A Radiation Model for Nonequilibrium Molecular Gases

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Solutions to the radiative transfer equation in a nonequilibrium gas are derived in a form paralleling the usual equilibrium solutions These nonequilibrium solutions are given in terms of an absorption coefficient and a Planck-like energy distribution, both of which are expressed as functions of effective electronic excitation temperatures and relative oscillator-strength distributions across the spectrum Approximate oscillator-strength distributions are presented which are functions of vibrational temperature only, and which give an averaged profile of the band produced by a given electronic transition Example calculations are made at vibrational temperatures of 1000°, 3000 , and 10,000°K for the strong molecular bands in nitrogen: namely, the N_2 first- and second-positive and the N_2^+ first-negative bands

Introduction

OPTICAL radiation from high-temperature gases is important in aerodynamics because it is one of the observables produced when a high-speed body traverses the atmosphere, and also because it may become the dominant mechanism of heat transfer when the body's speed exceeds escape velocity from earth Provided the flow field and the radiation are uncoupled (criteria for this condition have been established by Goulard,[1] for example), the problem can be treated in two steps First, the thermodynamic state of the gas is found at each point in the flow by methods such as those outlined by Hall, Eschenroeder, and Marrone [2] Then the radiation is calculated from knowledge of the emission and absorption coefficients, which are functions of the state variables

Where the excited gas is in equilibrium, the absorption coefficients are unique functions of any two state variables such as temperature and density; for equilibrium air these have been calculated by Meyerott, Sokoloff, and Nicholls,[3] whereas experimental values have been reported by Keck, Camm, Kivel, and Wentink [4] At low densities, such as may occur in expanded flow or at high altitude, the radiation may be from gases far out of equilibrium Then the state variables must include the population ratios of excited molecular and atomic species In principle, these may still be calculated by the methods of Hall et al ,[2] although it must be admitted that some of the collision cross sections required for electronic excitation are not well known However, even when the population ratios are given, the number of these variables involved becomes so large that it is impractical to tabulate radiation or absorption coefficients directly for nonequilibrium gases Thus, the aerodynamicist needs a method for treating nonequilibrium radiation for each specific flow problem where this occurs

It is the purpose of this paper to derive expressions for the nonequilibrium absorption and emission coefficients that are as simple as possible and to show how these coefficients enter the solution for radiative transfer The viewpoint is taken that the population numbers of excited species are available from a previous calculation It may be noted that the objective here is rather different from the objective of the spectroscopist, who seeks to establish a model that will reproduce the detailed structure of the spectrum, including the discontinuities observed at each rotational-vibrational band head Such a model for equilibrium air has been presented by Breene and Nardone,[5] for example The present objective is rather to retain only the essential average characteristics of the spectral distribution so that the model will be useful for engineering purposes but yet simple enough for a practical subroutine in calculations of radiation from complex flow fields For this purpose, the averaging procedures suggested by Meyerott et al [3] seem most practical, and these will be followed here

Absorption Coefficients

If radiation with intensity I_ν falls on a gas with N-absorbing molecules per unit volume, the energy absorbed each second per unit interval of the spectrum may be expressed:

$$4\pi N I\ \alpha_\nu = N I_\nu B_{nn} h\nu q \tag{1}$$

where I_ν is in units of erg/sec-cm²-steradian-unit frequency and α_ν is the absorption cross section per molecule The equivalent expression on the right-hand side of Eq (1) is given in terms of the Einstein probability coefficient B_{nn} , defined as the number of transitions each second per molecule from the quantum state n to the excited state n' when in an isotropic radiation field of unit intensity In general, the absorption is distributed over a finite portion of the spectrum because of factors such as the natural line-broadening, collision-broadening, Doppler shift, and in the case of molecular bands the vibration-rotation structure of the transition This is accounted for by the factor q, defined as the relative number of oscillators per unit frequency interval

The Einstein coefficient is given by[6 7]

$$B_{nn} = (4\pi^2 e^2/h\nu mc) f_{nn} \tag{2}$$

where f_{nn} is the absorption oscillator strength, or f number, for the transition It is a quantum mechanical correction to the classical result which signifies the probability that the absorbing particle will make the transition from n to n' in preference to all other possible transitions [It may be noted that B is sometimes defined[8] as the number of transitions induced when the radiant flux is limited to unit solid angle In this case, the coefficient is just $(4\pi)^{-1}$ times that given in Eq (2)]

