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Final Contractors Report

Radiative Coupled Nonequilibrium Flow Fields

Associated with Aeroassisted Orbital Transfer

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July 1984 - March 1986

ABSTRACT

The study outlines a procedure for adapting existing hyper-
sonic flow field programs to nonequilibrium conditions. The
procedure treats bound-bound transitions between electronic
levels in molecular species in which electron impact is
considered to be the dominant excitation mechanism. The
formulation of expressions for excited state population and the
radiative transfer equation are presented. The formulation
indicates how for nonequilibrium of the radiative transfer
equation can be written in terms of spectral source functions
and absorption coefficients so that existing programs for
radiative properties can be used as well as existing radiative
transfer solution programs.

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NOMENCLATURE

A_{21}	—Einstein coefficient for spontaneous emission $2 \to 1$
B_{21}	—Einstein coefficient for stimulated emission $2 \to 1$
B_{12}	—Einstein coefficient for stimulated absorption $1 \to 2$
$B_\nu(T)$	—Planck function at frequency ν and temperature T
c	—velocity of light
f_i	—fraction of the particles in an electronic state which are in the i'th vibrational state
g_i	—statistical weight factor of state i'th
h	—Planck constant
I_ν	—specific intensity at frequency ν
J_ν	—mean intensity at ν specific intensity averaged over direction
k	—Boltzmann constant
N_1	—concentration of particles in lower electronic state – number/unit volume
N_2	—concentration of particles in upper electronic state – number/unit volume
N_e	—concentration of electrons – number/unit volume
$Q_2(T)$	—vibrational partition function for the upper electronic state evaluated at temperature T
$Q_1(T)$	—vibrational partition function for the lower electronic state evaluated at temperature T
$q_{v'v''}$	—Franck-Condon factor for a transition between the v'' vibrational level of the lower electronic state and the v' vibrational level of the upper electronic state
S_ν	—Source function at frequency ν

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T_e	—translational temperature of free electrons
T_{E1}	—Boltzmann temperature of the lower electronic state
T_{E2}	—Boltzmann temperature of the upper electronic state
T_{v1}	—Boltzmann vibrational temperature of the lower electronic state
T_{v2}	—Boltzmann vibrational temperature of the upper electronic state
v'	—vibrational quantum number of the upper electronic state
v''	—vibrational quantum number of the lower electronic state
z	—depth coordinate
$\epsilon_{v'}$	—energy of the v' vibrational state relative to $v' = 0$
$\epsilon_{v''}$	—energy of the v'' vibrational state relative to $v'' = 0$
ϵ_2	—energy level of the upper electronic state $v' = 0$
ϵ_1	—energy level of the lower electronic state $v'' = 0$
ϵ_{12}	—energy difference between electronic states ($\epsilon_2 - \epsilon_1$)
μ	—cosine of polar angle between intensity and depth coordinate
μ_ν	—absorption coefficient per unit depth at frequency ν
ν	—frequency
τ_ν	—optical thickness at frequency ν
Φ_1	—normalized line shape profile for lower electronic state
Φ_2	—normalized line shape profile for upper electronic state
Ω_{12}	—collisional excitation rate $1 \rightarrow 2$
Ω_{21}	—collisional quenching rate $2 \rightarrow 1$
$(\ )^i$	—identifies an i'th electronic transition and/or specie

INTRODUCTION

Nonequilibrium occurs in a gas when an imbalance in excitation and quenching (de-excitation) processes results in state populations which deviate from the Boltzmann distribution characterized by the gas temperature. In the general case, the excitation and quenching processes include both kinetic (collisional) and radiative processes. For the molecular species, the subject of this study, each state is specified by a rotational quantum number, a vibrational quantum number, and the electronic level. Under the most sever nonequilibrium condition, each state is characterized by a different temperature which is not the translational temperature of the gas; in fact, the translational temperatures of the species are not necessarily equal.

A severe perturbation of atmospheric gases by an entry shock results in a nonequilibrium layer of gas adjacent to the shock. In this nonequilibrium layer, the rapid rise in random translational energy of the post-shock gas is re-distributed by kinetic processes into the internal states of the gas (rotational, vibrational, electronic, chemical change, and ionization).

The combination of hypersonic entry velocities with the low densities encountered in upper atmospheric entry produces a shock-layer characterized by high temperatures and low collision rates. For these conditions, the nonequilibrium region is extensive and the prediction of radiative transfer from this region is essential in prediction of the instantaneous heating from the shock-layer.

Nonequilibrium radiative heating is encountered by every body during the early portions of entry. During this portion of the trajectory, radiative heating of the body poses a more severe and uncertain problem

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than conventional equilibrium heating estimates would indicate. The problem was studied in the Apollo program. For Apollo, the nonequilibrium heating did not pose a severe problem in total system thermal management as Apollo plunged quickly through those conditions for which nonequilibrium dominates. A re-examination of the early flight and laboratory data has been presented by Sutton [1].

