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REVIEW OF EMISSIVITY CALCULATIONS FOR DIATOMIC GASES

by

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1. Introduction

The molecular absorption (or emission) spectra observed in the infrared results from the transitions of vibrating and rotating molecules to higher (or lower) energy levels. An absorption or emission spectra has only been observed for molecules which possess a permanent electric dipole moment (HCl, CO, CO_2, H_2O, etc). We note that we are not considering electronic transitions which are responsible for the visible and the ultraviolet band spectra. We classify the wavelength region extending from 0.8 to 20μ as the near infrared and from 20 to 80μ as the far infrared.

2. Coarse Structure of the Infrared Spectrum*

(a) The Rigid Rotator

The simplest model of the rotating molecule assumes the molecule to consist of several point masses which are rigidly connected by weightless rods. For the diatomic molecule there are only two point masses and the line joining them is an axis of symmetry, the internuclear distance, so that we have the so called dumbbell model.

The energy of rotation of a rigid body is given by

$$E = \frac{1}{2} I \omega^2 \tag{1}$$

where ω is the angular velocity and I is the amount of inertia defined by

$$I = \mu r^2 = \frac{m_1 m_2}{m_1 + m_2} r^2 \tag{2}$$

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* See Herzberg, reference 1.

It is convenient to write the energy of rotation E in the form

$$E = \frac{P^2}{2I}$$

where P is the angular momentum $I\omega$.

To obtain the possible energy levels according to quantum theory we determine the eigenvalues of the Schrodinger equation for the rigid rotator. The result is

$$E(j) = \frac{h^2 j(j + 1)}{8\pi^2 I} \quad ; \quad j = 0, 1, 2 \ldots . \quad (3)$$

where j is the rotational quantum number. We therefore have a series of discrete energy levels whose energy increases quadratically with j.

According to classical electrodynamics the rigid rotator will absorb or emit radiation if the rotation is accompanied by a changing electric dipole moment. This would occur for all diatomic molecules that consist of unlike atoms since these molecules have a permanent dipole moment in the direction of the internuclear axis.[*] Therefore during the rotation, the component of the dipole moment in a fixed direction changes periodically with a frequency equal to the frequency of rotation, $\nu_{rot} = \omega/2\pi$, which would result in the absorption or emission of light at this frequency. Thus the classical theory predicts a continuous absorption or emission spectrum for the rigid rotator since ν_{rot} can take all values.

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[*] Diatomic molecules consisting of two like atoms have no absorption or emission spectrum in the infrared.

According to the quantum theory absorption takes place only as a result of a transition from a lower to a higher energy level.[*] The wave number, $\nu(cm^{-1})$, of the spectral lines are given by (cf. Eq. 3)

$$\nu = \frac{E'}{hc} - \frac{E''}{hc} = Bj' \ (j' + 1) - B \ j'' \ (j'' + 1) \qquad (4)$$

where the primes ' and " correspond to the upper and lower states, respectively, and the constant, B, is given by

$$B = \frac{h}{8\pi^2 cI} \qquad (5)$$

The particular transition which give rise to absorption or emission are given by

$$\Delta j = j' - j'' = \pm 1$$

the so called selection rules of wave mechanics. Therefore, for the rigid rotator $j' > j''$ and $\Delta j = +1$ (consistent with our prime notation) so that

$$\nu = F \ (j'' + 1) - F \ (j'') = 2B \ (j'' + 1) \ ; \ j'' = 0, \ 1, \ 2 \ldots, \qquad (6)$$

where $F(j)$ represents the ratio $E(j)/hc$. Thus the spectrum of the rigid rotator consists of a series of equidistant lines (see Fig. 1). For convenience we write j for j''.

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[*] Recall the classical result for atomic spectra that energy is radiated when an electron moves in a single orbit about a charged nucleus while the quantum theory states there is no absorption or emission when the electron remains in one orbit, but occurs only when the electron jumps from one orbit to another.

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(b) The Harmonic Oscillator

The simplest model of the vibrating diatomic molecule assumes the atoms to be point masses which are acted on by a force that varies with the distance between them. This force corresponds to a potential energy, V,

$$V = + \frac{1}{2} kx^2$$

where k is the force constant. The motion of the atoms can be described by the harmonic motion of a single point mass, μ, about an equilibrium position, r_e, that is

$$\mu \frac{d^2(r-r_e)}{dt^2} = -k(r-r_e). \tag{7}$$

The frequency of oscillation is given by

$$\nu_{osc} = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2} \tag{8}$$

To obtain the energy levels of the harmonic oscillator, we determine the eigenvalues of the Schrodinger equation. The result is

$$\frac{E(v)}{hc} \equiv G(v) = \frac{\nu_{osc}}{c} (v + 1/2); \quad v = 0, 1, 2 \ldots \tag{9}$$

where v is the vibrational quantum number. The ratio ν_{osc}/c is denoted by $\omega(cm^{-1})$.

