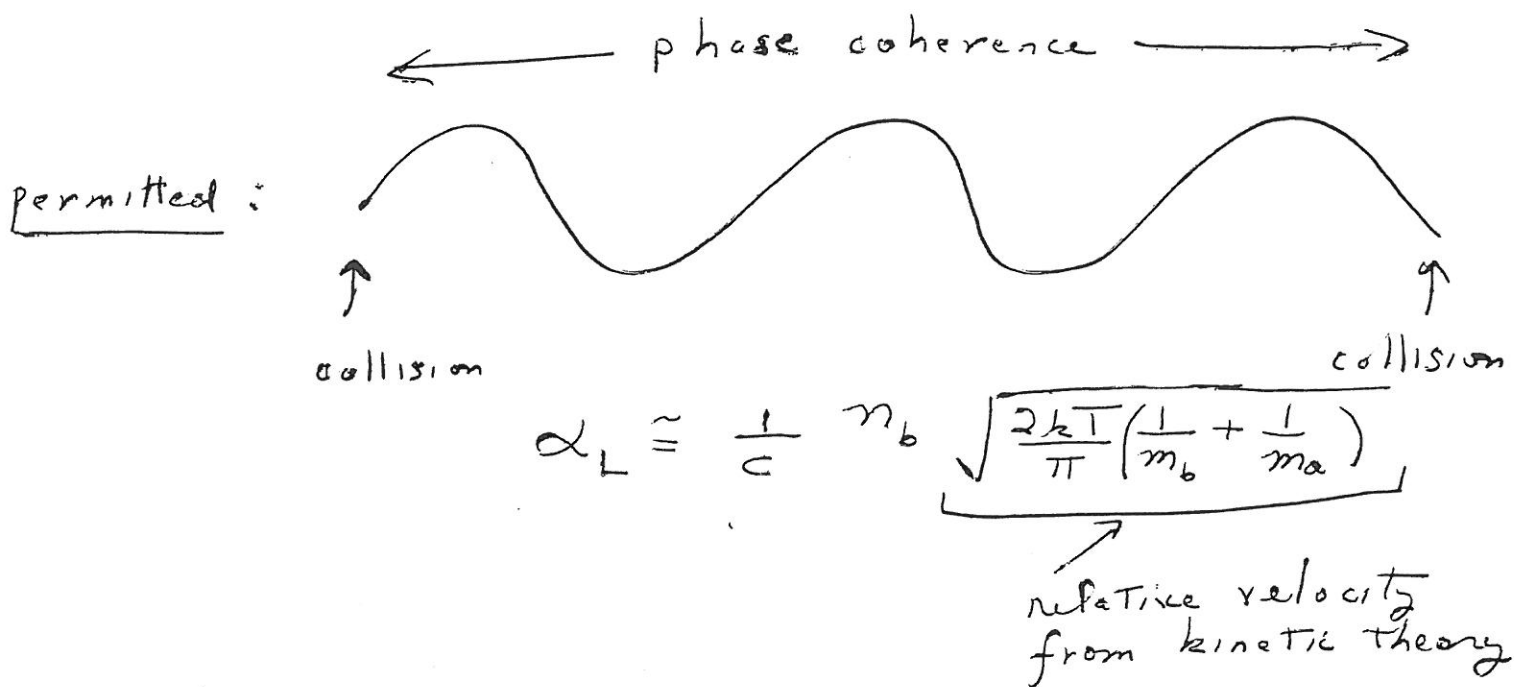
$$\alpha_Q = \frac{1}{2\pi c \tau_Q}$$

\uparrow Lifetime of excited state

— Collisions

$$\alpha = \frac{1}{2\pi c \tau_c}$$

τ_c = Time between collisions
 (permitted Transition)
 = Time during collision
 (pressure-induced)



(in reality - $\alpha_L \propto T^n$)