To date, the hypersonic shock layer heating has been handled by using either a chemical equilibrium or a chemical nonequilibrium flow field analysis to describe the spatial distribution of radiating species. An example of such a program (NEQ-VIS) is the viscous-shock-layer program of Moss [2] which has been extended for use in chemical nonequilibrium flow field analysis [3]. These applications are for conditions in which the collision rates are sufficiently high to assure kinetic equilibrium of the internal states to a common temperature and to assure kinetic rates exceed those of the radiative processes. For these conditions, the prediction of radiative transfer through the shock-layer follows the same procedure whether chemical nonequilibrium or equilibrium is considered, and programs such as Nicolet's (RAD) [4] can be used with the spatial distribution of temperature and radiating specie from the flow field programs.

Systems of current interest [5], Orbital Transfer Vehicles (OTV) or (AOTV), are proposed to operate in an entry-exit maneuver - "skipping" through the rarefied upper atmosphere. As a result, an OTV would dwell for a significant portion of its entry-exit trajectory in conditions for which nonequilibrium dominates [6]. As an example, consider an OTV entry of 10 to 11 km/sec which attains a minimum altitude of 80 km. For these conditions, the number density in the shock layer will be of the order of

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10^{15} particles/cm^3 (number density at STP is 10^{19} particles/cm^3) and the collision frequency would be 10^5 collisions/sec. Clearly, the collision quenching rate can be no larger than this; however, the radiative quenching rate can be several orders of magnitude larger. Thus, both radiative and kinetic rates govern state populations and nonequilibrium predictions of state populations are required.

The situation where kinetic rates are dominant but do not balance can be termed kinetic nonequilibrium. For such situations, one solves the kinetic rate equations to determine state populations. With the populations, one can solve the radiative transfer problem using procedures similar to those for the equilibrium. By contrast, those situations associate with OTV's in which radiative rates are significant the radiative terms must be considered in the rate equations.

To answer the question of the importance of nonequilibrium radiative transfer, one should solve the system of coupled rate equations for the state populations together with momentum, energy and radiative transfer equations for the complex shock-layer geometry of the OTV. This is a formidable problem. One approach, taken by Park [7], is to meticulously assess the rate processes in the context of a simplified flow field geometry.

Below, we approach the problem with the question: Can programs under development or existing programs similar to NEQ-VIZ and RAD be modified to solve the OTV problem to conserve the considerable effort required in code of development? The logic behind the question is that the form of the continuum conservation equation for mass, momentum and energy and their boundary conditions are the same regardless of the state of nonequilibrium. The treatment of chemical rate processes would seem

extendible to kinetic rate processes. Similarly, if the nonequilibrium radiative transfer problem can be stated in terms of spectral absorption coefficients and source functions, then the spectral and spatial integration procedure of existing computer codes can be used.

To explore the limitations associated with this approach, the character of a generic flow-field and radiative codes, will be briefly reviewed in the next section. A simple two level system is used to illustrate the conditions of nonequilibrium for the state population rate equation and the radiative transfer equation and to examine simplifications. The simplifications are then incorporated into general multi-state rate and radiative transfer equations. The result of this study is a procedure which enables one to modify existing codes for application to the nonequilibrium shock-layer of OTV's.

REVIEW OF CODES

The computational problem involving an entry shock-layer can be viewed in three, not necessarily equal parts:

Part (1) Satisfying conservation equations, boundary conditions and chemistry

Part (2) Computation of state populations for radiative properties

Part (3) Satisfy the radiative transfer equation

Usually, these parts are considered sequential; however, with radiative terms coupling all three together, a sequential solution must be considered as iterative.

The governing equations for the continuum regime of an OTV trajectory have been reviewed recently be Lee [8]. Comparing these equations, using order of magnitude arguments, with those incorporated into a program such as NEQ-VIS, one finds the governing equations satisfied to better than first order. This is not a surprise as the form of the conservation of mass, momentum and energy equations are basically the same, equilibrium or nonequilibrium. Certainly, kinetic nonequilibrium perturbs gas properties such as viscosity, conductivity, and specific heat; and these can be corrected, if one desires, in iterative cycles.

More important are three aspects of Part (1) which are not incorporated into the generic flow-field codes with nonequilibrium chemistry. These are:

(1) Computation of the translational temperature, T_e, for the electrons

(2) Computation of the vibrational temperatures, T_v, for the electronic states

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(3) Proper use of heavy particle translation temperature T, electron temperature T_e, and vibrational temperature T_v in the evaluation of the chemistry rate constants.

These three aspects can best be handled by the addition of the energy equation for electrons and rate equations for the vibrational states to the set of simultaneous equations treated by the program which handles Part (1). Adequate treatment of T_e in NEQ-VIS has been reported by Shinn [9]. The importance of incorporating vibrational temperatures is at this point, arguable. It can be done; however, in some of Park's work, arguments have been presented for T_e to T_v equilibrium. The proper use of T, T_v and T_e in the evaluation of chemical rate constants has been treated recently by Park [10]. Thus, Part (1) can be handled by existing programs with:

(1) the addition of an energy equation for electrons

(2) proper use of T_e, T and T_v in rate constant evaluations

(3) proper evaluation of radiative contribution in the energy equation

Part (1) will supply a flow field map of T_e, T, chemical specie concentration, and T_v's.