As a first approximation it is assumed that the dipole moment changes with a frequency equal to the oscillation frequency, $\nu_{osc}/c = \omega$. From the quantum theory we have that the wave number of the absorbed quantum is

given by

$$\nu = \frac{E(v') - E(v'')}{hc} = G(v') - G(v'') = \omega (v' - v'')$$ (10)

The transitions which absorb and emit radiation are given by

$$\Delta V = v' - v'' = \pm 1 \text{ so that } \nu = \omega = \nu_{osc}/c$$

which agrees with the classical result. The spectrum is shown in Fig. 2.

(c) **Quick Comparison with the Coarse Structure of the Observed Spectrum**

The observed spectrum in the far infrared consists of a series of nearly equidistant lines and is therefore primarily a rotation spectrum. The spectrum in the near infrared consists essentially of a single intense line and is therefore primarily a vibration spectrum.

3. Fine Structure of the Infrared Spectrum*

(a) The Anharmonic Oscillator

Recall that the harmonic oscillator is characterized by a parabolic potential curve. This would imply, however, that the potential energy and the restoring force continue to increase as the atoms move further and further apart. Practically, the attractive restoring force goes to zero for large distances so that the potential curve would approach a constant. As a first approximation to a more realistic potential energy curve we consider the following representation for an anharmonic oscillator:

$$V = f(r - r_e)^2 - g(r - r_e)^3$$ (11)

*See Herzberg[1].

For small anharmonicity the constant g is much smaller than f. The classical motion of the anharmonic oscillator is given by

$$x = x_{01} \sin 2\pi \, \nu_{osc} t + x_{02} (3 + \cos 2\pi \, 2\nu_{osc} t) + x_{03} \sin 2\pi \, 3\nu_{osc} t + \ldots$$

$$(12)$$

where x_{01}, x_{02}, x_{03} are the amplitudes of the fundamental, the first and the second overtone, respectively. For small anharmonicity $x_{02} \ll x_{01}$ and $x_{03} \ll x_{02}$.

For small anharmonicity, the energy levels of the anharmonic oscillator [Eq. (11)] as determined from the Schrodinger equation are given by[*]

$$\frac{Ev}{hc} = G(v) = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 + \ldots \quad (13)$$

where $\omega_e x_e \ll \omega_e$ and $\omega_e y_e \ll \omega_e x_e$. Note that the energy levels of the anharmonic oscillator are not equidistant like those of the harmonic oscillator; their separation decreases slowly with increasing v (Fig. 3). From Equation (13) for $v = 0$ we obtain the zero point energy of the anharmonic oscillator

$$\frac{Eo}{hc} = G(o) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e + \frac{1}{8} \omega_e y_e \quad (14)$$

For the anharmonic oscillator the selection rules for the spectrum are given by

$$\Delta v = \pm 1, \pm 2, \pm 3, \ldots \quad (15)$$

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[*] Note that using the Morse potential, which gives a good fit to the potential energy curve, the first two terms of Equation (13) are obtained.

although the greatest contribution is given by $\Delta v = \pm\ 1$ (which corresponds to the sole contribution for the harmonic oscillator). If all the molecules are initially in the lowest vibrational state, $v'' = 0$ (see Fig. 3), we obtain from Equations (13) and (14)

$$\nu = G(v') - G(o) = \omega_o v' - \omega_o x_o v'^2 + \omega_o y_o v'^3 + \ldots;\ v' = 1,2,3,\ \ldots \ . \tag{16}$$

where

$$\omega_o = \omega_e - \omega_e x_e + \frac{3}{4}\ \omega_e y_e + \cdots$$

$$\omega_o x_o = \omega_e x_e - \frac{3}{2}\ \omega_e y_e + \cdots$$

$$\omega_o y_o = \omega_e y_e$$

(b) The Nonrigid Rotator

Representing the rotating molecule by two point masses connected by a massless spring yields for the energy levels

$$\frac{E_r}{hc} = F(j) = Bj(j + 1) - Dj^2(j + 1)^2 \tag{17}$$

where the constant D reflects the influence of the centrifugal force. The effect of D is important at the higher rotational levels. The wave numbers of the spectral lines for the infrared rotation spectrum are given by

$$\nu = F(j + 1) - F(j) = 2B(j + 1) - 4D(j + 1)^3 \tag{18}$$

the selection rule, $\Delta j = \pm\ 1$, being unchanged.

(c) The Vibrating Rotator (or Rotating Oscillator)

We now consider the molecule to be rotating and oscillating at the same time. As a first approximation we could of course neglect the interaction

of vibration and rotation and simply add the independent contributions,
namely, Equations (13) and (17). An important interaction is the changing
moment of inertia resulting from the molecular vibration. This produces
changing values for the rotational constants B and D of Equation (17).
Since the period of vibration is much less than the period of rotation mean
values are used as approximations to the (changing) rotational constant and
are given by

$$B_v = B_e - \alpha_e \ (v + \frac{1}{2}) + \ \ldots \tag{19}$$

where B_e is the rotational constant based on the equilibrium internuclear
distance r_e,

$$B_e = \frac{h}{8 \ \pi^2 c \mu r_e^2} \quad \text{and} \quad D_v = D_e + \rho_e \ (v + \frac{1}{2}) + \ \ldots \tag{20}$$