- Doppler shift

$$f_D(\tilde{\nu} - \tilde{\nu}_0) = \left(\frac{1}{\alpha_D \pi^{1/2}} \right) \exp \left\{ - \left[\frac{(\tilde{\nu} - \tilde{\nu}_0)}{\alpha_D} \right]^2 \right\}$$

$$\alpha_D = \left(\frac{\tilde{\nu}_0}{c} \right) \left(\frac{2kT}{m_a} \right)^{1/2}$$

- Comparison of half widths

$$\alpha_Q \ll \alpha_D$$

$$\alpha_Q \ll \alpha_L \quad (\text{unless } P \ll 1)$$

$$\alpha_L > \alpha_D \quad P(\text{mb}) \gtrsim (1-10)$$

$$\alpha_D > \alpha_L \quad P(\text{mb}) \lesssim (1-10)$$

LINE DATABASES FOR PERMITTED TRANSITIONS

— CONTAIN

various molecules { $\tilde{\nu}_0$ — POSITION OF LINE CENTER
 S_L — LINE STRENGTH (T_{ref})
various transitions { α_L — PRESSURE HALF WIDTHS
(T_{ref} , n , broadener)
 E_{Low} — Energy of lower level of a transition
↑ temperature exponent

— EXAMPLES

Air Force ~~Geophysical~~
Geophysical Lab

HITRAN

— Put out by AFGL
Earth oriented

GEISA

— French, Earth +
outer Planets

HIGHT

— diatomies,] customized
 CO_2 , H_2O]

For high Temperatures
(Venus, rocket plumes,
cool stars)

DERIVATION

$$T_r(\Delta \tilde{\nu}) = \int_{\Delta \tilde{\nu}} e^{-k \cdot \tilde{\nu}} \frac{d\tilde{\nu}}{\Delta \tilde{\nu}}$$

↑
transmission
thru constant P, T

absorber
gas
amount

$$= \int e^{-k \cdot \tilde{\nu}} n(k) dk$$

($n(k) dk$ = probability of having
an absorption coefficient
between k and $(k + dk)$)

$$\text{Let } g(k) = \int_0^k n(k) dk$$

↑
cumulative probability that
absorption coefficient $\leq k$

$$\rightarrow T_r(\Delta \tilde{\nu}) = \int e^{-k(g) \cdot \tilde{\nu}} \frac{dg}{\Delta \tilde{\nu}}$$