The Part (2) computation of state populations is treated in a later section of this study. At this point, we should note that for the temperature and the level of ionization expected, the primary excitation mechanism will be from the ground electronic state and due to electron impact excitation. Due to their high speed, electrons are likely to dominate heavy particles in excitation. The excitations of rotational and vibrational states are sufficient fast to assure a Boltzmann distribution for each rotational and vibrational system. However, the

Boltzmann vibrational temperature for each electronic state may be different. Essentially, Part (2) converts the spatial distribution of T_e, chemical specie number density, and N_e into a spatial distribution of electronic state populations fractions or temperatures. In conclusion, recall that the stimulated emission and absorption processes result in a coupling of Part (2) to the solution for Part (3) and that for the assumption of an optically thin gas these stimulated terms are neglected.

For Part (3), codes such as RAD handle radiative transfer as two problems. One consists of computing the optical properties (absorption coefficients and source functions) for every spatial point based upon the temperature and number density field supplied. The second problem involves the integration of the radiative transfer equation to achieve +he spatial and spectral values of the radiative intensity or of the integrals of the intensity. From these quantities, radiative heating of the OTV can be determined as well as the radiative coupling terms which should be used for the next iteration through Parts (1) and (2).

The procedure for solving the radiative transfer equation and determining heating rates is independent of nonequilibrium considerations providing the radiative transfer equation for nonequilibrium can be written in the standard form involving a spectral absorption coefficient and source function. The problem posed by the standard form of the radiative transfer equation is not so much in the absorption coefficient as in the source function. It is clear that each absorption coefficient will contribute to the frequency interval associated with its electronic state and it is clear how to sum the absorption coefficients spectrally. What is not clear is: What does one replace the Planck source function with to achieve the classic form of the radiative transfer equation?

This source function and its logical development is treated in a later section devoted to the radiative transfer equation. It will be shown that taking simple combinations of absorption coefficients and Planck functions evaluated at the nonequilibrium state temperatures will enable the spectral and spatial solution procedure of the RAD code to operate as if solving an equilibrium problem with spatial variation of absorption coefficients and source function.

Returning to the former problem of optical properties, several approaches are available. First, a line by line computation has been used by several investigators. Such an approach requires a knowledge of the line broadening mechanisms to be used with an extensive data base and accounting procedures. Second, a JORL "just overlapping-rotational-line" band model [11] and [12] has been used extensively. This model portrays a simple variation in absorption coefficient within a vibrational band by summing over each rotational line which is assigned a line width conforming to the line spacing. A third procedure which is referred to as the "bandless model" or average absorption coefficient model considers the coefficient to be constant in and evaluated by averaging over a frequency interval $\Delta\nu$. In this way, sums over all rotational lines lead to expressions which are independent of rotational temperature and parameters. This procedure was used in the early work of Meyerott [13] with $\Delta\nu = 6000$ cm^{-1} and the frequently cited work of Biberman [14] with $\Delta\nu = 3000$ cm^{-1}. These frequency intervals would sum together several vibrational transitions. To be consistent with the average coefficient assumption the spectral variation should be portrayed as a series of steps; however, the variation of amplitude is frequently represented by a smooth curve with the amplitude associated with the center of the

frequency interval. This model and procedure are incorporated into RAD [4] and will be used in a later section in which the nonequilibrium radiative transfer equation is examined. The result of this examination indicates that the nonequilibrium optical properties can be computed to the same accuracy as equilibrium optical properties using the procedures of RAD providing the properties are evaluated at the proper nonequilibrium temperatures supplied by Part (2). Thus, the use of proper sums and temperatures allows RAD to be used without major modifications.

TWO-LEVEL ILLUSTRATION

A two-level system similar to that used in an earlier investigation [15], provides a simple illustration of the problem of predicting state populations for nonequilibrium and for observing the consequences of these populations on the radiative transfer problem. This will allow critical points to be observed uncluttered by the complex notation inherent in a multi-level system. Later sections will apply the findings of this section to more complex multi-level systems.

For a radiating specie possessing two nondegenerate states between which both radiative and kinetic transitions occur, the rate equation and the radiative transfer equation take the form:

$$\frac{DN_2}{Dt} = -N_2(A_{21} + B_{21}\bar{J} + N\,\Omega_{21}^{(h)} + N_e\Omega_{21}^{(e)}) \qquad (1)$$

$$+ N_1(B_{12}\bar{J} + N\,\Omega_{12}^{(h)} + N_e\Omega_{12}^{(e)})$$

$$\mu\frac{dI_\nu}{dz} = -(h\nu\Phi_\nu/4\pi)\,[N_1 B_{12}I_\nu - N_2(A_{21} + B_{21}I_\nu)] \qquad (2)$$

The terms of the RHS of Eq. (1) are the rate of quenching of the population N_2 of the upper state and the rate of excitation from N_1 the lower state. The quenching processes are spontaneous emission, stimulated emission, collisional de-excitation by heavy particles, and collisional de-excitation by electrons. The excitation processes are stimulated absorption, excitation by heavy particles, and excitation by electrons. The differentiation is the material derivative associated with the stream lines of the flow. The differentiation of Eq. (2) is along a ray path.