where

$$D_e = \frac{4 B e^3}{\omega_e^2}$$

The constants α_e and ρ_e are much smaller than B_e and D_e, respectively.
The energy levels of the vibrating rotator are then given by

$$\frac{E}{hc} = G(v) + F_v(j) = \omega_e \ (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + \omega_e y_e (v + \frac{1}{2})^3$$

$$+ \ \ldots \ B_v \ j(j + 1) - D_v j^2 (j + 1)^2 + \ \ldots \tag{21}$$

The energy levels are shown in Fig. 4. For each vibrational level there
are a number of possible rotational levels, the level $j = 0$ corresponding
to the pure vibrational level (no rotation). The wave number of the spectral

lines resulting from a particular vibrational transition v'' to v' are given by

$$\nu = G(v') - G(v'') + F_v'(j') - F_v''(j'')$$

$$= \nu_o + B_v'j'(j'+1) - B_v''j''(j''+1)* \qquad (22)$$

where $\nu_o = G(v') - G(v'')$. With $\triangle j = +1$ and $\triangle j = -1$ we obtain two branches, the R and P branches, given by

$$\nu_R = \nu_o + 2B_v' + (3B_v' - B_v'')j + (B_v' - B_v'')j^2; \quad j = 0,1 \ .. \quad (23)$$

$$\nu_P = \nu_o - (B_v' + B_v'')j + (B_v' - B_v'')j^2; \quad j = 1, 2 \ . \ . \ . \quad (24)$$

where we replace j'' by j. The spectrum is shown in Fig. 5. Equations (23) and (24) give good agreement with the observed spectrum in the near infrared. For sufficiently large values of j a reversal of the R branch occurs corresponding to the vertex of the parabola in Equation (23). This reversal or band head is responsible for the sharp drop in intensity observed in band absorption. We note that any absorption observed beyond the band head is from the wings of broadened lines whose centers lie below this wave number.

The wave numbers for the R and P branches are frequently written in the form

$$\nu = \nu_o + (B_v' + B_v'')m + (B_v' - B_v'')m^2 \begin{cases} m = 1,2,\ldots R(m=j+1) \\ m = -1,-2,\ldots P(m=-j) \end{cases} \quad (25)$$

For the most intense absorption transition, $v' - v'' = 1$, Equation (25)

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*We neglect the influence of the centrifugal force on the rotational energy.

becomes

$$\nu = \nu_o + 2 \left[Be - \alpha_e (v'' + 1) \right] m - \alpha_e m^2 \qquad (26)$$

The average spacing between the lines is given by

$$d = \frac{\nu(m + 1) - \nu(m) + \nu(m) - \nu(m-1)}{2} = 2 \left[Be - \alpha_e (v''+1+m) \right] \qquad (27)$$

4. <u>The Calculation of Absorption and Emission in the Infrared Spectrum</u>

(a) Band Models

Before discussing the calculation of the absorption and emission of

spectral lines we briefly review some basic results. The one-dimensional

equation of transfer for a radiating gas is given by

$$dI_\nu = -I_\nu k_\nu du + I_{b\nu} k_\nu du^* \qquad (28)$$

where

$$du = \rho dz \qquad (29)$$

and I_ν is the intensity, k_ν is the spectral absorption coefficient, and u

is the amount of material per unit area. For a single radiating gas at

uniform temperature and pressure we obtain

$$I_\nu = I_{b\nu} \left[1 - e^{-k_\nu u} \right] + I_\nu(o) e^{-k_\nu u} \qquad (30)$$

where $I_{b\nu}$ is the black body spectral intensity, and $I_\nu (o)$ is the inci-

*The corresponding notation of Penner[2] is given by $dX = pdz$ with an
absorption coefficient P_ν related to k_ν according to $P_\nu = \rho \, k_\nu/p$

dent intensity at u = 0. For negligible emission of radiation we obtain

$$I_\nu = I_\nu(o)e^{-k_\nu u} \tag{31}$$

Under atmospheric conditions the spectral lines in the infrared spectrum are primarily affected by Lorentz (pressure) broadening resulting from molecular collisions. Under these conditions, the line shape is given by [2,3,4]

$$b_\nu = \frac{k_\nu}{S} = \frac{1}{\pi} \frac{\alpha}{(\nu - \nu_o)^2 + \alpha^2} \tag{32}$$

where S is the total line intensity

$$S = \int_o k_\nu d\nu \tag{33}$$

and α is the half-width. For negligible emission the total energy absorbed by a single line over a frequency interval $\Delta\nu$ is given by

$$\int_{\Delta\nu} (I_\nu(o) - I_\nu) = I_{\nu o}(o) \int_{\Delta\nu} (1 - e^{-k_\nu u}) d\nu \tag{34}$$

where we have assumed $I_\nu(o)$ to have the constant value of $I_{\nu o}(o)$ over the interval $\Delta\nu$. We define the fractional absorption in $\Delta\nu$ by