$$= \sum_i w_i e^{-k(g_i) \cdot \tilde{\nu}}$$

↑
gauss weight

↑
gauss point

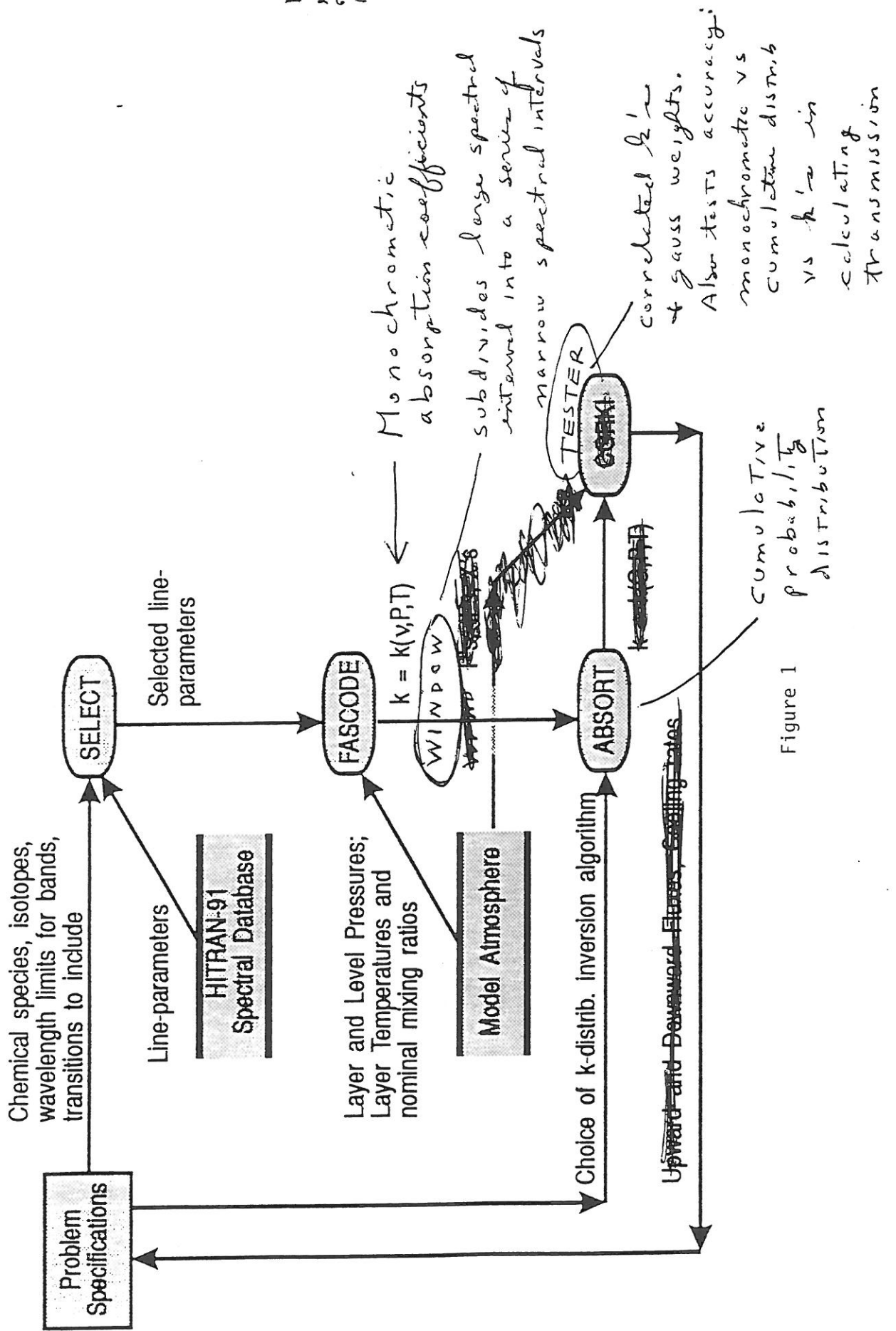