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Rearranging Eq. (2) yields the classical radiative transfer equation:

$$\mu \frac{dI_\nu}{dz} = (h\nu\Phi_\nu/4\pi) \; (N_1 B_{12} - N_2 B_{21}) \; [S_\nu - I_\nu] \qquad (2b)$$

where the source function

$$S_\nu = N_2 A_{21}/(N_1 B_{12} - N_2 B_{21}) = (2h\nu^3/c^2)/[(N_1/N_2)-1]$$

using $B_{12} = B_{21}$ and $A_{21}/B_{21} = 2h\nu^3/c^2$, and one recognizes the

absorption coefficient as:

$$\mu'_\nu = (h\nu\Phi_\nu/4\pi) \; [(N_1 B_{12}(1 - N_2/N_1)]$$

Now for many applications the optically thin assumption is used.
This is based upon the assumption that the optical depth τ_ν is small.
For a uniform gas, the optical depth is proportional to the produce of
the absorption coefficient and the ray path length. Recall that the
absorption coefficient is inversely proportional to the photon mean free
path. Thus, large mean free paths compared to the characteristic ray
path dimensions implies small optical depths and photons escape the
emitting volume without participation in the stimulated absorption or
emission processes.

For the optically thin assumption, Eq. (2b) is conventionally written
as:

$$\mu \frac{dI_\nu}{dz} = \mu'_\nu \; S_\nu \qquad (3)$$

implying that the stimulated absorption and emission processes are negligible. Reconsidering the definition of the absorption coefficient and source function yields a more useful form of Eq. (3) for the optically thin gas.

$$\mu \frac{dI_\nu}{dz} = h\nu\Phi_\nu A_{21}N_2/4\pi \qquad (3b)$$

The quantity $h\nu A_{21}N_2$ is the radiative power emitted per unit volume and will be noted by Q/v.

Returning to Eq. (1) for the population of the upper state N_2 and seeking the steady state population i.e., the maximum population to which the process relaxes, we have set Eq. (1) equal to 0 to achieve the steady state result.

$$\frac{N_2}{N_1} = \frac{N_e\Omega_{12}^{(e)} + B_{12}\bar{J}(1 - N_2/N_1)}{N_e\Omega_{21}^{(e)} + A_{21}} \qquad (4)$$

where we have neglected the heavy particle collision terms based upon the argument that the columbic interaction by the electrons results in cross sections larger than heavy particle cross sections by an order of magnitude, that the speed of the electrons is over 250 times those of the heavy particles and that for a degree of ionization of 1% or more, the electron impact process exceeds the heavy particle process by more than an order of magnitude. Clearly, the heavy particle kinetics could have been retained; however, we would require the rate constants for them.

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Now, if the numerator and denominator of Eq. (4) were divided by A_{21} we would find the term $[J\,B_{12}\,(1 - N_2/N_1)/A_{21}]$ to be of the order of the terms which were considered negligible in the optically thin approximation. Thus, we shall neglect these stimulated processes and re-write Eq. (4) as:

$$\frac{N_2}{N_1} = \frac{\left[\dfrac{\Omega_{12}N_e}{A_{21}}\right]\left[\dfrac{\Omega_{12}}{\Omega_{21}}\right]}{\left[\dfrac{\Omega_{12}}{\Omega_{21}}\right] + \left[\dfrac{\Omega_{12}N_e}{A_{21}}\right]} \tag{5}$$

$$= \frac{(\Omega_{12}N_e/A_{21})}{1 + (\Omega_{21}N_e/A_{21})}$$

Both Ω_{12} and Ω_{21} are functions of the temperature of the electrons and by the usual kinetic arguments relating forward and reverse rates:

$$\Omega_{12}/\Omega_{21} = (N_2/N_1)_{eq} = \exp\,(-\epsilon_{12}/kT_e) \tag{6}$$

Before examining Eq. (5) further, let us compare Eqs. (4) and (5) and ask the question: how does neglecting the stimulated absorption and emission terms influence the state population? Clearly, the dominant absorption process is an excitation mechanism which tends to increase the upper state population and so estimates in which these stimulated absorption terms are neglected, such as Eq. (5), will tend to under predict the excited state population.

Returning to Eq. (5), notice that $(\Omega_{12}N_e/A_{21})$ is the ratio of the

rate of kinetic quenching to the rate of radiative quenching and that at large electron concentrations, kinetic quenching will dominate and at low electron concentrations, radiative quenching will dominate.

For large electron concentrations, i.e., $N_e \gg (A_{21}/\Omega_{21})$ Eq. (5) reduces to:

$$N_2/N_1 = \frac{(\Omega_{12}N_e/A_{21})}{(\Omega_{21}N_e/A_{21})} = \frac{\Omega_{12}}{\Omega_{21}} = \exp\ (-\epsilon_{12}/kT_e) \qquad (7)$$
$$= (N_2/N_1)_{eq}$$

using Eq. (6). This is the equilibrium solution which is maintained in equilibrium with the electrons by balancing of kinetic excitation and kinetic quenching.

As the electron concentration is reduced, the kinetic quenching rate is reduced until it is below the radiative quenching rate. Thus, for $N_e \ll A_{21}/\Omega_{21}$ Eq. (5) reduces to:

$$N_2/N_1 = \Omega_{12}N_e/A_{21} \qquad (8)$$

where excitation by electron collision is balanced by radiative quenching. This solution is frequently referred to as "collision limiting."