$$A = \frac{\displaystyle\int_{\Delta\nu} (I_\nu(o) - I_\nu) d\nu}{\displaystyle\int_{\Delta\nu} I_\nu(o) \, d\nu} = \frac{1}{\Delta\nu} \int_{\Delta\nu} (1 - e^{-k_\nu u}) d\nu \tag{35}$$

and an equivalent width of the single line by

$$W_{s\ell} = A\Delta\nu$$

Using the Lorentz line shape and extending the frequency interval to infinity we obtain

$$W_s = 2 \pi \alpha f(x) = 2 \pi \alpha x e^{-x} [I_0(x) + I_1(x)] \qquad (37)$$

where I_0 and I_1 are the Bessel functions of imaginary argument and

$$x = \frac{Su}{2\pi\alpha} \qquad (38)$$

For small x we obtain the so-called linear approximation

$$W_{s\ell} = 2 \pi \alpha x = Su = d \beta x \qquad (39)$$

where

$$\beta = \frac{2 \pi \alpha}{d} \qquad (40)$$

with d equal to the average spacing between the spectral lines. In this section it has been assumed that the spectral lines are spaced sufficiently far apart so that there are no effects due to overlapping. Therefore the total absorption from several (non-overlapping) spectral lines is obtained by simply adding the absorption from the individual lines.

For large x we obtain the so-called square root approximation

$$W_{s\ell} = \sqrt{8\pi\alpha^2 x} = 2 \sqrt{S\alpha u} = d \sqrt{2\beta^2 x/\pi} \qquad (41)$$

Now, to calculate the absorption of a band a specific model describing the spectral lines must be considered. The Elsasser model assumes a band consists of an infinite number of spectral lines of equal intensity, S, half width, α, and line spacing, d. For this band, the fractional ab-

sorption <u>integrated over a frequency range d</u> is given by

$$A = 1 - \frac{1}{2\pi} \int_{\pi}^{\pi} \exp\left[- \beta x \sinh \beta / (\cosh \beta - \cos z)\right] dz \qquad (42)$$

For $x > 1.25$ and $\beta < 0.3$

$$A \approx \text{erf} \left[\left(\frac{1}{2} \beta^2 x\right)^{1/2} \right] \qquad (43)$$

and for $\beta > 3$ for all x

$$A \approx 1 - e^{-\beta x} \qquad (44)$$

We note that the fractional absorption of an Elsasser band does not in general equal the fractional absorption of a single line. The difference is due to the effect of the overlapping of lines in an Elsasser band.[*]

The statistical model of a band[5,6] assumes that the position and intensity of the spectral lines are randomly distributed. For an infinite number of equally spaced lines the statistical method gives

$$A = 1 - \exp\left(- \bar{W}_{s\ell} / d\right) \qquad (45)$$

where

$$\bar{W}_{s\ell} = \int_{0}^{\infty} W_{s\ell} (S, \beta) P(S) dS \qquad (46)$$

$$W_{s\ell} / d = \beta f(x) = \beta x e^{-x} \left[I_{o}(x) + I_{1}(x) \right] \qquad (47)$$

$P(S)dS$ denotes the probability that a spectral line of intensity S, is in the interval dS.

Still another model for band absorption may be obtained by a random superposition of Elsasser bands. Each Elsasser band consists of an in-

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[*]We shall later discuss overlapping effects in detail.

finite number of spectral lines of equal intensity, S, half width, α, and line spacing d, although the bands may have different intensities, half widths and line spacings. The absorption from a random superposition of N Elsasser bands is given by

$$A = 1 - \prod_{i=1}^{N} (1- \frac{\bar{W}_{E,i}}{\triangle_i}) \tag{48}$$

where $\triangle_i$ is the separation of the spectral lines in the ith band and $\bar{W}_{E,i}$ is the average value of the equivalent width of the ith Elsasser band, given by

$$\bar{W}_{E,i} = \int_0^\infty W_{E,i} \, P(S) \, dS \tag{49}$$

(b) Regions of Validity for Absorption Calculations

(i) Strong Line Approximation

When the absorption is virtually complete near the centers of the strongest lines in the band (x large) the absorption is a function of the single variable $\beta^2 x = 2 \pi \alpha \, Su/d^2$. The strong line approximation corresponds to the case of complete absorption near the center of the strong lines and is valid even when there is overlapping of the spectral lines. The resulting absorption, as calculated by the strong line approximation, is dependent on the spectral arrangement of the lines in the band. This must be so because overlapping near the strong line centers cannot result in increased absorption. It should be noted that the strong line approximation is not the same as the square root

approximation discussed previously, which is valid only for non-overlapping lines.