If the molecular wave functions are separable into the product of functions involving only the electronic, vibrational, or rotational coordinates, then the oscillator strength can be expressed as the product of three factors:

$$f = f\ f\ f \tag{3}$$

where each of these factors is a probability normalized to unity when summed over all possible electronic, vibrational, and rotational transitions, respectively Thus the summation over all vibration and rotation transitions yields just the value f , and this quantity will be used as the oscillator strength

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required in the definition of B, Eq (2) The wave functions are not strictly separable, of course, and so the quantity f_e varies somewhat across the band This variation may be treated by Fraser's method of r centroids as described by Nicholls and Jarmain[9] [10] However, if the band is reasonably compact, the f number usually varies but weakly across the band,[3] and in the interests of simplicity a constant value will be assigned here

With f_e assumed constant, the oscillator distribution function q is the density of the product $f_v f_r$ per unit frequency interval Following the suggestion of Meyerott,[3] an interval of frequency $\Delta\nu$ is chosen (2000 cm^{-1} in wave-number units), and the average oscillator density over this interval is calculated For a compact band, this interval is broad enough to include a reasonable number of vibrational transitions so that the average has statistical meaning The rotational line structure of the band is neglected except to assume that, together with the collision and Doppler broadening, it spreads the absorption uniformly across the interval $\Delta\nu$ Then the oscillator distribution function is given by

$$q = \frac{1}{\Delta\nu}\sum_{v}\sum_{v'} q \quad \frac{N_v}{N} \tag{4}$$

The summation is understood to include only those lines that lie within the interval $\Delta\nu$ The quantity $q_{vv}{}'$ is the Franck-Condon factor[11] giving the fraction of electronic transitions that occur from vibrational quantum number v in the lower state to the vibrational quantum number v' in the upper state:

$$q_{vv'} = [\int \psi \, \psi_v \, dr]^2 \tag{5}$$

where ψ and ψ are the vibrational wave functions of the lower and upper state, respectively The ratio N_v/N is the fraction of the N-absorbing molecules that are in the vibrational quantum level v It is generally assumed that the vibrational states are approximately in Boltzmann distributions even when they are out of equilibrium with other energy modes Accordingly, a vibrational temperature Θ is assigned to characterize the vibrational state To the approximation that the molecules behave like harmonic oscillators with the frequency ω, the population fractions are

$$N_v/N = e^{-vh\omega/k\Theta}(1 - e^{-h\omega/k\Theta}) \tag{6}$$

Absorbing molecules are most often in the ground state or a metastable state, where it is generally adequate to use the Boltzmann-type distribution given by Eq (6) Another form suitable for excited-state molecules in very low-density gases will be considered in the following section on emission coefficients The oscillator distribution function q, Eq (4), is a convenient parameter to tabulate for use in computing the absorption in gases From Eqs (1) and (2) it follows that the average absorption coefficient per unit frequency is

$$\alpha_\nu = (\pi e^2/mc)f_e q \tag{7}$$

when q is given in seconds

Emission Coefficients

At equilibrium, the emission coefficient is related in a simple way to the absorption coefficient[8] However, for the case of interest here, where the gas may be out of equilibrium, the emission coefficient needs to be calculated separately, because the radiation process and the collisions are competing to populate the vibrational levels in different ways For the moment, neglect the radiation-induced downward transitions and consider only the spontaneous transitions from excited to lower states Then the energy emitted each second per unit interval of frequency by each unit volume may be expressed:

$$4\pi N'\epsilon_\nu = N'A_{n\ n}h\nu q' \tag{8}$$

where N' is the number of excited molecules per unit volume and ϵ_ν is the emission coefficient in erg/sec-steradian-molecule-unit frequency Again, the equivalent expression on the right-hand side of the equation is given in terms of an Einstein coefficient $A_{n\ n}$, defined as the number of spontaneous transitions each second per molecule from the excited state n' to a lower state n The two Einstein coefficients are related[8] by

$$A_{n'n} = \frac{g}{g'}\frac{2h\nu^3}{c^2}B_{nn} \tag{9}$$

where g and g' are the degeneracies of the lower and upper states, respectively The emission oscillator distribution function is given by

$$q' = \frac{1}{\Delta\nu}\sum_{v}\sum_{v'} q_{vv'}\frac{N_v}{N'} \tag{10}$$

where the Franck-Condon factors q_{vv} are the same as for Eq (4), and the sum is over the same lines of the spectrum lying in the interval $\Delta\nu$ Only the terms N_v/N' giving the fraction of excited molecules with vibrational quantum number v' are different

