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RESONANCE ABSORPTION BAND MODEL

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ABSTRACT

A model is derived for the resonance absorption of molecular bands composed of Lorentzian lines that is suitable for calculating fluorescence from irradiated air. The model is based on an explicit functional form derived for the resonance absorption of a single Lorentzian line which properly accounts for the possibility of unequal emission and absorption line widths. A procedure for rapid numerical computation of this function is given. This function yields a model for the resonance absorption of molecular bands composed of either overlapping or separate lines. A significant savings in computation time is obtained by using the model in place of exact expressions for resonance absorption. Examples are given for the resonance absorption of the N_2^+ First Negative band system.

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1. INTRODUCTION

The main features of the fluorescence spectrum from irradiated air are strong bands of N_2 and N_2^+ (see, for example, Gaydon and Pearse[1]). Most laboratory measurements of air fluorescence are made at low pressures using relatively weak radiation sources. Under these conditions, fluorescence is a valuable tool for studying excitation and ionization processes and the related molecular structure.[2,3] Relatively few measurements have been made at pressures near one atmosphere. Notable exceptions are deactivation measurements by Davidson and O'Neal[4] and by Mitchell.[5] These investigators find that the fluorescence efficiencies of the First and Second Positive bands of N_2 and the First Negative bands of N_2^+ are reduced at high pressure by factors of 10^3-10^4 relative to the low pressure regime.

Very few quantitative measurements of air fluorescence have been made at high pressure using intense radiation sources that strongly excite the air but produce negligible heating. Fluorescence is commonly observed from strongly excited air in the vicinity of high current pulsed electron beams, high flux nuclear reactors, and atmospheric nuclear explosions. In this regime, processes not normally encountered in the laboratory play a major role in producing and transporting air fluorescence. For example, deactivation of ion states through electron-ion recombination can be important as well as collisions with neutrals.[2,6] Molecular species produced by nonequilibrium processes in strongly irradiated air can absorb the fluorescence.[6] In particular, lower states of the nitrogen fluorescence transitions are metastables. This suggests that resonance absorption is important. We are concerned here with the latter effect.

Radiation that exits from a volume of gas that is both emitting and absorbing in the same transitions is called resonance radiation. The absorbing process is called resonance absorption. The process whereby absorbed radiation is re-emitted, called resonance scattering, will be neglected here since the fluorescence from air at high pressure is strongly quenched by collisions.[4,5] Mitchell and Zemansky[7] treated the resonance absorption of isolated lines in atomic gases. Our goal is to formulate a model for the resonance absorption of molecular bands applicable to numerical calculations of fluorescence from irradiated air. In a separate report,[8] the model will be applied to the N_2^+ First Negative bands.

In previous work, Bennett and Holland[9] considered the resonance scattering of fluorescence from high altitude nuclear explosions. They estimated average absorption coefficients for bands composed of lines with Doppler profiles. These coefficients were used in the exponential (Beer's Law) formula of absorption. The approach here is closer to the development of band models for the absorption of continuum radiation by molecular bands.[10,11,12] The resonance absorption of a single Lorentz line is first formulated in Section 2. The approach is similar to that given in Reference 7. The effect of unequal emission and absorption line widths is examined in detail, and convenient expressions for numerical computation are given. In Section 3, the two cases of bands composed of separated and overlapping Lorentz lines are considered. Approximate expressions of the single line form are derived for both cases.

2. SINGLE LINE WITH LORENTZ PROFILE

Band models that approximate the absorption by molecular bands of continuum light sources are based on functional forms for absorption by isolated lines.[10,11,12] Similarly, a model for resonance absorption by molecular bands must be based on functional forms for the resonance absorption of a single line associated with an isolated electronic-vibrational-rotational molecular transition. The resonance absorption of such a line has the added complexity that it depends on both the emission and absorption line shapes and strengths.[7] The dependence on line shapes can be understood by solving the equation of radiative transfer[10,13] restricted to the case of resonance absorption.

A formal solution to the equation of radiative transfer is the spectral radiance that would be observed along a column through a radiating volume. In the special case where scattering can be neglected, and for a spatial distribution of isotropic radiators, the spectral radiance can be written

$$N_\nu(\nu,L) = \frac{1}{4\pi}\int_0^L dx\ j_\nu(\nu,x)\ \exp\left(-\int_x^L dx'\ k_\nu(\nu,x')\right) \tag{1}$$

N_ν : spectral radiance, $W/cm^2 \cdot sr \cdot$ frequency
j_ν : volume emission coefficient, $W/cm^3 \cdot$ frequency
k_ν : volume absorption coefficient, cm^{-1}
L : column length, cm

For a single line with Lorentz profile associated with an isolated molecular transition, the spectral dependence of j_ν and k_ν can be written explicitly in terms of the Lorentz function

$$b(\nu) = \frac{\gamma}{\pi\left[(\nu-\nu_o)^2 + \gamma^2\right]},\ \text{frequency}^{-1} \tag{2}$$

γ : half width at half maximum, frequency
ν_o : line center, frequency

where

$$\int_0^\infty d\nu \; b(\nu) = 1$$

and the coefficients are

$$j_\nu(\nu,x) = j(x) \; b_e(\nu,x)$$
$$k_\nu(\nu,x) = S(x) \; b_a(\nu,x) \tag{3}$$

j : integrated volume emission, W/cm^3
S : absorption line strength, frequency/cm
b_e : emission line shape
b_a : absorption line shape

The line shapes b_e and b_a are functions of position through foreign gas and self broadening collisions. In general, both the Lorentz half-width γ and the line center frequency ν_o depend on collisional effects.[14] The integrated volume emission j and absorption line strength S are functions of position through the concentrations of emitting and absorbing states, respectively.