We first consider the strong line approximation for the statistical model.. For large x for the Lorentz line shape we have

$$\frac{W_{s\ell}}{d} = \beta \ f(x) = \beta \ (2x/\pi)^{1/2} \tag{50}$$

If all the lines are equally intense, (uniform statistical model) the intensity distribution is given by

$$P(S) = \delta(S - S_o) \tag{51}$$

where δ is the Dirac delta function. Therefore the absorption is given by

$$A = 1 - \exp \ [-(2\beta^2 x_o/\pi)^{1/2} \ ] \tag{52}$$

with

$$x_o = S_o u/2 \ \pi \ \alpha \tag{53}$$

For the statistical model with an exponentially decreasing intensity,

$$P(S) = \frac{1}{S_1} e^{-S/S_1} \tag{54}$$

which gives

$$A = 1 - \exp \ [\ - \beta x_1 \ /(1+2x_1)^{1/2}] \tag{55}$$

with

$$x_1 = \frac{S_1 u}{2\pi \ \alpha} \tag{56}$$

To compare the uniform statistical model with the exponential intensity model we must make some connection between the two

intensity parameters, S_o and S_1. If S_o is chosen to be $S_1 \frac{\pi}{4}$ the absorption is seen to be only slightly affected by the two intensity distributions.

For the Elsasser band, the strong line approximation gives

$$A = \text{erf} \ (\ \frac{1}{2} \ \beta^2 x)^{1/2} \tag{57}$$

The Elsasser band gives more absorption than the statistical model. This is due to the fact that there is more overlapping of the spectral lines in the statistical model than in the Elsasser model. Since the absorption is almost complete at the strong line centers overlapping in these regions cannot result in additional absorption. Thus for a given total intensity, the more prominent overlapping associated with the statistical model results in less absorption than the Elsasser model.

(ii) Weak Line Approximation

When the absorption is small (x small) at all frequencies in the band (including the centers of the strongest lines) the absorption is a function of the single variable $\beta_x = Su/d$. This condition is valid even when there is overlapping of the spectral lines. It is therefore not the same as the linear approximation which is valid only for non-overlapping lines.

When the weak line approximation is valid, the absorption is sufficiently small at all frequencies so that the effect of the different spectral lines is additive. Therefore for the weak line

approximation, in contrast to the strong line approximation, the absorption does not depend on the spectral arrangement of the lines in the band.

For small x we obtain

$$\frac{W_{s\ell}}{d} = \beta \ f(x) = \beta \ x \tag{58}$$

and

$$A = 1 - e^{-\beta \ x} \tag{59}$$

for the absorption for both the statistical and the Elsasser models.

(iii) Nonoverlapping Line Approximation

The regions of validity for the strong and weak line approximations depend only on whether the absorption is large or small at the line centers. The regions of validity for these approximations do not depend on overlapping effects. On the other hand, the only requirement for the validity of the non-overlapping approximation is that the spectral lines do not overlap appreciably. This approximation does not depend on the value of the absorption at the line centers and since there is no overlapping effect, the absorption is the same for regular or for random spacing. For the Elsasser model and the uniform statical model the absorption is given by

$$A = \beta \ f(x) \tag{60}$$

The values of x and β for which the three line approximations, strong, weak, and non-overlapping, are valid to within 10% have been determined by Plass.

(c) Emissivity Calculations

The actual calculation of the emissivity or absorptivity within the appropriate region of validity requires the determination of the intensity, line spacing, etc. To date, the best calculations for the emissivity of diatomic gases have been made by Stull and Plass[8] and by Malkmus and Thomson[9] employing the rotating anharmonic oscillator model previously discussed. Recall that the energy levels of the rotating anharmonic oscillator are given by

$$E(v,j) = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 + \omega_e z_e(v + \tfrac{1}{2})^4$$

$$+ B_e j(j + 1) - \alpha_e(v + 1/2) \, j \, (j + 1) \tag{61}$$

The effect of the centrifugal force on the energy levels has been omitted.[*] The frequency of a transition for $\Delta v = 1$ is given by[**]

$$\omega_{vj}^{v+1 \; j'} = E(v + 1, j') - E(v,j) \tag{62}$$

$$= \omega_v + B_e \left[\, j'(j' + 1) - j(j + 1) \, \right] - \alpha_e \left[\, (v + \tfrac{3}{2})j'(j' + 1) \right.$$

$$\left. -(v + 1/2)j(j + 1) \, \right] \tag{63}$$

We represent both the R and P branches by one equation

$$\omega = \omega_v + 2B_e m - \alpha_e \left[\, m(m + 1) + 2(v + \tfrac{1}{2})m \, \right] \tag{64}$$

which gives a band head in the R branch. The average line spacing is

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[*] Stull & Plass do not neglect this effect in their calculation.

[**] In our notation $\omega_v = \nu_o$

given by

$$d(\omega) = 2 \left[\left[B_e - \alpha_e (v + 1) \right]^2 - \alpha_e (\omega - \omega_v) \right]^{1/2} \tag{65}$$

The energy levels $F_v(J)$ are given by[9]

$$F_v(J) \gtrless E_v(j) \approx \left[B_e - \alpha_e (v + \tfrac{1}{2}) \right] j(j + 1) \tag{66}$$

$$= \frac{B_e - (v+1)\alpha_e}{\alpha_e^2} \left[2 \left[B_e - (v + 1) \alpha_e \right] \left[B_e - (v + 1) \alpha_e \right.\right.$$

$$\mp \sqrt{\left[B_e - (v + 1) \alpha_e \right]^2 - \alpha_e (\omega - \omega_v)}$$

$$- \left(1 + \frac{\tfrac{1}{2} \alpha_e}{B_e - (v + 1) \alpha_e} \right) \cdot \alpha_e (\omega - \omega_v) \left.\right] \tag{67}$$