If the gas density is high enough so that collision frequency is much larger than the radiative transition rate, a vibrational population distribution of the same form as Eq (6) may be used The oscillator-strength distribution for this case will be designated by q_∞':

$$q_\infty' = \frac{1}{\Delta\nu}\sum_{v}\sum_{v'} q_{vv'}e^{-v'h\omega'/k\Theta}(1 - e^{-h\omega/k\Theta}) \tag{11}$$

To determine the densities for which Eq (11) applies, consider the ratio of the radiative transition and collision frequencies The radiative transition frequency may be expressed as

$$A = 3\gamma f\, g/g' \tag{12}$$

where γ is the classical damping constant $8\pi^2\nu^2e^2/3mc^3$ and f_e is the oscillator strength for the transition Typically, f_e is the order of 10^{-1} to 10^{-3} for strong molecular bands, γ is about $10^8\ \mathrm{sec}^{-1}$ in the optical region of the spectrum, and so A lies in the range about 10^6 transitions/sec

The collision rate may be written as

$$Z = NS\bar{u} \tag{13}$$

where N is the molecule number density, S is the cross section, and $\bar{u}$ is the mean molecular velocity $(8kT/\pi\mu)^{1/2}$, with μ the reduced mass of the colliding particles The cross section S is the order of $30 \times 10^{-16}\ \mathrm{cm}^2$ for most molecules, and $\bar{u}$ is typically in the range from 10^5 to 10^6 cm/sec for the temperatures and molecular weights of interest Thus Z is the order of $10^{-9}N$ Then, for collision frequency to be large compared to radiative transition rate, it is necessary that

$$N \gg \frac{3\gamma f}{S\bar{u}}\frac{g}{g'} \simeq 10^{15} \tag{14}$$

On the other hand, if gas densities are much less than the foregoing, radiation will occur from the upper states which are initially produced by the excitation processes Excited diatomic molecular states may be produced by three different mechanisms as follows:

Two-Body Collision

$$AB + M \rightarrow AB^* + M \tag{15}$$

Radiation Absorption

$$AB + h\nu \rightarrow AB^* \tag{16}$$

Three-Body Recombination

$$A + B + M \rightarrow AB^* + M \tag{17}$$

The ratio of three-body collision rate to the two-body collision rate is the order of VN, where the volume V is the sphere of influence for the potential function between two of the colliding atoms This volume is about 10^{-22} cm^3, so that when three-body recombination becomes appreciable, the number density N is large enough to effect a collision randomized vibrational population according to the criterion of Eq (14) Consequently, at low density, only the two-body collision and radiation absorption excitations are considered

If radiation of uniform spectral intensity is absorbed, the ground-and upper-state vibrational populations are related by

$$\frac{N}{N'} = \sum_{v=1}^{\infty} q \ \frac{N_v}{N} \tag{18}$$

where the summation includes all vibrational quantum numbers v of the ground state The same population should be produced by electron bombardment, as an electron can scarcely be more effective than a quantum of absorbed radiation in changing the instantaneous momentum or position of the heavy atomic nuclei These atoms suddenly find themselves with their original momentum and position operating in a different potential field, and the probabilities that the molecules then arrive at the new vibrational quantum numbers v' are just the Franck-Condon factors used in Eq (18) In the case of collision with heavier particles, it is possible for vibrational quantum jumps to be produced by the same collision that causes electronic excitation However, it will be assumed that the distribution of Eq (18) applies to this case as well, on the grounds that excitation of multiple-energy modes by a single event is generally less probable than excitation of a single mode Then the emission oscillator strength distribution for low densities may be expressed:

$$q_0' = \frac{1}{\Delta\nu} \sum_{v} \sum_{v'} q_{vv} \left(\sum_{v=1}^{\infty} q_{vv} \ \frac{N_v}{N} \right) \tag{19}$$

At intermediate densities where Z and A are the same order of magnitude, part of the molecules will suffer collision before they radiate The probability that the molecule does not radiate in the time t will be taken as $\exp(-At)$ An interval, the order of Z^{-1}, is required to transfer the excited molecule from one distribution to the other, and it will therefore be assumed that the fraction $\exp(-A/Z)$ has been transferred by collision to the Boltzmann vibrational distribution before radiating, whereas the remaining fraction radiates from the initial states produced by the excitation process The total effective oscillator distribution function may then be expressed:

$$q' = (1 - e^{-A/Z})q_0' + e^{-A/Z}\, q_\infty' \tag{20}$$

The factors q_0' and q_∞' are convenient parameters to tabulate for use in computing the emission from nonequilibrium gases The average molecular emission coefficient per unit frequency interval is related as follows to the total emission oscillator distribution given by Eq (20):

$$\epsilon_\nu = \frac{g}{g'} \frac{2h\nu^3}{c^2} \left(\frac{\pi e^2}{mc} f_e \right) q' \tag{21}$$