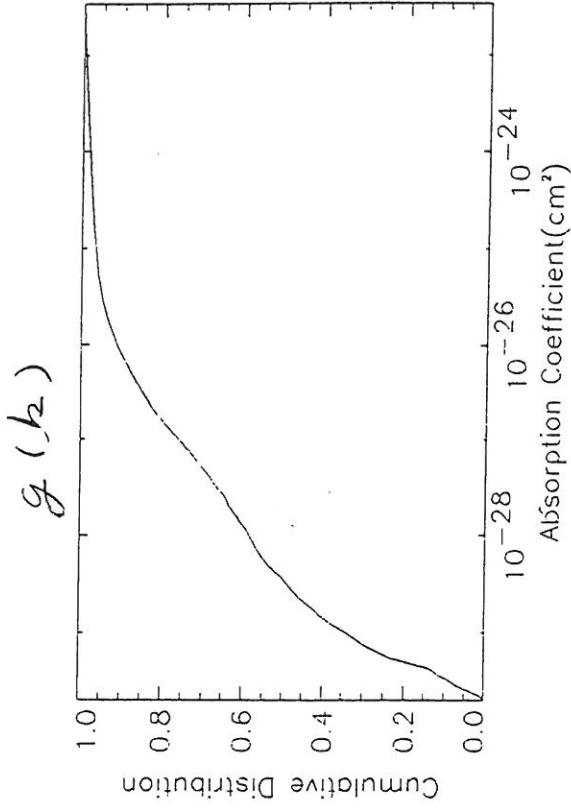
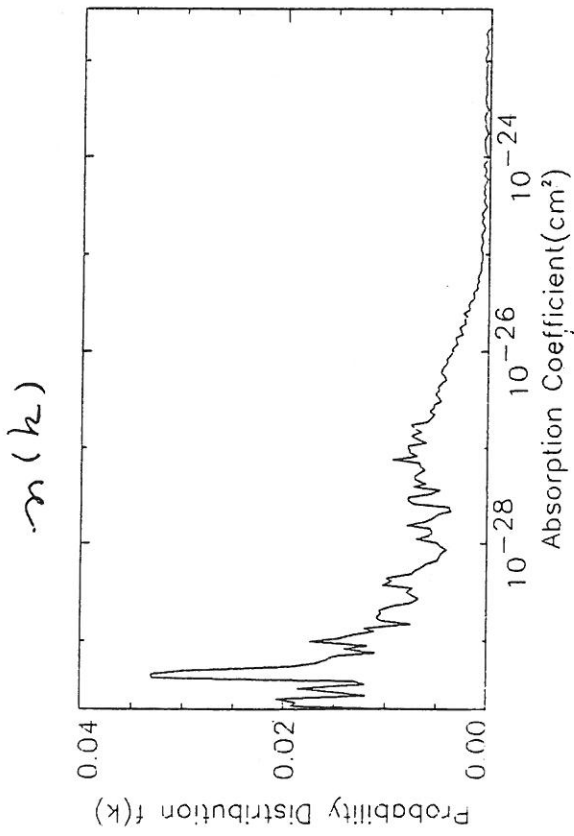