The equation for the integrated absorption of a vibration rotation line per unit pressure (c_m^{-2} atm^{-1}), $(1/p) \int_0^\infty k(\nu)d\nu$, is given by (Penner[8],[2], p. 135)

$$S_{vj}^{v'j'} = (8\pi^3/3hc) \, (N/Gp)\omega_{vj}^{v'j'}$$

$$\times \exp[-E(v,j)hc/kT] \left| M_{vj}^{v'j'} \right|^2$$

$$\times [j\delta_{j-1,j'} + (j+1)\delta_{j+1,j'}]$$

$$\times [1 - \exp(-hc\omega_{vj}^{v'j'}/kT)], \tag{68}$$

for the transition $vj \rightarrow v'j'$. In this equation N is the number of molecules per unit volume, p is the pressure in the atmosphere, G is the partition function, $\left| M_{vj}^{v'\,j'} \right|^2$ is the square of the vibration rotation matrix elements of the dipole moment, and δ is the Kronecker delta. A number of

approximations must be made[8,9] to obtain the final result

$$S_{vj}^{v'j'} = [\alpha_v^{v'}/G_R(v,T) \langle \Omega_v^{v'} \rangle_{av}] \omega_{vj}^{v'j'} F_{vj}^{v'j'}$$

$$X exp[-E_v(j)hc/kT]$$

$$X[j\delta_{j-1,j'} + (j+1)\delta_{j+1,j'}]$$

$$X[1-exp(-\omega_{vj}^{v'j'}hc/kT)] \tag{69}$$

The total band absorption (neglecting overlapping) is given by

$$\alpha_v^{v'} = \sum_{jj'} S_{vj}^{v'j'} = (8\pi^3/3hc)(N/Gp) \left| R_v^{v'} \right|^2 \langle \Omega_v^{v'} \rangle_{av}$$

$$X G_R(v,T) \ exp[-E(v)hc/kT], \tag{70}$$

where

$$\langle \Omega_v^{v'} \rangle_{av} G_R(v,T)$$

$$= \sum_{jj'} \omega_{vj}^{v'j'} F_{vj}^{v'j'} [1-exp(-\omega_{vj}^{v'j'}hc/kT)]$$

$$X exp[-E_v(j)hc/kT][j\delta_{j-1,j'} + (j+1)\delta_{j+1,j'}], \tag{71}$$

The amplitude $\left| M_{vj}^{v'j'} \right|^2$ has been written as $\left| R_v^{v'} \right|^2 F_{vj}^{v'j'}$[2,8,9]. Note that $S_{vj}^{v'j'}$ can be calculated for any temperature as long as $\alpha_v^{v'}$ has been measured at one temperature.[8,9]

Thus the frequency and the intensity may be calculated at different temperatures for the important transitions $(v,j \rightarrow v + 1, j \pm 1)$. The quantities $\sum_i S_i$ and $\sum_i (S_i)^{1/2}$ may then be calculated as functions of the frequency.

Now, in the weak line approximation we have

$$\epsilon_\omega = 1 - \exp\,[-\beta x] = 1 - \exp\,[\,-\,p1S(\omega)/d(\omega)\,] \tag{72}$$

$$= 1 - \exp\,[\,-p1\bar{S}/d\,]$$

where

$$\bar{S}/d = \sum_i S_i/Nd = \sum_i S_i/\Delta\nu \tag{73}$$

and N is the number of spectral lines in a small frequency interval $\Delta\nu$. The quantity $\sum_i S_i/\Delta\nu$ is obtained as a function of frequency and temperature as discussed previously so that the emissivity may be then calculated according to Equations (72) and (73).

In the strong line approximation (for the uniform statistical model)

$$\epsilon_\omega = 1 - \exp\,[\,-\,(2\beta^2 x/\pi)^{1/2}\,] \tag{74}$$

$$= 1 - \exp\,[\,-\,(2\pi\,\alpha_0)^{1/2}\,(\sum_i S_i^{1/2}/\Delta\nu)(p^2 1)^{1/2}\,] \tag{75}$$

where α_0 is the average half width of the line at one atmosphere pressure and the quantity $\sum_i S_i^{1/2}/\Delta\nu$ is obtained as a function of frequency and temperature as discussed previously. The strong line absorption for the Elsasser model follows directly from the above.

Calculations were made for HCl, HF, CO and No over a temperature range from 300 to 7000 $^\circ$K.[9] There is good agreement with other published calculations of the spectral emissivity.

We have had to omit certain details in our discussion of the emissivity calculations. An important point which warrants consideration is the determination of the line width, $2\,\alpha$. As was recently demonstrated by

Malkmus, Maclay and Babrov[10] for the HCL band at room temperature, the correct use of the available data on line strengths and line widths is more important than even the choice of a particular band model. There remains a definite need for further work on the temperature dependence of molecular line widths.