Clearly for any prediction, Eq. (5) would be used with Eq. (6). However, it is useful to keep these two limiting solutions in mind. To achieve some understanding of the magnitudes involved in these two limits consider the conditions for $\Omega_{21}(N_e)^*/A_{21} = 1$

$$(N_e)^* = A_{21}/\Omega_{21} = (A_{21}/\Omega_{12})\ (\Omega_{12}/\Omega_{21}) \tag{9}$$

In Figure 1, the radiative lifetime and excitation rate data from [16] and [17] have been used to compute the "limiting electron concentration" $(N_e)^*$ for 4 band systems: the first-positive (1+), the second-positive (2+), and the Lyman-Birge-Hopfield (LBH) of Nitrogen and the Schumann-Runge (SR) of Oxygen. The radiative lifetime is that of the optical transition while the excitation is always the resonant transition from the ground state.
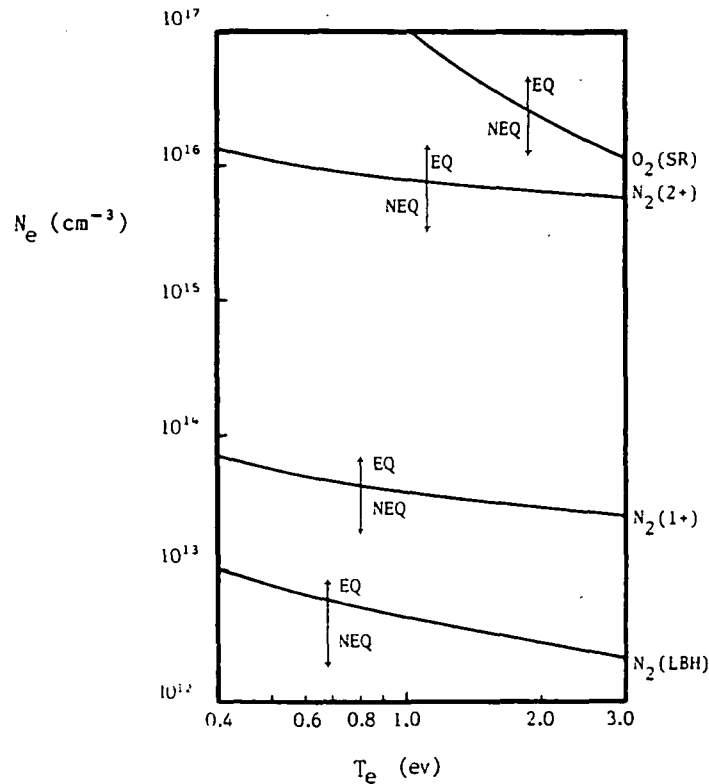
Figure 1. Nonequilibrium Criterion Curves. The curve for each specie-transition represents the "limiting electron concentration" for which population fractions of the upper electronic state of the transition is 1/2 the equilibrium value. Conditions above a curve approach equilibrium, while conditions below a curve indicate nonequilibrium.

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In interpreting Fig. 1 electron concentrations well above the $(N_e)^*$ curve assure equilibrium population fractions while electron concentrations well below the $(N_e)^*$ indicate collision limited nonequilibrium populations. Thus, for $N_e = 10^{15} cm^{-3}$ the (2+) and the (SR) are in nonequilibrium while the (1+) and the (LBH) are in equilibrium.

In Table 1, a comparison of the population fractions predicted by Eq. (5) is given for $N_2(1+)$ over a range of temperatures and at two electron concentrations.

TABLE 1

Population Fraction Prediction of Equation (5)
for the Upper STate of the $N_2(1+)$ Transition

T_e(ev)	$(N_2/N_1)_{eq}$	$\Omega_{12}N_e/A_{21}$		N_2/N_1	
		$N_e = 10^{15}$	$N_e = 10^{13}$	$N_e = 10^{15}$	$N_e = 10^{13}$
.4	2.1×10^{-8}	2.8×10^{-7}	2.8×10^{-9}	1.9×10^{-8}	2.5×10^{-9}
.5	8.3×10^{-7}	1.4×10^{-5}	1.4×10^{-7}	7.8×10^{-7}	1.2×10^{-7}
1.0	1.3×10^{-3}	3.5×10^{-2}	3.5×10^{-4}	1.2×10^{-3}	2.8×10^{-4}
2.0	5.1×10^{-2}	1.9	1.9×10^{-2}	4.9×10^{-2}	1.4×10^{-2}
3.0	1.7×10^{-1}	6.8	6.8×10^{-2}	1.7×10^{-1}	4.9×10^{-2}

In the second column above the equilibrium predictions of Eq. (7) are listed. Recall these are also the ratios of the collisional excitation and quenching. The third and fourth column list the collision limited

solution, Eq. (8), for the two electron concentrations considered. Note the ratio of the third or fourth columns to column two is the ratio of collision to radiative quenching which appears in the denominator of Eq. (5). An electron concentration of $10^{15} cm^{-3}$ is well above the $(N_e)*$ limit for $N_2(1+)$ and we find the population fraction from Eq. (5) in column 5 very close to the equilibrium value in column 2. By contrast, an electron concentration of $10^{13} cm^{-3}$ is below $(N_e)*$ for the $N_2(1+)$ and the predictions of Eq. (5) in column 6 are close to the collision limited solutions of Eq. (8) in column 4.