Figure 1

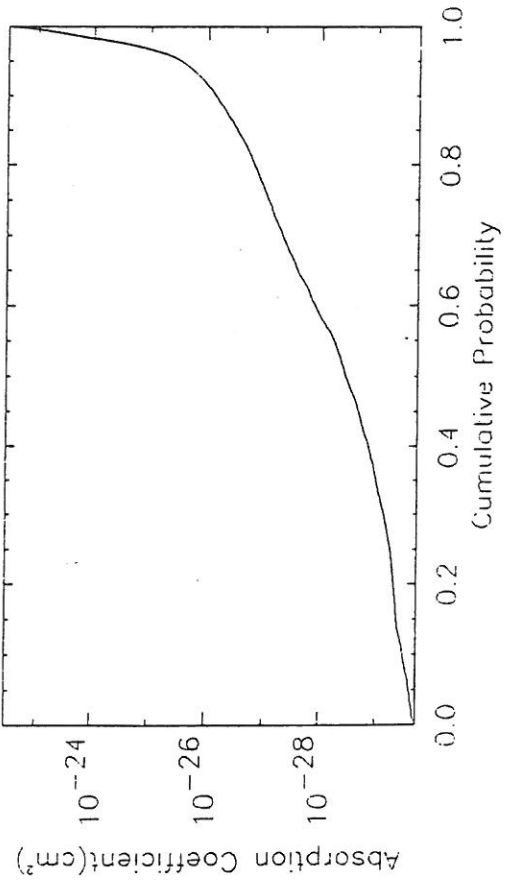
CH₄



(a)

(b)

$h(g)$



(c)

| | | |
|-------------|--------|-----|
| Pressure | 1.480 | bar |
| Temperature | 272.23 | |
| Band Low | 1300.0 | |
| Band High | 1320.0 | |

Figure 2 ...