(d) Experimental Considerations

The use of experiments in conjunction with band models in order to determine the emissivity of gases has been discussed by Oppenheim and Ben-Aryeh.[11] They consider the statistical model for the linear triatomic gas CO_2. We briefly outline their discussion.

From experiments at one temperature, the variation of $-\ln T/P$ may be obtained as a function of wave number, ν, and path length ℓ .   T is the transmittance. Now, for the uniform statistical model with Lorentz line shape, we have

$$- \frac{\ln T}{p} = \frac{-\ln(1-A)}{p} = \frac{W_{s\ell}}{d} = \frac{2 \pi \alpha\gamma}{d} \, f(x) \tag{76}$$

By plotting Equation (76) vs. path length, 1 , at one wavenumber (the so called curve of growth) we obtain $\frac{S}{d}$, $\frac{2 \pi \gamma}{d}$ and $\frac{x}{1}$ at one wavenumber. The procedure is carried out over a range of wave numbers so that $\frac{S}{d}$, $\frac{2 \pi \gamma}{d}$ and $\frac{x}{1}$ are obtained over a range of wavenumbers. These parameters constitute the fundamental spectroscopic parameters so that the transmittance can now be calculated for any pressure and path length. In detail, for a given path length we obtain $\frac{2 \pi \gamma}{d}$ and x. Then, for the uniform

statistical model

$$\frac{\overline{W}_{s\ell}}{d} = \frac{W_{s\ell}}{d} = \frac{2 \pi \gamma}{d} = f(x)p \tag{77}$$

so that the transmittance, T, or absorption 1-T, can then be obtained from

Equation (76) as a function of wavenumber and pressure.

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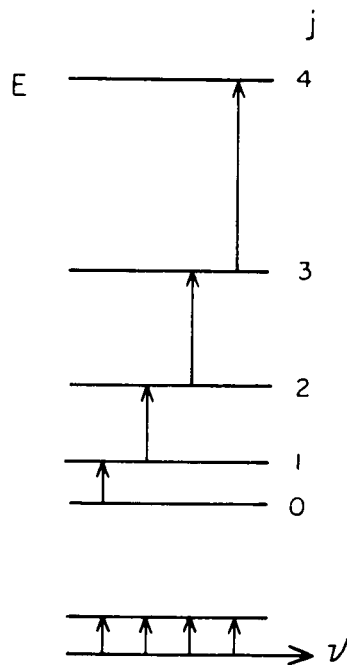
FIG. 1   ENERGY LEVELS AND INFRARED
          TRANSITIONS OF A RIGID ROTATOR
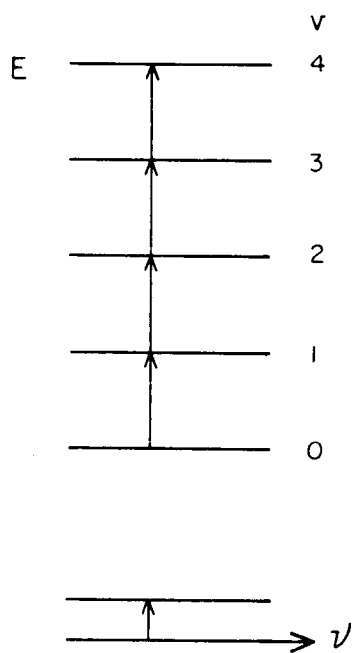

FIG. 2   ENERGY LEVELS AND INFRARED
          TRANSITIONS OF A HARMONIC
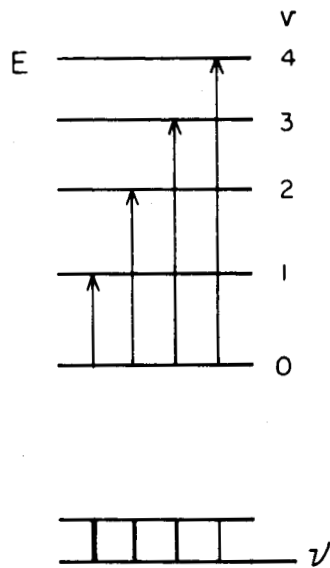   OSCILLATOR