It may be noted that the foregoing oscillator distribution factors have the same purpose as the averaged ϕ functions used by Keck et al [4] Both give the spectral shape of the band The band head discontinuities are obliterated in the q factors, since these are obtained by Meyerott's scheme of averaging, which ignores the rotational structure These discontinuities appear sharply in models where rotational structure is included, as it can be in Keck's ϕ function or in the model used by Breene and Nardone [5] However, at the high temperatures where radiation becomes important, the neglected broadening effects often smear out the structure, and the simpler averaging procedure used to obtain q is judged to be adequate for many engineering purposes

Radiative Transfer in Nonequilibrium Gas

The solutions to radiative transfer in a nonequilibrium gas can be worked out in a manner almost exactly analogous to the equilibrium gas solutions[8] if the parameters involved are defined properly With scattering neglected, the equation of transfer for a steady-state medium can be written:

$$\frac{dI_\nu}{ds} = \frac{Ah\nu}{4\pi} N'q' - \frac{Bh\nu}{4\pi} I_\nu N q + \frac{B'h\nu}{4\pi} I_\nu N' q' \tag{22}$$

where ds is the element of path length through the gas The last term on the right side of Eq (22) accounts for the downward transitions induced by the radiation of intensity I_ν This must be included as well as the spontaneous transition rate given by the first term on the right side of Eq (22) The factor B' is the Einstein probability coefficient for these induced emissions Like the other Einstein coefficients, it is a property of the molecule or atom independent of the state of the gas Thus its value can be determined from a relation that must obtain in an equilibrium gas; namely, the ratio of induced emission to absorption probability is proportional to the ratio of lower- to upper-state degeneracy[8]:

$$B'/B = g/g' \tag{23}$$

Then the equation of transfer becomes

$$\frac{dI_\nu}{ds} = \frac{Bh\nu}{4\pi} Nq \left[\frac{A}{B} \frac{N'}{N} \frac{q'}{q} - \left(1 - \frac{N'}{N} \frac{g}{g'} \frac{q'}{q} \right) I_\nu \right] \tag{24}$$

If an electronic temperature T_e is defined such that

$$N'g/Ng' = e^{-h\nu/kT} \tag{25}$$

and if this, together with the definition of α [Eq (7)] is substituted in Eq (24), there results

$$\frac{dI_\nu}{ds} = N\alpha_\nu \left[\frac{2h\nu^3}{c^2} \frac{q'}{q} e^{-h\nu/kT} - \left(1 - \frac{q'}{q} e^{-h\nu/kT_e} \right) I_\nu \right] \tag{26}$$

Furthermore, if the electronic temperature T_e is used to define a Planck-like function J_ν,

$$J_\nu = \frac{2h\nu^3}{c^2} \frac{q'}{q} e^{-h\nu/kT} \left(1 - \frac{q'}{q} e^{-h\nu/kT_e} \right)^{-1} \tag{27}$$

Then the transfer equation may be written as

$$\frac{dI_\nu}{ds} = N\alpha_\nu \left(1 - \frac{q'}{q} e^{-h\nu/kT} \right) (J_\nu - I_\nu) \tag{28}$$

It may be noted that, as defined, the function J_ν could be negative at frequencies where $(q'/q) \exp(-h\nu/kT_e)$ is greater than unity At these same frequencies the effective absorption coefficient $N\alpha_\nu[1 - (q'/q) \exp(-h\nu/kT_e)]$ would also be negative, so that both sides of the radiative transfer equation, Eq (28), are positive The physical meaning of the negative absorption coefficient is that the radiation of intensity I_ν induces more transitions in emission than in absorption This can happen, of course, only when the relative population of excited states is large, corresponding to a large electron temperature T_e, so as to take advantage of the situation where q' is greater than q As will be seen later, this occurs only in one of the wings of the band and not near the peak intensity