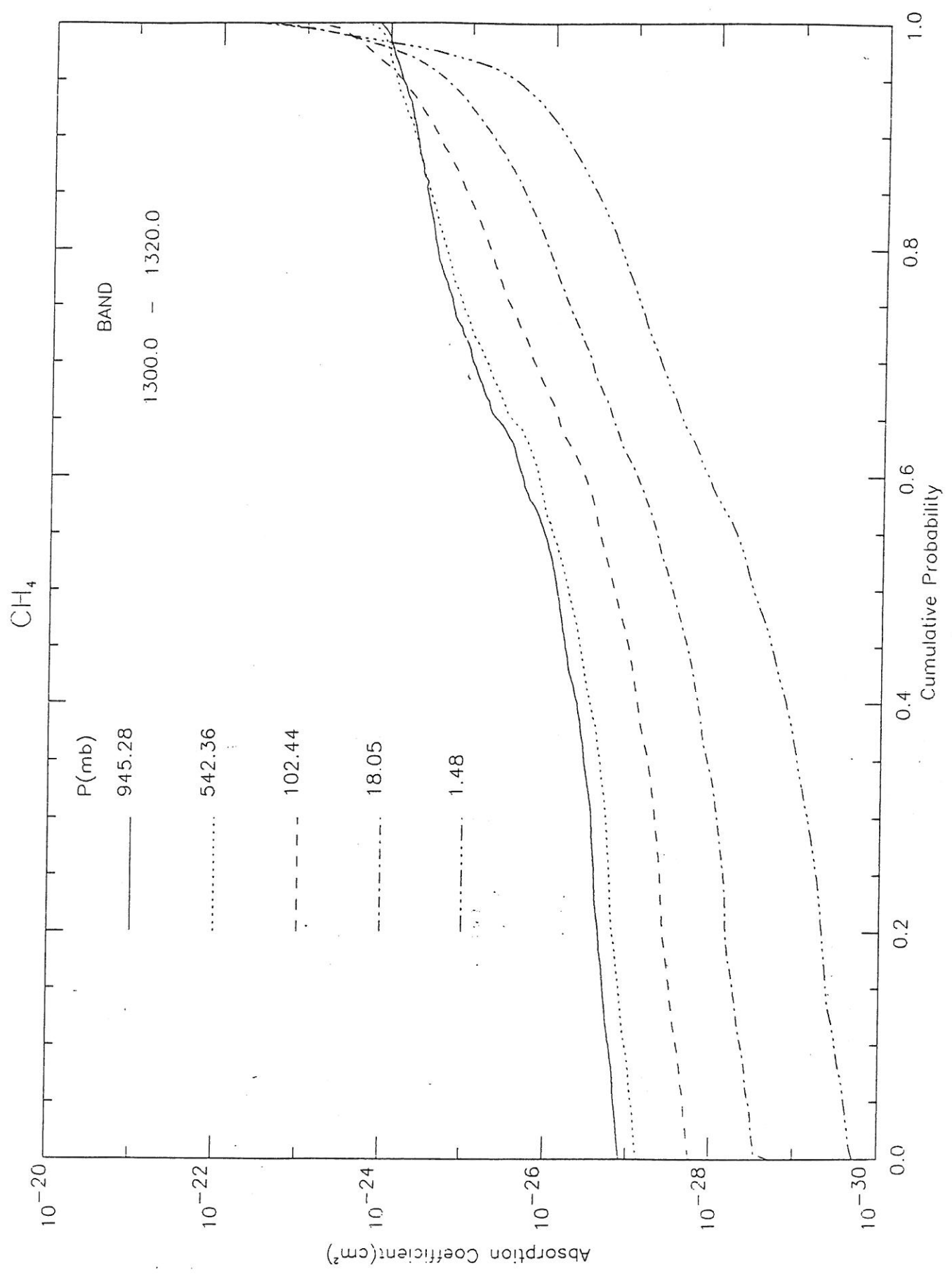


Figure 4 ...

TESTS OF ACCURACY OF CORRELATED k 's (vs monochromatic)