FIG. 3   ENERGY LEVELS AND INFRARED
TRANSITIONS OF A HARMONIC
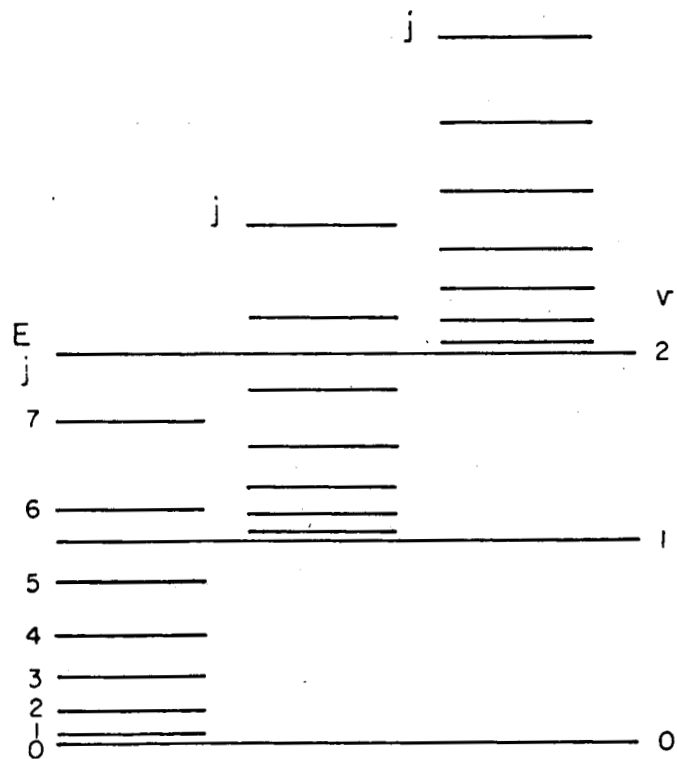OSCILLATOR

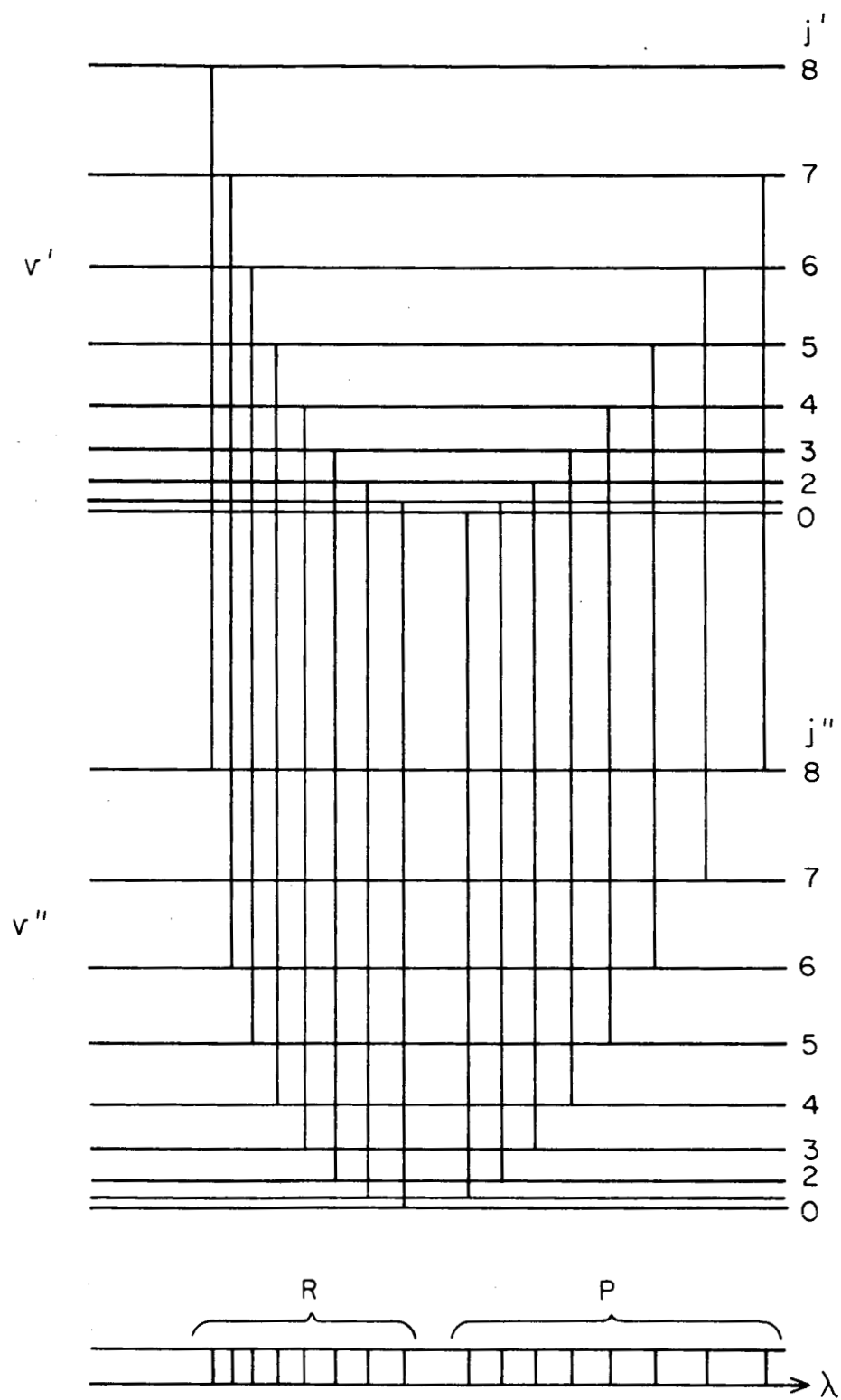FIG. 4   ENERGY LEVELS OF THE VIBRATING ROTATOR

FIG. 5 ENERGY LEVELS AND INFRARED TRANSITIONS
OF A ROTATION-VIBRATION BAND