In terms of the Einstein spontaneous emission probability, $A_{if}(s^{-1})$, and the Einstein absorption coefficient, B_{fi} (cm^2/J · s), for transitions between upper state i and lower state f, j and S are given by[13,15]

$$j(x) = n_i(x) \; h\nu_o \; A_{if}$$
$$S(x) = n_f(x) \; h\nu_o \; B_{fi} \tag{4}$$

and

$$B_{fi} = \frac{c^2}{8\pi \; h\nu_o^3} A_{if}$$

n_i, n_f : emitter, absorber concentrations, cm^{-3}

A small variation of j and S with transition frequency has been neglected in Eq. 4. By combining Eqs. 1-4 and integrating over frequency, an expression is obtained for the line radiance, $N(W/cm^2 \cdot sr)$.

$$N(L) = \int_0^\infty d\nu\, N_\nu(L) \tag{5}$$

$$= \frac{1}{4\pi} h\nu_o\, A_{if} \int_0^L dx\, n_i(x) \int_0^\infty d\nu\, b_e(\nu,x)\, \exp\left(-h\nu_o\, B_{fi} \int_x^L dx'\, n_f(x')\, b_a(\nu,x')\right)$$

From Eqs. 4 and 5, the integrated transmittance of a resonance absorbed line is

$$T(x) = \int_0^\infty d\nu\, b_e(\nu,x)\, \exp\left(-\int_x^L dx' S(x')\, b_a(\nu,x')\right) \tag{6}$$

The line integrated radiance in terms of T is

$$N(L) = \frac{1}{4\pi} \int_0^L dx\, j(x)\, T(x)$$

In the remainder of this section, functional forms for T are derived for important special cases of Eq. 6. Limiting forms of these T-functions are found which are convenient for numerical computation. In all cases, the emission and absorption line center frequencies are assumed to be the same. The line shape functions, b_e and b_a, are at first restricted to be constant over the radiating volume; these results are then generalized to account for spatially varying line shapes.

CASE A. Homogenous radiating volume, equal line widths ($\gamma_a = \gamma_e = \gamma$).

In this case, the line shapes are identical, $b_a = b_e = b$, and are not functions of position. The transmittance, Eq. 6, becomes

$$T(\chi) = \int_0^\infty d\nu \; b(\nu) \; \exp\left(-\chi b(\nu)\right) \tag{7}$$

where χ is defined by

$$\chi(x) = \int_x^L dx \; S(x) = S \cdot (L-x)$$

The integration over frequency can be performed by expressing it in terms of the equivalent width, W, for the absorption line.

$$W(\chi) = \int_0^\infty d\nu \left[1 - \exp\left(-\chi b(\nu)\right)\right] \tag{8}$$

For absorption lines with Lorentz profile, W is the Ladenberg and Reiche function.[10,11,12]

$$W(\chi) = \chi \exp\left(-\chi/2\pi\gamma\right) \left[I_o\left(\frac{\chi}{2\pi\gamma}\right) + I_1\left(\frac{\chi}{2\pi\gamma}\right)\right] \tag{9}$$

I_o, I_1 : zeroth, first order Bessel functions
of imaginary argument[16]

It is apparent from Eqs. 7 and 8 that

$$T(\chi) = \frac{dW(\chi)}{d\chi}$$

The Ladenberg and Reiche function, Eq. 9, is easily differentiated using properties of the Bessel functions[16], and T is found to be

$$T(Z) = \exp(-Z) \; I_o(Z) \tag{10}$$

where $Z \equiv \dfrac{\chi}{2\pi\gamma}$

The T-function, Eq. 10, has well-known weak line (linear) and strong line (square root) limits.[10,11,12]

$$\begin{aligned} T(Z) &\xrightarrow[Z \to o]{} 1 - Z \text{ (weak line, linear)} \\ T(Z) &\xrightarrow[o \ll Z]{} \left(\frac{1}{2\pi Z}\right)^{1/2} \text{ (strong line, square root)} \end{aligned} \tag{11}$$

Percentage errors incurred by using these limiting forms for small and large values of the argument have been fully discussed by Plass, Ref. 11. Figure 1 is a plot of the T-function, Eq. 10, as a function of the dimensionless variable, Z. The linear and square root regions are evident in the figure.