CH₄ 40 points

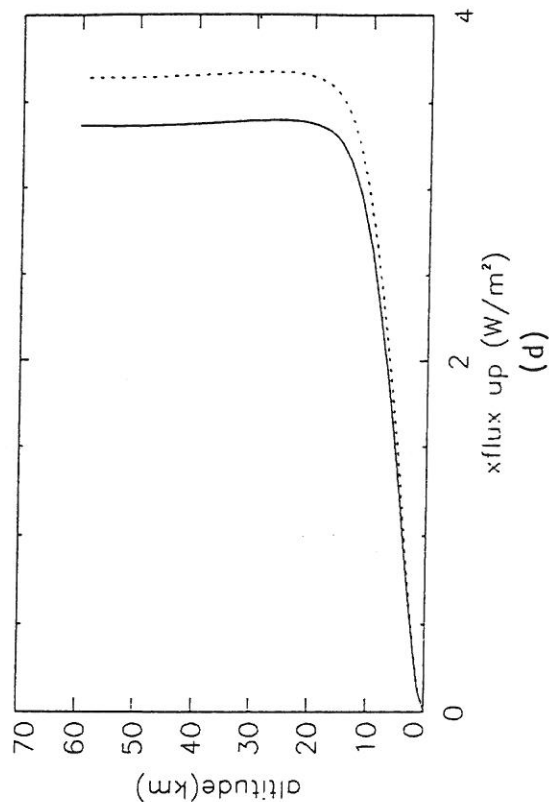
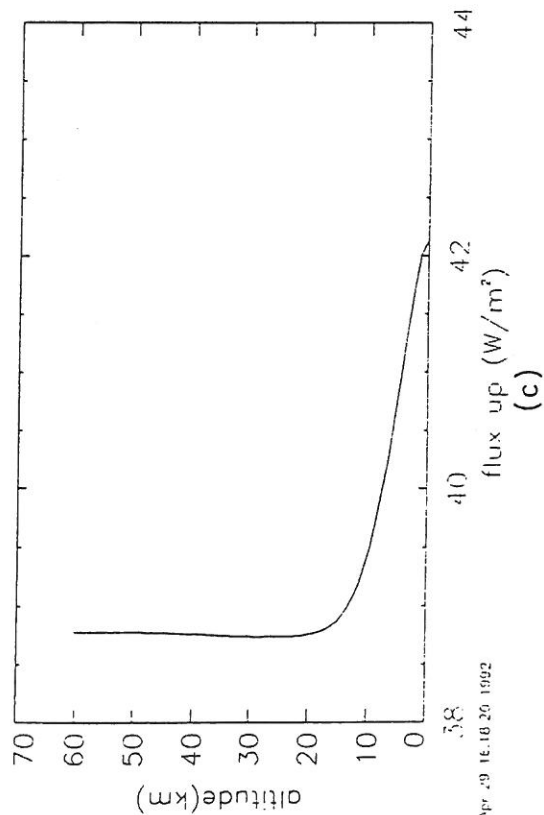
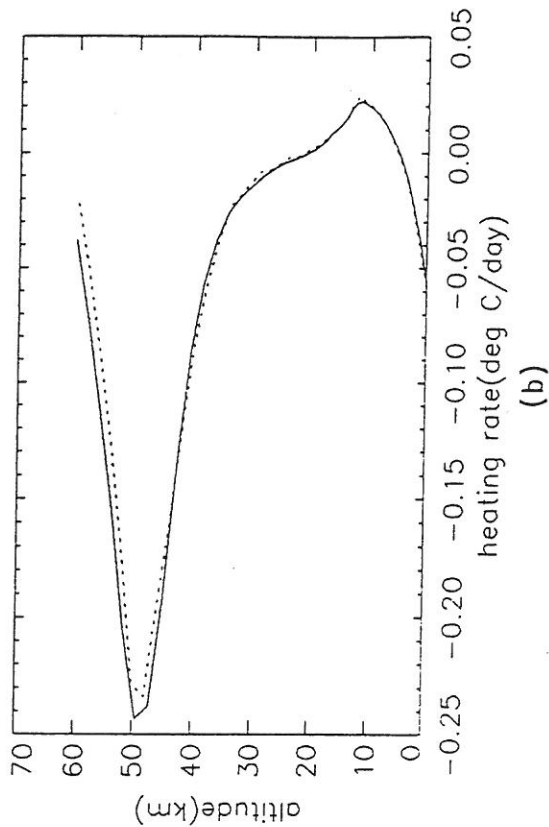
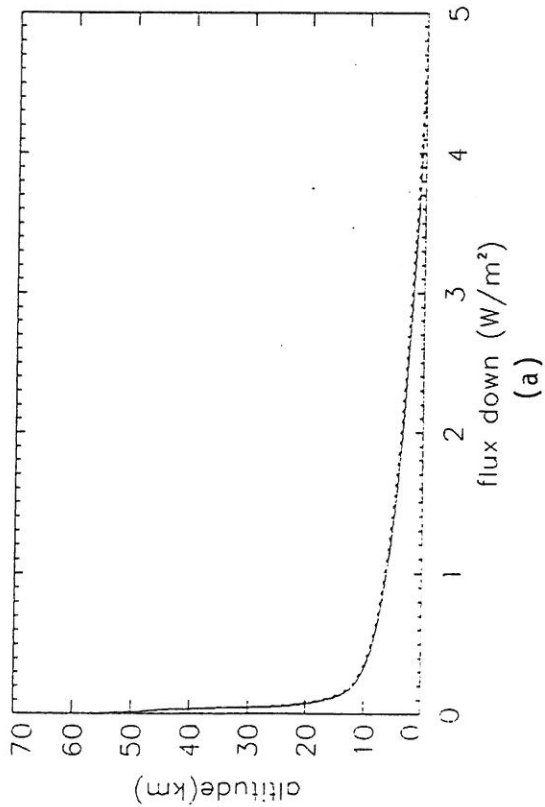