At equilibrium, the upper states are populated to an appreciable extent only when the temperature is the order of $h\nu/k$ This is generally much larger than the characteristic vibrational temperature $h\omega/k$, and in this case the population of vibrational states is approximately uniform [see Eq (6)]:

$$N_v/N \xrightarrow[T \to \infty]{} hw/kT \ll 1 \tag{29}$$

Moreover, to the order of approximation that the partition functions are separable, the vibrational frequencies of the

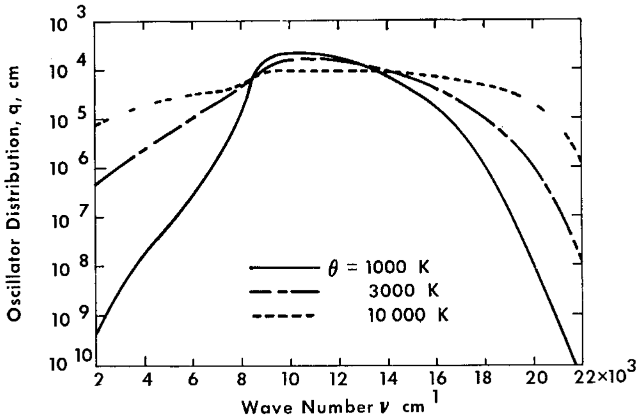

Fig 1a N₂ first-positive band absorption

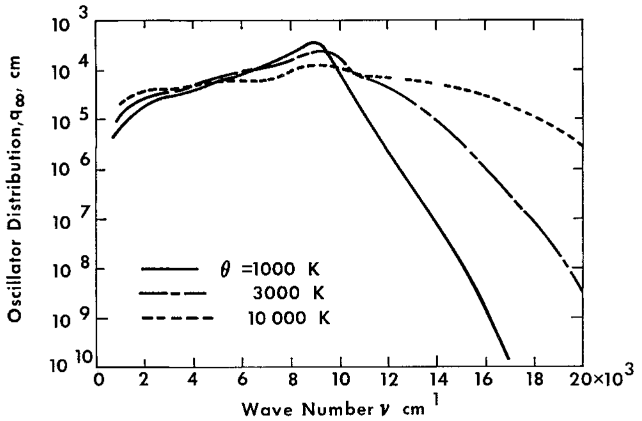

Fig 1b N₂ first-positive band emission

upper and lower states are equal Then the oscillator-strength spectral-distribution functions q and q' are equal, J_ν reduces to the blackbody intensity-distribution function, and the effective absorption coefficient is just the value for a gas in local thermodynamic equilibrium, as given by Chandrasekhar[8]

The solution to Eq (28) is

$$I_\nu = \int_0^{\tau_m} J_\nu e^{-\tau} d\tau \tag{30}$$

where τ is the integrated absorption path length

$$\tau(x,y,z) = \int_0^{x\,y\,z} N\alpha_\nu \left(1 - \frac{q'}{q} e^{-h\nu/kT}\right) ds \tag{31}$$

The upper limit of the integral in Eq (30), τ_m, is just the value of τ at the gas boundary This would, of course, be infinity in a gas of infinite extent The physical meaning of Eq (30) is that the intensity at a given point in the gas and in a given direction is the sum of emission from all volume elements, less the absorption suffered, up to the point considered

For the special case where the medium has constant properties, J_ν is a constant, and the solution for I_ν at a distance s from the gas boundary is

$$I_\nu = J_\nu(1 - e^{-\tau_m}) \tag{32}$$

$$\tau_m = N\alpha_\nu \left(1 - \frac{q'}{q} e^{-h\ /kT}\right) s \tag{33}$$

When the gas density N, or the absorption coefficient α_ν, or the path length s is very small so that $\tau_m \ll 1$, then

$$I_\nu \simeq \tau_m J_\nu \tag{34}$$

Table 1 Spectroscopic constants for air molecules

Band	Lower state	Upper state
N_2 first positive	$A^3\Sigma_u{}^+$	$B^3\Pi_g$
f_e = 0 0028	$v_{\max}$ = 16	$v_{\max}{}'$ = 21
ν_e	50206 0	59626 3
ω_e	1460 37	1734 11
$\omega\, x_e$	13 891	14 47
$\omega\, y$	−0 025	0
N_2 second positive	$B^3\Pi_g$	$C^3\Pi_u$
f = 0 07	$v_{\max}$ = 21	$v_{\max}{}'$ = 4
ν_e	59626 3	89147 3
ω_e	1734 11	2035 1
$\omega\, x_e$	14 47	17 08
$\omega\, y_e$	0	−2 15
$N_2{}^+$ first negative	$X^2\Sigma_g{}^+$	$B^2\Sigma_u{}^+$
f = 0 20	$v_{\max}$ = 21	$v_{\max}{}'$ = 29
ν_e	0	25461 5
ω	2207 19	2419 84
$\omega\, x$	16 136	23 19
$\omega\, y$	−0 0400	−0 5375