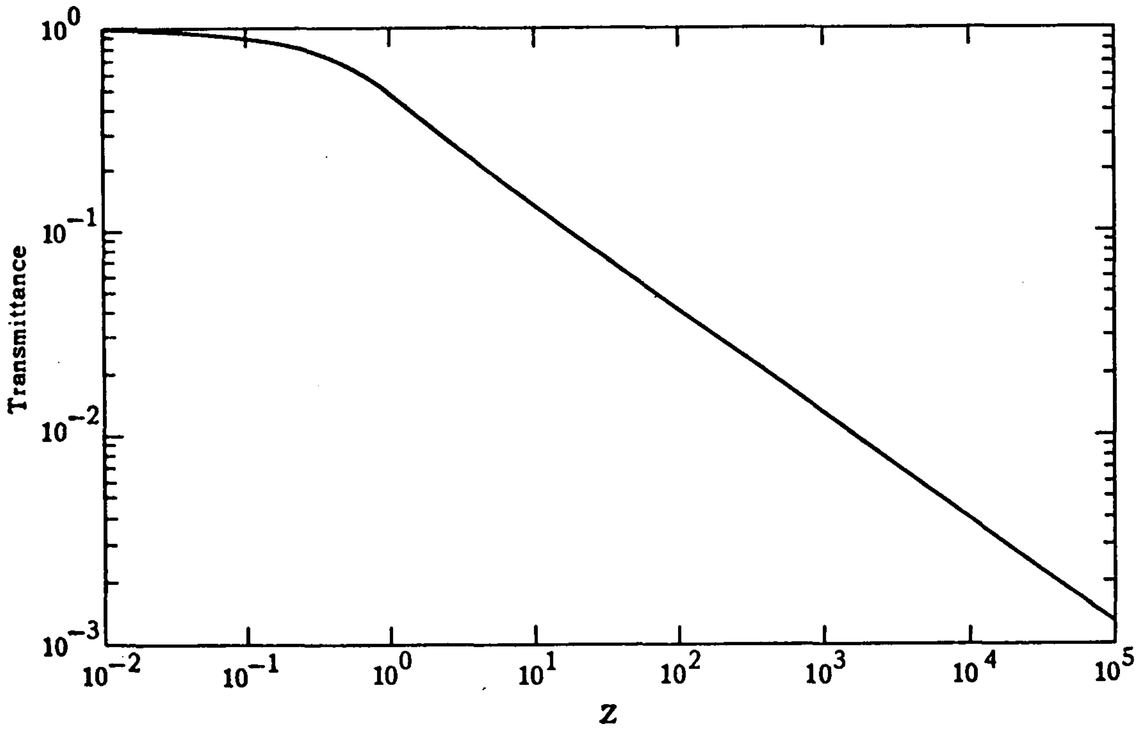

Figure 1. Transmittance function, Eq. 10, for the resonance absorption of an isolated Lorentz line, with $\gamma_a = \gamma_e$ and $Z = \chi/2\pi\gamma_a$.

CASE B. Homogenous radiating volume, unequal line widths ($\gamma_a \neq \gamma_e$).

In this case, the line shapes, b_a and b_e are not functions of position, but $b_a \neq b_e$ so that Eq. 6 becomes

$$T(\chi) = \int_0^\infty d\nu \; b_e(\nu) \; \exp\Big(-\chi \; b_a(\nu)\Big) \tag{12}$$

where, as in Case A, $\chi(x) = S \cdot (L-x)$

A series representation can be found for the integral in Eq. 12 by expressing it in terms of a generalized Ladenberg and Reiche function, W_1.

$$W_1(\chi) = \int_0^\infty d\nu \; \frac{b_e(\nu)}{b_a(\nu)} \left[1 - \exp\Big(-\chi \; b_a(\nu)\Big)\right] \tag{13}$$

$$T(\chi) = \frac{dW_1(\chi)}{d\chi}$$

By substituting the explicit form for the Lorentz functions, Eq. 2, and making a trigonometric change of variable, Eq. 13 can be recast in the form

$$T(Z) = \frac{2\beta}{1+\beta^2} \exp(-Z) \; \frac{1}{\pi} \int_0^\pi d\Theta \; \frac{\exp(-Z \; \cos\Theta)}{1 + \left(\frac{1-\beta^2}{1+\beta^2}\right) \cos\Theta} \tag{14}$$

where

$$Z = \frac{\chi}{2\pi\gamma_a}$$

and

$$\beta \equiv \frac{\gamma_a}{\gamma_e}$$

The parameter β measures the departure from equal (β=1) emission and absorption line widths.

If the denominator in the integrand of Eq. 14 is expanded in geometric series, one can identify an integral representation of the Bessel function, I_o, and an infinite sequence of derivatives of I_o.[16]

$$T(Z) = \frac{2\beta}{1+\beta^2} \exp(-Z) \sum_{n=0}^{\infty} \left(\frac{1-\beta^2}{1+\beta^2}\right)^n I_o^{(n)}(Z) \tag{15}$$

$I_o^{(n)}$: n^{th} derivative of I_o

The n^{th} derivative of I_o can be expressed as a linear combination of Bessel functions of imaginary argument.[16]

$$I_o^{(n)} = \frac{1}{2^n} \sum_{m=0}^{n} \binom{n}{m} I_{n-2m} \tag{16}$$

$\binom{n}{m}$: binomial coefficient

By substituting Eq. 16 into Eq. 15 and rearranging the series, one can verify that

$$T(Z) = \frac{2\beta}{1+\beta^2} \exp(-Z) \left[C_o I_o(Z) + 2 \sum_{n=1}^{\infty} C_n I_n(Z) \right] \tag{17}$$