Notice that the collision limited population fraction "prediction" is not always below the equilibrium fraction; however, only those values below the equilibrium value are valid. Collision limited solutions are valid only for $N_e < (N_e)*$. Thus, if we make a computation of equilibrium and collision limited fractions, we may be assumed that the smaller fraction is the valid fraction and Eq. (5) would predict a fraction which is below the valid limit. Note that stimulated absorption and cascading from higher excited states could raise the fraction above the prediction of Eq. (5).

Now, using the optically thin form of the radiative transfer equation, consider the implications of Eq. (5). Combining the two equations yields:

$$Q/v = h\nu A_{21} N_2$$
$$= h\nu (\Omega_{12} N_e N_1)/[1+(\Omega_{21} N_e/A_{21})] \qquad (10)$$

For the equilibrium limit achieved with $N_e \gg (N_e)*$

$$(Q/v)_{eq} = h\nu A_{21} N_2 \qquad\qquad (11)$$

and for the collision limited with $N_e \ll (N_e)^*$

$$(Q/v)_{cl} = h\nu \Omega_{12} N_1 N_e \qquad\qquad (12)$$

The first expression applicable to equilibrium conditions indicates the emission from a unit volume is proportional to the number of emitters and is limited by the radiative decay rate. The collision limit indicates the emission from a unit volume is proportional to the excitation rate. Note also that the equilibrium emission scales linearly with density of the specie while the collision limit scales as the square of the density. When predicting Q/v, it is possible for the equilibrium prediction to exceed the collision limiting prediction as it is also possible for the reverse to occur. The valid Q/v is the lower of the two predictions. The cross over point for Q/v predictions is $(N_e)^*$.

As an illustration of the variation of Q/v with N_e, consider Table 2.

The first column indicates the band system. The electron temperature was fixed at 1ev and the specie ground state concentration was 10^{15} cm^{-3}. Column 2 indicates the equilibrium solution. Columns 3, 4, and 5 indicate the solution of Eq. (10). For the lowest N_e only the (LBH) band of nitrogen is close to equilibrium with the other transitions well below equilibrium. The $N_e = 10^{15}$ cm^{-3} indicates the (1+) joins the (LBH) in equilibrium. At the highest electron concentration considered $N_e = 10^{17}$ cm^{-3} all states are approaching equilibrium emission. Note the relation of these three N_e's to the $(N_e)^*$ for the bands of Figure (1).

In the above, we have used the optically thin assumption to effectively de-couple the population prediction from the radiative

transfer process while retaining the nonequilibrium character of the problem. In doing this, we may be under predicting state populations slightly.

Table 2
Prediction of Volumetric Emission at $T_e = 1ev$ and $N_1 = 10^{15} \, cm^{-3}$
by Equation (10) for Different Electron Concentrations

Transition		$Q/v \, watts/cm^{-3}$		
	Equilibrium	$N_e = 10^{13}$	$N_e = 10^{15}$	$N_e = 10^{17}$
$N_2(1+)$	0.39×10^{-2}	0.08×10^{-2}	0.37×10^{-2}	0.39×10^{-2}
$N_2(2+)$	0.37	0.11×10^{-2}	0.08	0.37
$N_2(LBH)$	0.31×10^{-2}	0.21×10^{-2}	0.3×10^{-2}	0.31×10^{-2}
$O_2(SR)$	260	0.02	2.8	130

Next, we shall consider how this simple model can be transferred into a simple expression for electronic state temperature while considering the vibrational and rotational states of a molecular sources.

POPULATION FRACTIONS FOR ELECTRONIC STATES

Applying the optically thin assumption and considering electron impact kinetics to dominate heavy particle kinetics, the expression determining the population, N_u, of the upper state, u, from the rate processes between states u and lower state ℓ, of a molecule is:

$$\frac{DN_u}{Dt} = \sum_\ell (\Omega_{\ell u} N_\ell N_e - \Omega_{u\ell} N_u N_e - A_{u\ell} N_u) \tag{13}$$

where $\Omega_{\ell u}$ and $\Omega_{u\ell}$ are the kinetic rate coefficients for excitation and de-excitation of state u by electron impact and $A_{u\ell}$ is the spontaneous emission coefficient between u and ℓ.

The total population N_2 of the upper electronic state which is designated by "2" is obtained by summing over all the upper states associated with the upper electronic level. So

$$\frac{DN_2}{Dt} = \sum_u \frac{DN_u}{Dt} = N_e \sum_u \sum_\ell \Omega_{\ell u} N_e - N_e \sum_u \sum_\ell \Omega_{u\ell} N_u - \sum_u \sum_\ell A_{u\ell} N_u \tag{14}$$

Considering that the upper state u is designated by the electronic state number 2 and the vibrational state number v' and that the lower state ℓ is designated by the electronic state number 1 and the vibrational state number v'', it is clear that the summations in Eq. (14) are over all the v'' and the v' associate with the (2,1) transition. Although the rotational structure of the states has not been considered, to be consistent with the bandless model used with the radiative transfer equation, the summation over rotational states would yield expressions identical to those below.