Multicomponent Gases with Overlapping Bands

In the general case, there will be overlapping band systems and continua that may arise from different species in the gas, each of which may be populated according to a different characteristic electronic temperature For this general case, Eq (22) may be written

$$\frac{dI}{ds} = \frac{h\nu}{4\pi} \sum_i (A_i N_i' q_i' - IB_i N_i q_i + IB_i' N_i' q_i') \tag{35}$$

where the summation is over all i components in the gas If an absorption coefficient for the ith component is defined by

$$\alpha_i = (h\nu/4\pi) B_i q_i \tag{36}$$

and again the population numbers define effective electronic temperatures T_i and Planck-like functions J_i,

$$N_i'/N_i = (g_i'/g_i) e^{-h\nu/kT_i} \tag{37}$$

$$J_i = \frac{2h\nu^3}{c^2} \frac{q_i'}{q_i} e^{-h\ /kT_i} \left(1 - \frac{q_i'}{q_i} e^{-h\nu/kT_i}\right)^{-1} \tag{38}$$

then the radiative transfer equation (35) may be expressed as

$$\frac{dI}{ds} = \sum_i N_i \alpha_i \left(1 - \frac{q_i'}{q_i} e^{-h\nu/kT_i}\right)(J_i - I) \tag{39}$$

The solution for this differential equation is

$$I = \int_0^{\tau_m} \bar{J} e^{-\tau}\, d\tau \tag{40}$$

where the absorption path length τ is now the summation

$$\tau = \sum_i \int_0^{x\,y\,z} N_i \alpha_i \left(1 - \frac{q_i'}{q_i} e^{-h\nu/kT_i}\right) ds \tag{41}$$

and the value of $\bar{J}$ is an averaged Planck-like function given by

$$\bar{J} = \frac{\sum_i N_i \alpha_i \left(1 - \frac{q_i'}{q_i} e^{-h\nu/kT_i}\right) J_i}{\sum_i N_i \alpha_i \left(1 - \frac{q_i'}{q_i} e^{-h\nu/kT_i}\right)} \tag{42}$$

It can be seen from the equations in the preceding sections that once the population numbers N_i and N_i' are determined for a nonequilibrium gas, the radiation intensity can be expressed as functions of the factors q_i and q_i', which are dependent on vibrational temperatures only Note that, in the general case, each species may have its own vibrational temperature The calculated values of these oscillator distribution functions are given in the next section for some of the important band systems in nitrogen

Oscillator Distribution Functions for Nitrogen

The strong bands in high temperature nitrogen are the N_2 first- and second-positive bands and the N_2^+ first-negative band The Franck-Condon factors for these bands have been computed by Nicholls[12] from vibrational wave-function solutions to the Morse potential The energy levels of the electronic-vibrational states were calculated from

$$E = \nu + \omega (v + \tfrac{1}{2}) - \omega x (v + \tfrac{1}{2})^2 + \omega y (v + \tfrac{1}{2})^3 \quad (43)$$

where the spectroscopic constants ν , ω_e, ωx_e, and ωy are taken from Herzberg[13] and are in wave-number units of cm^{-1} These are summarized in Table 1 for the three bands considered here Also shown are the estimates of the electronic oscillator strength f taken from Meyerott,[3] except for the N_2 first-positive band where the f number is that reported by Wurster [14]

The energy differences for the transitions were grouped in class intervals of 2000 cm^{-1} The Franck-Condon factors were then multiplied by the vibrational population numbers for vibrational temperatures equal to 1000°, 3000°, and 10,000°K These were then summed for the class interval and divided by 2000 to give the average oscillator distribution per unit wave number The results of these calculations are plotted in Figs 1, 2, and 3, where q is now given in units of centimeters rather than seconds Figure 1 gives the oscillator-strength distribution as a function of wave number for the N_2 first-positive band, Fig 2 for the N_2 second-positive band, and Fig 3 for the N_2^+ first-negative band Tabulated numerical results of these calculations are available in Ref 15