The coefficients, C_n, are given by

$$C_o = \sum_{m=0}^{\infty} \binom{2m}{m} \left(\frac{\Lambda}{2}\right)^m$$

$$C_1 = \frac{1}{\Lambda} (C_o - 1)$$

$$C_n = \frac{2}{\Lambda} C_{n-1} - C_{n-2}, \ 2 \leq n \tag{18}$$

where

$$\Lambda = \frac{1-\beta^2}{1+\beta^2}$$

The series for C_o can be summed using Series No. 899 in Jolley.[17] The rest of the coefficients can then be evaluated using the recursion formula in Eq. 18. The result of this procedure is

$$C_n = \frac{1+\beta^2}{2\beta}\left(\frac{1-\beta}{1+\beta}\right)^n \quad , \; 0 \leq n \tag{19}$$

Combining Eqs. 17 and 19 yields a series representation for the T-function in the case that $\gamma_a \neq \gamma_e$.

$$T(Z) = \exp(-Z)\left[I_o(Z) + 2\sum_{n=1}^{\infty}\left(\frac{1-\beta}{1+\beta}\right)^n I_n(Z)\right] \tag{20}$$

It is easy to verify that Eq. 20 holds for all values of β, $0 \leq \beta < \infty$. In particular, for $\beta = 1(\gamma_a = \gamma_e)$, the T-function reduces to that of Case A, Eq. 10. Several useful limiting forms of the T-function have been derived and are summarized in Eq. 21.

(a) $\beta = 1$, arbitrary Z, (21)

$$T(Z) = \exp(-Z)\; I_o(Z)$$

(b) $\beta \to 0$, arbitrary Z,

$$T(Z) \to 1$$

(c) $1 << \beta$, arbitrary Z,

$$T(Z) = \exp(-2\,Z)$$

(d) $Z \to 0$, arbitrary β

$$T(Z) = 1 - \frac{2\beta}{1+\beta} Z \qquad \text{(weak line, linear)}$$

(e) $0 << Z$, arbitrary β

$$T(Z) = \frac{1}{\beta}\left(\frac{1}{2\pi Z}\right)^{1/2} \qquad \text{(strong line, square root)}$$

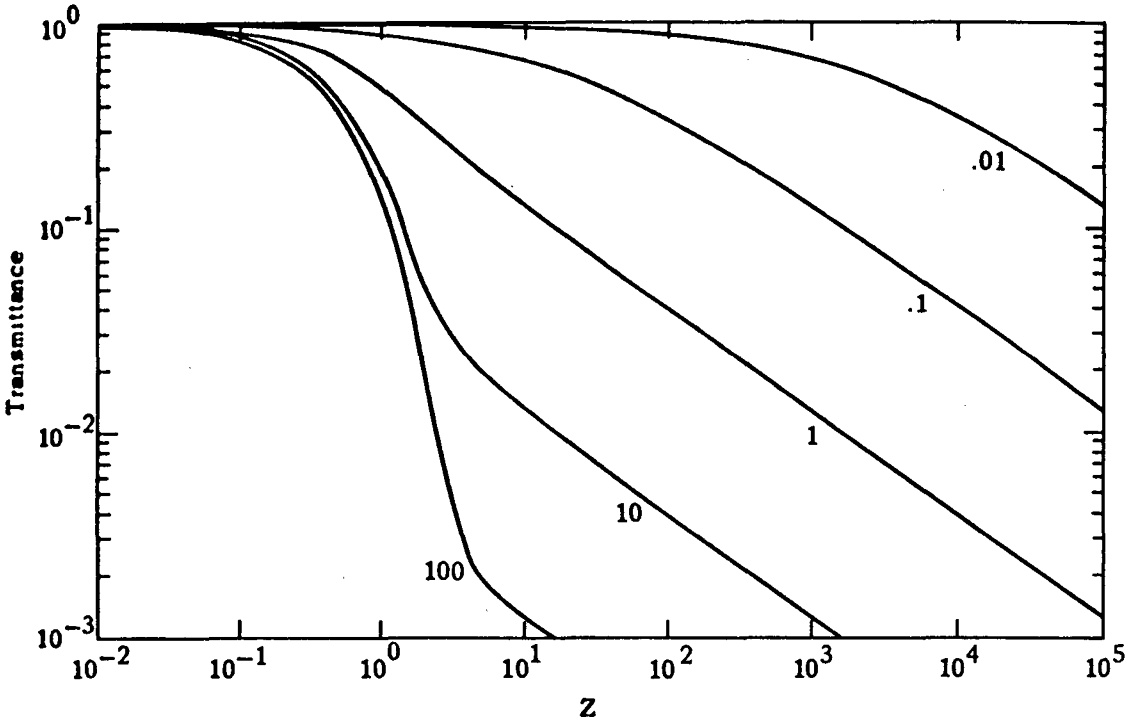

Fig. 2. Transmittance function, eqn (20), for the resonance absorption of an isolated Lorentz line plotted as a function of $Z = \chi/2\pi\gamma_a$ for fixed values of $\beta = \gamma_a/\gamma_e$.