Now using the Boltzmann distribution for the fraction $f_{v'}$ of the population of an electronic state which is in the specific vibrational state v'

$$N_u/N_2 = f_{v'} = N_{2v'}/N_2 = \exp{(-\epsilon_{v'}/kT_{v2})}/Q_2(T_{v2}) \qquad (15a)$$

and $f_{v''}$ for the lower electronic state fraction

$$N_\ell/N_1 = f_{v''} = N_{1v''}/N_1 = \exp{(-\epsilon_{v''}/kT_{v1})}/Q_1(T_{v1}) \qquad (15b)$$

Where the Q's are the vibrational partition functions for the respective electronic states which are evaluated at the Boltzmann vibrational temperatures: T_{v2} for the upper electronic state and T_{v1} for the lower electronic state.

Recall that the spontaneous emission coefficient can be factored into an electronic transition probability A_{21} and a Franck-Condon factor $q_{v'v''}$, so that

$$A_{u\ell} = A_{21} \, q_{v'v''} \qquad (16)$$

Thus, using Eqs. (15) and (16), terms such as

$$\sum_u \sum_\ell A_{u\ell}N_u = A_{21}N_2 \sum_{v'} \sum_{v''} q_{v'v''} \, f_{v'} \qquad (17)$$

The sum of the Franck-Condon factors over any column or row is unity so

$$\sum_{v''} q_{v'v''} = 1$$

The sum of the vibrational state population fractions over all upper electronic state vibrational levels is also unity so the double sum on the right side of Eq. (17) is unity and the equation reduces to:

$$\sum_u \sum_\ell A_{u\ell} N_u = A_{21} N_2 \qquad (18)$$

Similar arguments can be used for the collisional rate coefficients so Eq. (14) can be re-written as:

$$\frac{DN_2}{Dt} = \Omega_{12} N_1 N_e - \Omega_{21} N_2 N_e - A_{21} N_2 \qquad (19)$$

Where N_1 and N_2 are the populations of the lower and upper electronic states and Ω_{12}, Ω_{21} and A_{21} are the collisional excitation rate coefficient, collisional quenching rate coefficient, and the radiative (spontaneous) quenching rate coefficient.

The steady state population ratio is achieved by setting Eq. (19) equal to zero so:

$$N_2/N_1 = \Omega_{12} N_e / (A_{21} + \Omega_{21} N_e) \qquad (20)$$

which is identical in form to the illustration in the previous section. The equation will be written as:

$$N_2/N_1 = (R_1 R_2)/(R_2 + R_1) \qquad (21)$$

where $\tau = A_{21}^{-1}$ is the radiative lifetime and $R_1 = \tau \Omega_{12} N_e$ and

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$$R_2 = (N_2/N_1)_{eq} = (g_2 Q_2 (T_{v2})/g_1 Q_1 (T_{v1})) \exp (-\epsilon_{12}/kT_e) = \Omega_{12}/\Omega_{21}$$

The quantity R_1 is ratio of collisional excitation to radiative quenching rates, the quantity R_2 is the ratio of upper to lower electronic state populations in equilibrium*, and the ratio R_1/R_2 is the ratio of collisional to radiative quenching rates.

Rather than an expression for populations such as Eq. (21), it is more useful in radiative transfer applications to express a population as an electronic state temperature, T_{E2}

$$T_{E2} = (\epsilon_{12}/k) \ln [(N_1/N_2) (Q_2/Q_1) (g_2/g_1)] \qquad (22)$$

Although developed for a resonant transition, i.e. 1 is the ground state and 2 is an excited state, radiative quenching to other excited states may be considered simply by substituting an appropriate radiative lifetime for τ in Eq. (21).

In closing, note the relationships between individual state rate constants and electronic state rate constants are:

$$\Omega_{u\ell} = \Omega_{21} q_{v'v''} f_{v'}$$

$$(23)$$

$$A_{u\ell} = q_{v'v''} f_{v'}/\tau$$

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* Note equilibrium is in terms of the electron temperature T_e and the upper and lower electronic states vibrational temperatures T_{v2} and T_{v1}.

RADIATIVE TRANSFER EQUATION

This section is devoted to an examination of the radiative transfer equation and shall show how the standard or classic form of this equation in terms of source function and absorption coefficient can be constructed for nonequilibrium conditions from a modification of the conventional absorption coefficients and source functions computed by equilibrium computer codes. Solution procedures for the classic radiative transfer equation will not be considered as adequate treatment is available in the form of computer codes and their documentation. Similarly, we will not review the computation of absorption coefficients as the procedure for computing the bandless model is incorporated into the same codes. We shall concentrate on the necessary modifications and their logical development. The development is easily extended to more complex models such as the JORL.