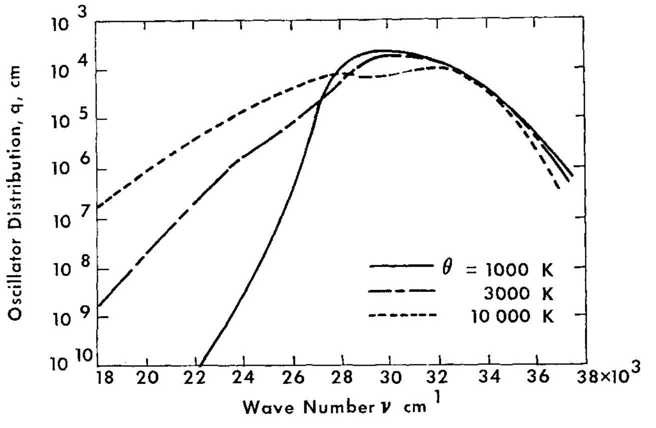

Fig 2a N_2 second-positive band absorption

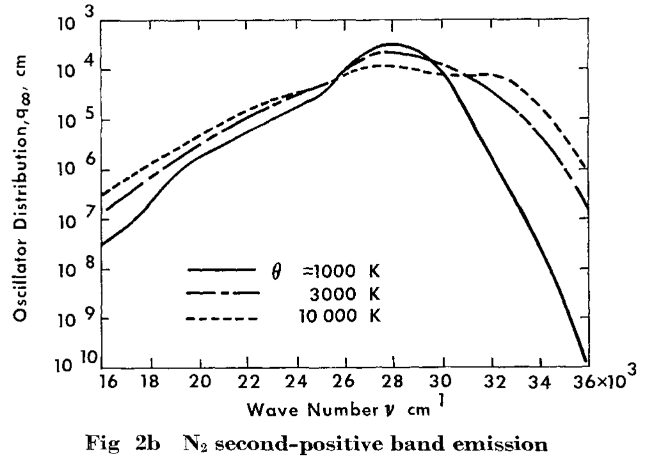

Fig 2b N_2 second-positive band emission

Because of the sum rules,

$$\sum_v \frac{N}{N} = \sum_{v'} \frac{N_v}{N'} = \sum_v q_v = \sum_{v'} q = 1 \quad (44)$$

the integration of the oscillator distribution curves must total unity:

$$\int q d\nu = 1 \quad (45)$$

Equation (45) is approximately satisfied in each case except for the N_2 second-positive band at Θ = 10,000°K, where the integration totals about 0 7 This means that the Franck-Condon array used has not been quite extensive