The T-function, Eq. 20, is plotted in Figure 2 as a function of the dimensionless variable Z for several values of β in the range 10^{-2} to 10^2. The shape of the T-function depends significantly on the value of β; in particular, the regions of validity of the weak and strong line limits change dramatically as β is varied. Clearly, this β dependence cannot be neglected in resonance absorption calculations. The series for the T-function, Eq. 20, converges slowly for values of β such that the expansion parameter, $\left(\frac{1-\beta}{1+\beta}\right) \to \pm 1$. For example, if $Z = 400$ and $\beta = 10^{-2}$ or 10^2, approximately 100 terms are required for convergence (absolute error $< 10^{-6}$). This is not a severe problem for large β values since the strong line limiting form, Eq. 21(e), is applicable over the range of large Z values where convergence is slow. To circumvent the convergence problem for small β values ($\beta < 10^{-1}$), approximations to the infinite series, Eq. 20, have been derived in terms of finite series based on expansions of the Bessel functions for small and large values of the argument.[16]

A prescription will now be given for evaluating the T-function which has been found to be particularly useful in numerical calculations of resonance absorption.[8] It is based on the exact expression Eq. 20, the limiting forms Eq. 21, and the approximations by finite series mentioned previously. Convergence is rapid for all values of the β parameter. The accuracy of the approximations has been checked, and a relative error less than 1% has been found over the following ranges,

$$10^{-2} \leq Z \leq 10^{5}$$

$$10^{-3} \leq \beta \leq 10^{3}$$

$$10^{-3} \leq T \leq 1$$

In the calculational procedure, the T-function is evaluated as a function of the variable $Z = \frac{\chi}{2\pi\gamma_a}$. The following parameters are defined for fixed values of β,

$$Z_w \equiv 0.02 \left(\frac{1+\beta}{2\beta}\right) \qquad (22)$$

$$Z_s \equiv 50 \left(\frac{1+\beta}{2\beta}\right)^2$$

$$Z_{w1} \equiv 0.4 \left(\frac{1+\beta}{2\beta}\right)^2$$

$$Z_{s1} \equiv 4 \left(\frac{1+\beta}{2\beta}\right)^2$$

and,

(a) for $Z < Z_w$ and arbitrary β,

$$T(Z) = 1 - \frac{2\beta}{1+\beta} Z$$

(b) for $Z_s < Z$ and arbitrary β,

$$T(Z) = \frac{1}{(2\pi Z)^{1/2}\beta}$$

(c) for $\beta = 1$ and $Z_w \leq Z \leq Z_s$

$$T(Z) = e^{-Z}\, I_o(Z)$$

(d) for $\beta < 0.1$ and $Z_w \leq Z < Z_{w1}$,

$$T(Z) = 1 - \left(\frac{2\beta}{1+\beta}\right)A_1(Z) + \left(\frac{2\beta}{1+\beta}\right)^2 A_2(Z) - \left(\frac{2\beta}{1+\beta}\right)^3 A_3(Z)$$

where

$$A_1(Z) = Ze^{-Z}(I_o(Z) + I_1(Z))$$

$$A_2(Z) = \frac{Z}{2}\left[1 - e^{-Z}(I_o(Z) + I_1(Z))\right]$$

$$A_3(Z) = \frac{Z^2}{3}\, e^{-Z}(I_1(Z) + I_2(Z)) - \frac{Z}{2}\left[1 - e^{-Z}(I_o(Z) + 2I_1(Z))\right]$$

(e) for $\beta < 0.1$ and $Z_{s1} < Z \leq Z_s$

$$T(Z) = \frac{1}{(2\pi Z)^{1/2}} \cdot \frac{1}{(1-B)(1+B)^2}$$

where

$$B(\beta, Z) = \left(\frac{1-\beta}{1+\beta}\right)\left(\frac{1-\beta}{2\beta}\right)^2 \frac{1}{Z}$$

(f) for $0.1 \leq \beta$ and $Z_w \leq Z \leq Z_s$,

and for $\beta < 0.1$ and $Z_{w1} \leq Z \leq Z_{s1}$,

$$T(Z) = e^{-Z}\left[I_o(Z) + 2\sum_{n=1}^{N} \left(\frac{1-\beta}{1+\beta}\right)^n I_n(Z)\right] .$$

Terms in the series are monotonically decreasing; the series is terminated by dropping terms smaller than 10^{-6}. After evaluating I_o and I_1, the Bessel functions I_n, $2 \leq n$ are generated using the recurrence relation[16]

$$I_n(Z) = I_{n-2}(Z) - \frac{2(n-1)}{Z} I_{n-1}(Z)$$

CASE C. Inhomogeneous radiating volume.

In this case, the line shapes, b_a and b_e, and the emitter and absorber concentrations, n_i and n_f, are functions of position. The general form, Eq. 6, must be integrated to find the transmittance for each radiating point in the column. Note that one cannot proceed by dividing the inhomogeneous volume into homogenous subvolumes and then taking products of T-functions because $T(Z_1)T(Z_2) \neq T(Z_1 + Z_2)$. A complete numerical simulation of the problem is possible, but this would require evaluating the spectral radiance, Eq. 1, on many frequency subintervals, and then summing over the line profile.

Instead, we apply the Mean Value Theorem of the calculus to the integral in the exponent of Eq. 6.

$$\int_x^L dx' \; S(x') \; b_a(\nu,x') \tag{23}$$

$$\equiv \bar{b}_{ax}(\nu) \; \chi(x)$$

$\bar{b}_{ax}$: mean value of b_a on the subinterval $[x,L]$

$$\chi(x) = \int_x^L dx' \; S(x')$$

The problem is then one of evaluating the mean value of the absorption line shape $\bar{b}_{ax}$ on any subinterval of the column. An estimate of $\bar{b}_{ax}$ can be obtained in the following way. First, find an average absorption line width $\bar{\gamma}_{ax}$ using the density of absorbers n_f as a weighting function.

$$\bar{\gamma}_{ax} = \frac{\int_x^L dx' \; \gamma_a(x') \; n_f(x')}{\int_x^L dx' \; n_f(x')} \tag{24}$$

Then, assign to the mean line shape $\bar{b}_{ax}$ the average width $\bar{\gamma}_{ax}$ on each subinterval [x,L). In this way, the T-function, Eq. 20, is specified for every radiating point along the column, and can be evaluated using the procedure given in Case B, Eq. 22.