Figure 5

N₂O 40 points

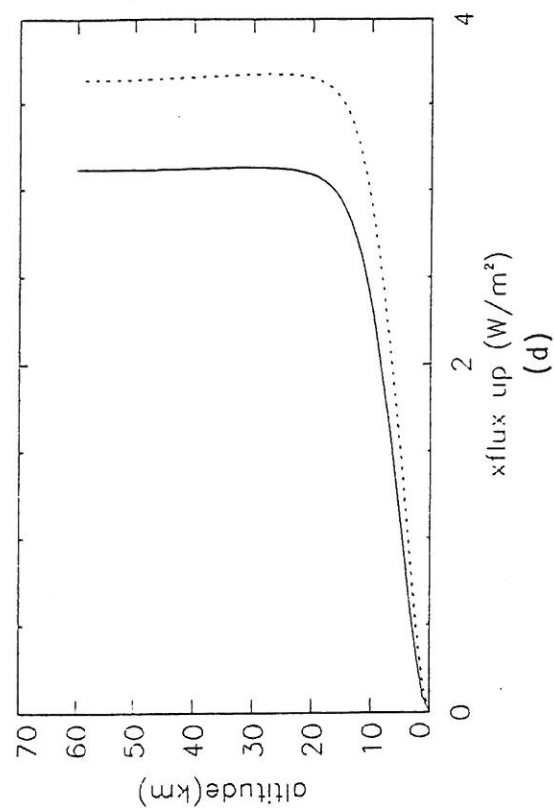
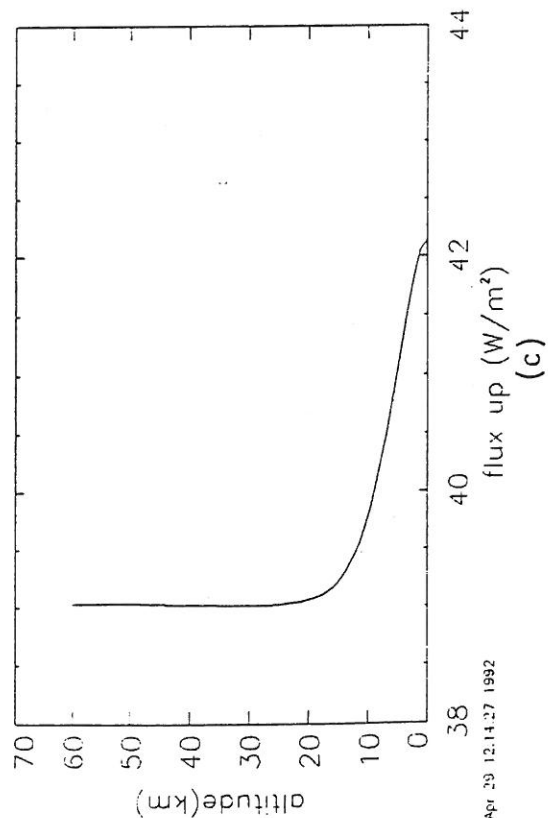
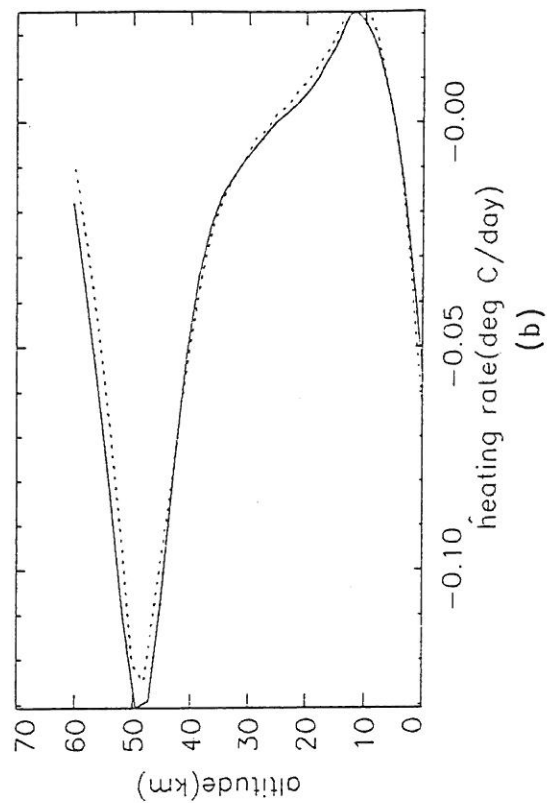
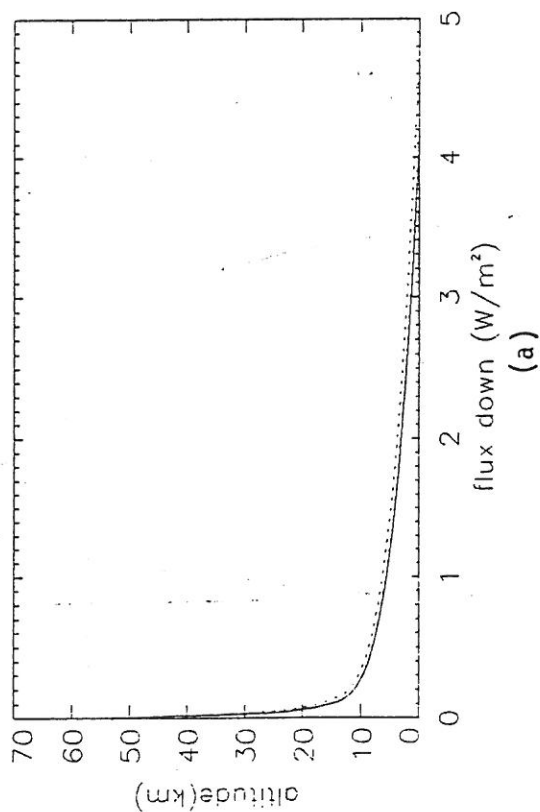


Figure 6 ...

SPECTRAL MAPPING TRANSFORMATION (SMT)

— DEFINITION: WHEN BINNING TOGETHER ~~EXACTLY~~ WAVELENGTHS THAT HAVE VERY SIMILAR VALUES OF k , DEMAND THAT THE SIMILARITY HOLD AT ALL P, T LEVELS IN THE ATMOSPHERE

— VS CORRELATED k :

- WITH CORRELATED k WE BIN ONE LEVEL AT A TIME
- SMT MORE ACCURATE FOR INHOMOGENEOUS ATMOSPHERES ($P(z), T(z)$)
- BUT REQUIRES MORE CALCULATIONS PER SPECTRAL INTERVAL (~ 100 - SEVERAL 100 VS 6-12 FOR CORRELATED k)
- BETTER ACCURACY ($\leq 1\%$ VS $\leq 5\%$ FOR CORRELATED k)
+ RARE SITUATIONS WITH LARGER ERRORS FOR CORRELATED k .

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