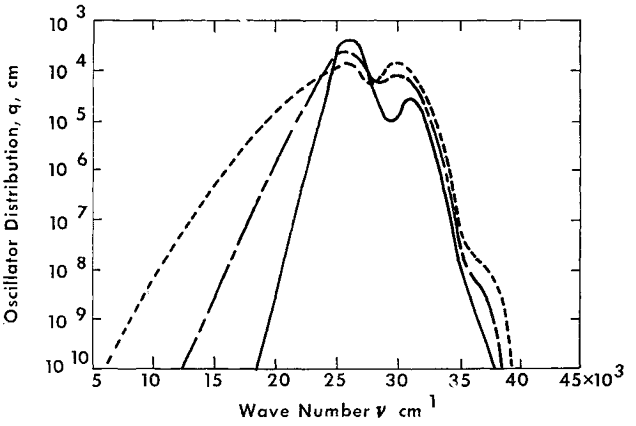

Fig 3a N_2^+ first-negative band absorption

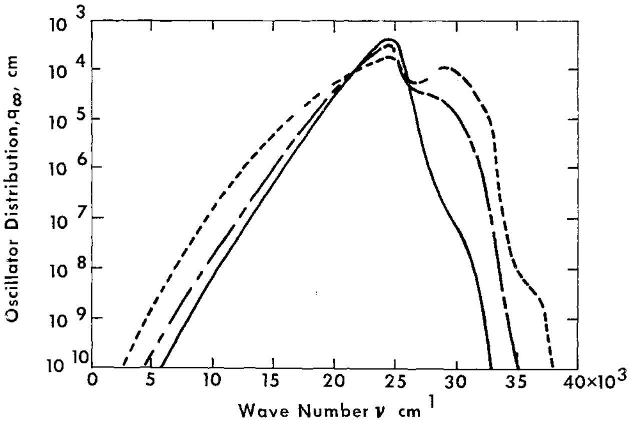

Fig 3b N_2^+ first-negative band emission for high-density gas

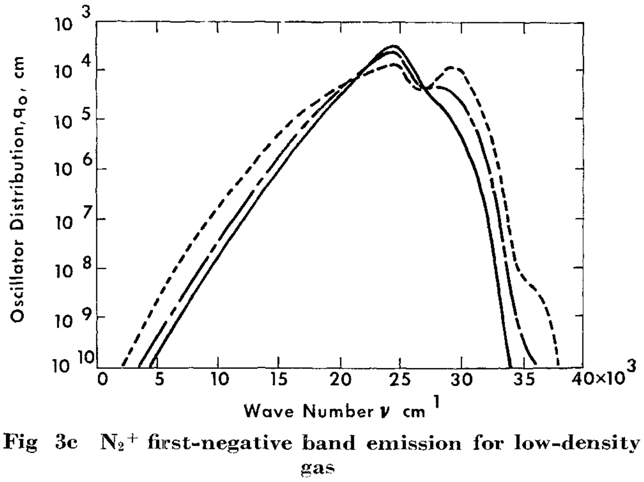

Fig 3c N_2^+ first-negative band emission for low-density gas enough to give all the strong transitions when higher vibrational quantum numbers are excited, or that some of the strong transitions from upper vibrational levels may lie in the continuum region Thus there is need for a calculation of these continuum oscillator-strength distributions

The oscillator distribution functions plotted in Figs 1–3 are the profiles of relative intensity across the band At low vibrational temperatures, where only low quantum states occur, the band is relatively compact As vibrational temperatures and the population of upper vibrational states increase, the radiation spreads across a wider band with some loss of intensity near the maximum

The maximum transition probabilities lie along a parabolic-like contour in a $v - v'$ plot,[11] so that transitions from low vibrational quantum numbers in the ground state tend to occur to somewhat higher quantum numbers in the excited state On the other hand, spontaneous transitions occur most frequently from low quantum levels in the excited state to higher quantum levels in the ground state As a result, the absorption profiles are weighted toward higher frequencies relative to the 0-0 transition It is in the low-frequency wing that the ratio q'/q is larger than unity, and the possibility of a negative absorption coefficient exists

The low-density limit for an emission oscillator distribution function, Eq (19), is illustrated by the calculations for the N_2^+ band given in Fig 3c The N_2 bands represent a special case inasmuch as the ground state is not involved in the transitions, and the populations produced in the excited states at very low density are difficult to estimate However, for the N_2^+ band, the low-density oscillator distribution is similar in appearance to the high-density limit (Fig 3b) This suggests that the approximations involved in compounding the two distributions, as in Eq (20), may not be too serious The principal difference between the two limiting profiles is that the low-density profile is weighted more in the high-frequency wing of the band at low vibrational temperatures This occurs because high vibrational quantum numbers are produced relatively more frequently by the excitation processes than when the molecules are in a low-temperature Boltzmann distribution

Concluding Remarks

In conclusion, it has been shown that solutions to the radiative transfer equation for a steady-state, nonequilibrium gas can be expressed in a form paralleling the usual equilibrium solutions In these nonequilibrium solutions, the population of excited electronic states is used to define an effective electron temperature, and the populations of vibrational states are used to weight the Franck-Condon factors to give the distribution of oscillator strength across the spectrum These distribution functions are designated by q and q' for the absorption and emission process, respectively; and they are functions of vibrational temperature only, to a first approximation The solutions for intensity are then given in terms of an effective absorption coefficient allowing for radiation-induced emission, and of a Planck-like energy distribution This absorption coefficient and the Planck-like distribution are both functions of the electron temperature and the factors q and q'

The oscillator distribution functions have been calculated for the strong molecular bands in nitrogen: the N_2 first- and second-positive and the N_2^+ first-negative These are presented for vibrational temperatures of 1000°, 3000°, and 10,000°K

It would be of value to determine the distribution functions q and q' for other strong bands that occur in air, such as the O_2 Schumann-Runge and the NO β and γ bands The Franck-Condon arrays for these bands have been calculated,[16, 17] but there is also a strong continuum that needs to be included Consequently, the calculation of these functions is deferred until values of the continuum oscillator strengths are available The presence of a strong continuum indicates also a strong coupling between vibrational and electronic states, so for such cases it will be desirable to include a correction for variation in the electronic oscillator strength across the band In addition, the population numbers would be more accurately given if based on the actual partition function for the anharmonic molecule, rather than on the harmonic oscillator approximation

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