3. MOLECULAR BAND COMPOSED OF LINES WITH LORENTZ PROFILES

In Section 2, the resonance absorption of a single Lorentz line was described. Those results will be used here to construct a model which approximates the resonance absorption of a molecular band composed of Lorentz lines. Two cases will be considered: first, a band composed of separated lines, and then the more general case of a band with overlapping lines. It is assumed that the profiles of all lines forming either an emission or absorption band are identical and that the line center frequencies of emission and corresponding absorption lines are the same.

CASE A. Separated lines.

Consider a molecular band composed of rotational lines produced in transitions between upper state (U, v, J) and lower state (X, v', J') where U,X denote electronic states; v,v' denote vibrational levels; J,J' denote rotational levels. For an isolated rotational line, the development in Section 2 for the line integrated radiance of a single resonance absorbed line can be applied. In particular, the integrated volume emission j and the line strength S (Eq. 3) become

$$j(x)_{vv'jj'} = n_U(x)\; P_v(x)\; P_J(x)\; h\nu_{vv'}\; A_{vv'JJ'} \tag{25}$$

$$S(x)_{vv'JJ'} = n_X(x)\; P_{v'}(x)\; P_{J'}(x)\; h\nu_{vv'}\; B_{vv'JJ'}$$

n_U, n_X : concentrations of molecules in electronic states U,X

$P_v P_J$: fraction of U-state molecules in vibration-rotation level (v,J)

$P_{v'} P_{J'}$: fraction of X-state molecules in (v',J')

$\nu_{vv'}$: transition frequency of the (v,v') band

$A_{vv'JJ'}, B_{vv'JJ'}$: Einstein spontaneous emission probability absorption coefficient

The decomposition of the A-coefficient into electronic-vibrational and rotational transition probabilities is (see, for example, Herzberg[18])

$$A_{vv'JJ'} = A_{vv'} \frac{M_{JJ'}}{2J+1} \tag{26}$$

$A_{vv'}$: total transition probability for the (v,v') band

$M_{JJ'}$: rotational transition probability

and

$$B_{vv'JJ'} = \frac{c^2}{8\pi h\nu^3_{vv'}} \frac{2J+1}{2J'+1} A_{vv'JJ'}$$

$$= \frac{c^2}{8\pi h\nu^3_{vv'}} A_{vv'} \frac{M_{JJ'}}{2J'+1}$$

Combining Eqs. 25 and 26, one obtains the following useful expressions for j and S

$$\begin{aligned} j(x)_{vv'JJ'} &= n_U(x)\ P_v(x)\ h\nu_{vv'}\ A_{vv'}\ F_J(x) \\ S(x)_{vv'JJ'} &= n_X(x)\ P_{v'}(x)\ \frac{c^2}{8\pi\nu^2_{vv'}}\ A_{vv'}\ G_{J'}(x) \end{aligned} \tag{27}$$

where

$$F_J(x) = P_J(x) \frac{M_{JJ'}}{2J+1}$$

$$G_{J'}(x) = P_{J'}(x) \frac{M_{JJ'}}{2J'+1}$$

For an isolated rotational line the line radiance Eqs. 5 and 6 becomes

$$N(L)_{vv'JJ'} = \frac{1}{4\pi} \int_0^L dx\ j(x)_{vv'JJ'}\ T(x)_{vv'JJ'} \tag{28}$$

where

$$T(x)_{vv'JJ'} = \int_0^\infty d\nu b_e(\nu,x) \exp\left(-\int_x^L dx' \; S(x')_{vv'JJ'} \; b_a(\nu,x)\right)$$

For a band composed of separated rotational lines, the band radiance is merely the sum of line radiances

$$\begin{aligned} N(L)_{vv'} &= \sum_J N(L)_{vv'JJ'} \\ &= \frac{1}{4\pi}\int_0^L dx \; j(x)_{vv'} \; T(x)_{vv'} \end{aligned} \qquad (29)$$

The following definitions have been used in Eq. 29.

$$T(x)_{vv'} = \sum_J F_J(x) \int_0^\infty d\nu \; b_e(\nu,x) \exp\left(-\int_x^L dx' \; S(x')_{vv'} \; G_{J'}(x') \; b_a(\nu,x')\right)$$

$$j(x)_{vv'} = n_U(x) \; P_v(x) \; h\nu_{vv'} \; A_{vv'} \qquad (30)$$

$$S(x)_{vv'} = n_X(x) \; P_{v'}(x) \; \frac{c^2}{8\pi\nu^2_{vv'}} \; A_{vv'}$$

In Eq. 30, $T_{vv'}$ is the transmittance due to resonance absorption of the (v,v') band. By applying the Mean Value theorem, we replace the sum over rotational lines in the expression for $T_{vv'}$ by a single term. In this way, the resonance absorption T-function for a band composed of separated Lorentz lines has the same form as the T-function for a single Lorentz line with an additional parameter, g_s that accounts for the average line strength in the band.

$$T_{vv'}(Z_{vv'}) = T_{s\ell}(g_s\, Z_{vv'},\ \beta) \tag{31}$$

$T_{s\ell}$: single line T-function, Eqs. 20-22 and Figure 2

g_s : average rotational line strength for separated lines

and

$$Z_{vv'} = \frac{X_{vv'}}{2\pi\gamma_a}$$

$$X_{vv'}(x) = \int_x^L dx'\ S_{vv'}(x')$$

$$\beta = \frac{\gamma_a}{\gamma_e}$$

If g_s is a function of position through the rotational state population fractions P_J and $P_{J'}$ (Eq. 27), then average values along the column must be used in Eq. 31, in the same manner that average values for the absorption line width γ_a were previously defined, Eq. 24.

We have computed T-functions for the N_2^+ First Negative bands assuming that the rotational states are populated in thermal equilibrium.[8] For example, if β=1 and the rotational temperatures are 300°K, the T-function computed via Eq. 31 with $g_s = 0.026$ is a good fit to the exact result, Eq. 30, over the range $10^{-3} \leq T_{vv'} \leq 1$ (standard error = 3%). Note that some improvement in accuracy could be obtained by evaluating separate T-functions for the P and R branches of the First Negative bands.[9,18]

CASE B. Overlapping lines.

Models which describe the absorption of continuum radiation by molecular bands[10,11,12] account for line overlap by introducing a parameter for the average line spacing. Heaton[19] has given a formulation for combining the equivalent widths of two Lorentz lines in the square root region. His results show the transition from the separated line case to the coincident line case as a function of line width and spacing, and line strength.

For the resonance absorption of a molecular band with overlapping lines, the band transmittance, Eq. 30, must be rewritten summing the contributions from neighboring absorption lines to the absorption of each emission line.

$$T_{vv'}(x) = \sum_J F_J(x) \int_0^\infty d\nu b_e(\nu,x) \exp\left(-\int_x^L dx' \; S_{vv'}(x') \sum_{J'} G_{J'}(x') b_{a,J'}(\nu,x')\right) \quad (32)$$

Note that in Eq. 32, the subscript J' on the absorption line shape function denotes the variation of line center frequency with J', while the absorption line shapes are still taken to be equal. Approximate solutions to Eq. 32 of the single line form, Eq. 20, are easily obtained in the two limits of separated lines and coincident lines. The solution for separated lines was given in Eq. 31. For the case of coincident lines, the absorption line shape function no longer depends on J', and a solution obtains by making the following replacement in Eq. 31

$$g_s \rightarrow g_c = \sum_{J'} G_{J'}$$

For intermediate cases, we replace the parameter g_s in Eq. 31 by a parameter g which varies continuously as a function of $Z_{vv'}$ between the separated and coincident line limits, i.e.,

$$g_s \leq g \leq g_c$$

The parameter g is a complicated function of the absorption line width and average spacing and the magnitude of $Z_{vv'}$. For a particular band with fixed absorption line width and average spacing, g approaches the separated line limit for $Z_{vv'}$ small, and the coincident line limit for $Z_{vv'}$ large.[19] We shall assume a simple (nonunique) functional form for g which has the proper limits,

$$g(Z_{vv'}) = g_s + \left(\frac{\alpha Z_{vv'}}{1+\alpha Z_{vv'}}\right)(g_c - g_s) \qquad (33)$$

$$g \xrightarrow[Z_{vv'} \to 0]{} g_s \quad \text{(separated lines)}$$

$$g \xrightarrow[Z_{vv'} \to \infty]{} g_c \quad \text{(coincident lines)}$$

Thus, a T-function that approximates the resonance absorption of a molecular band with overlapping Lorentz lines is given by

$$T_{vv'}(Z_{vv'}) = T_{s\ell}\left(g(Z_{vv'}) \cdot Z_{vv'}, \beta\right) \qquad (34)$$

$T_{s\ell}$: single line T-function, Eqs. 20-22 and Figure 2

$g(Z_{vv'})$: Eq. 33

$Z_{vv'}, \beta$: Eq. 31

The parameter α in Eq. 33 depends on the absorption line width and average spacing. The value of α determines the region of transition, $\alpha Z_{vv'} \sim 1$, between separated and coincident line regimes. The parameter α must be evaluated for the particular band of interest by fitting it to numerical calculations using the exact form of the transmittance, Eq. 32, or by fitting it to experimental data.

We have compared the T-function, Eq. 34, with the exact expression, Eq. 32, evaluated for the N_2^+ First Negative bands assuming that the rotational states are populated in thermal equilibrium.[8] In this case, g_c is equal to 0.5 for both the P and R branches. If $\beta=1$ and $T = 300°K$, we find reasonable agreement over a broad range of γ_a values by writing α in the form, $\alpha = \text{constant} \cdot \gamma_a^2$. The value of the constant was found to be $\simeq 0.015$ cm^2 with γ_a in cm^{-1}. Standard errors obtained by comparing numerical calculations of Eqs. 32 and 34 over the range $1 \leq Z_{vv'} \leq 10^5$ for fixed values of γ_a are

$\gamma_a (cm^{-1})$	Standard Error (%)
0.001	3
0.01	6
0.1	10
1.0	12

Rotational lines of the First Negative bands were found to be essentially independent for $\gamma_a < 0.01\ cm^{-1}$. The exact expression, Eq. 32 and the T-function, Eq. 34 are plotted in Figure 3 as functions of $Z_{vv'}$, for $\gamma_a = 0.1\ cm^{-1}$. Errors incurred by using the T-function, Eq. 34, will be acceptable for many applications. Use of Eq. 34 in place of Eq. 32 results in tremendous savings of computation time.

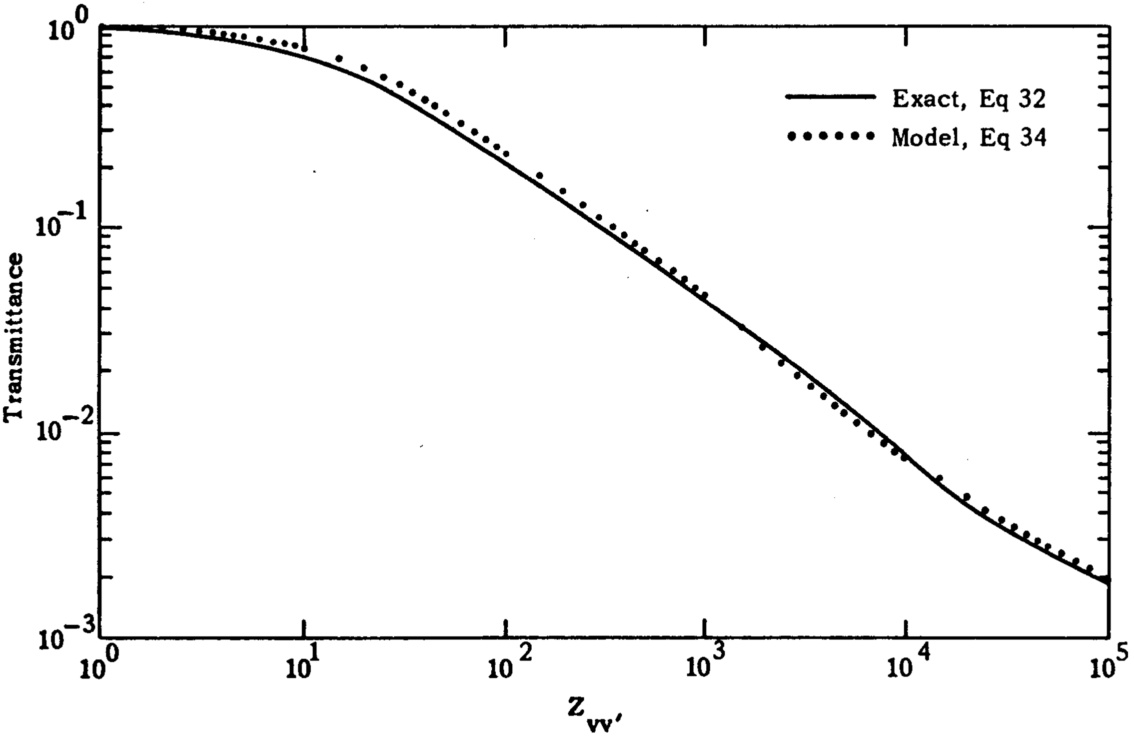

Figure 3. Transmittance due to resonance absorption of the N_2^+ first negative bands: rotational states populated in thermal equilibrium, $g_s(300^\circ K) = 0.026$; $g_c = 0.5$ for P and R branches; equal emission and absorption line widths, β=1; line overlap parameter $\alpha = 0.015\ \gamma_a^2$, $\gamma_a = 0.1\ cm^{-1}$; $Z_{vv'} = \chi_{vv'}/2\pi\gamma_a$.

4. CONCLUSIONS

A band model of resonance absorption has been derived that is suitable for numerical calculations of fluorescence from strongly irradiated air at high pressure. In Section 2, a functional form, Eq. 20, was obtained for the transmittance produced by the resonance absorption of an isolated Lorentz line. This function properly accounts for differences in emitting and absorbing line widths. A prescription, Eq. 22, was given for rapid numerical computation of this function. In Section 3, a transmittance function, Eq. 34, based on the single line form was derived for the resonance absorption of molecular bands composed of overlapping or nonoverlapping Lorentz lines. For clarity, Eq. 34 is reproduced here along with the definitions of the parameters.

$$T_{vv'}(Z_{vv'}) = T_{s\ell}(g(Z_{vv'}) \cdot Z_{vv'}, \beta)$$

$T_{s\ell}$: single line form, Eq. 20, to be evaluated by the prescription given in Eq. 22

$$Z_{vv'} = \frac{1}{2\pi\gamma_a} \int_x^L dx' \; S(x')_{vv'}$$

x, L : emission point, column length

$S_{vv'}$: absorption band strength, Eq. 30

γ_a, γ_e : absorption, emission line width

$$\beta = \frac{\gamma_a}{\gamma_e}$$

$$g(Z_{vv'}) = g_s + \frac{\alpha Z_{vv'}}{1+\alpha Z_{vv'}} (g_c - g_s)$$

g_s : average rotational line strength for separated lines

g_c : sum of rotational line strengths for coincident lines

α : line overlap parameter

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