Assuming that either excited state population fractions or temperatures are available from solutions of the state population rate equations, the starting point is the "microscopic" radiative transfer equation expressed in terms of the Einstein relations for bound-bound transitions. The equation, Ref. [18], for the rate of change of radiative intensity I_ν in the frequency range $\Delta\nu$ at frequency ν, in the direction z per unit solid angle, considering the processes of spontaneous emission, stimulated absorption and stimulated emission between an upper electronic state 2 with population N_2 and a lower state 1 with a population N_1 is:

$$\mu \frac{dI_\nu}{dz} = (h\nu/4\pi) \sum_i [A_{21}^{(i)} N_2^{(i)} \Phi_2^{(i)} - I_\nu (B_{12}^{(i)} N_1^{(i)} \Phi_1^{(i)} - B_{21}^{(i)} N_2^{(i)} \Phi_2^{(i)})] \quad (24)$$

where the summation over i includes all species and bands which
contribute to the $\Delta\nu$ interval and where Φ_1 and Φ_2 which may be though of
as "line" shape functions for the transition, are:

$$\Phi_2 = \sum_{\Delta\nu} q_{v'v''} f_{v'} / \Delta\nu \tag{25a}$$

$$\Phi_1 = \sum_{\Delta\nu} q_{v'v''} f_{v''} / \Delta\nu \tag{25b}$$

where the sums are over all vibrational-electronic transitions with
centers in the interval $\Delta\nu$. Recall the quantity μ is the direction
cosine between the intensity ray and the direction z. The above
expression is consistent with the bandless model which assumes the
interval $\Delta\nu$ to be small enough so that properties are constant in the
interval but broad enough to encompass all of the rotational lines
associated with the transition.

Recognizing that the terms multiplied by I_ν comprise the absorption
coefficient including stimulated emission:

$$\mu'_\nu = \sum_i \mu_\nu^{(i)} \ (1 - \delta_\nu^{(i)}) \tag{26a}$$

with

$$\delta_\nu^{(i)} = (B_{21}N_2\Phi_2 / B_{12}N_1\Phi_1)^{(i)} \tag{26b}$$

and the absorption coefficient

$$\mu_\nu^{(i)} = (h\nu/4\pi) \ (B_{12}N_1\Phi_1)^{(i)} \tag{26c}$$

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Factoring this term in Eq. (24) yields the standard form:

$$\mu \frac{dI_\nu}{dz} = \mu'_\nu (S_\nu - I_\nu) \tag{27a}$$

where the source term takes the form:

$$S_\nu = \sum_i (A_{21} N_1 \Phi_1)^{(i)} / \mu'_\nu \tag{27b}$$

With the use of the relationship between the Einstein coefficients:

$$A_{21} = (2h\nu^3/c^2) B_{21} \quad ; \quad B_{12} = (g_2/g_1) B_{21} \tag{28}$$

the terms

$$A_{21} N_2 \Phi_2 = (B_{12} N_2 \Phi_2)(2h\nu^3/c^2)(g_1/g_2) \tag{29a}$$

which comprise the sum and the numerator of the source function. Now multiply and divide by $N_1 \Phi_1$ which are evaluated at the lower electronic state vibration temperature T_{v1} yielding:

$$(B_{12} N_1 \Phi_1) = (2h\nu^3/c^2)(g_1 N_2 \Phi_2 / g_2 N_1 \Phi_1) \tag{29b}$$

with the introduction of a term, Eq. (26b), $\delta_\nu = g_1 N_2 \Phi_2 / g_2 N_1 \Phi_1$, the above can be written as:

$$[(B_{12} N_1 \Phi_1)(1 - \delta_\nu)] \, [(2h\nu^3/c^2) \delta_\nu / (1 - \delta_\nu)] \tag{29c}$$

which one recognizes as the product of the absorption coefficient μ_ν' and

the Planck or Blackbody source function provided δ_ν reduces to the simple

exponential of frequency and temperature. The source function becomes:

$$S_\nu = \sum_i (\mu_\nu')^{(i)} (S_\nu)^{(i)}/\mu_\nu' \tag{30}$$

where the absorption coefficient for the individual band interval for the

i'th transition:

$$(\mu_\nu')^{(i)} = (h\nu/4\pi) (B_{12}N_1\Phi_1)^{(i)}(1 - \delta_\nu^{(i)})$$

and the source function for the individual band interval from the i'th

transition is:

$$S_\nu^{(i)} = (2h\nu^3/c^2) \, \delta_\nu^{(i)}/(1 - \delta_\nu^{(i)})$$

with

$$\delta_\nu^{(i)} = (g_1N_2\Phi_2/g_2N_1\Phi_1)^{(i)} \tag{31}$$

First note that the ratio of upper electronic state population to

lower electronic state population:

$$N_2/N_1 = (g_2/g_1) (Q_2(T_{v2})/Q_1(T_{v1}) \exp(-\epsilon_2/kT_{E2})/\exp(-\epsilon_1/kT_{E1}) \tag{32}$$

which is not a simple function of temperature and frequency.

Furthermore, re-examining the sums of Φ_1 and Φ_2, Eqs. (25 a & b), it is not obvious that these sums over the $\Delta\nu$ band interval are equal other than under the conditions that $\Delta\nu$ encompasses the entire band so that the sum encompasses all upper and lower states. To explore the relationship between Φ_1 and Φ_2, it is convenient to recall that for frequencies ν in the $\Delta\nu$ interval are represented by the upper and lower state vibrational energy terms satisfying:

$$h\nu = \epsilon_{12} + \epsilon_{v'} - \epsilon_{v''} \tag{33}$$

which can be used to solve for $\epsilon_{v'}$ and used with Eqs. (25) to yield a ratio

$$\Phi_2/\Phi_1 = [\Phi_1(T_{v2})/\Phi_1(T_{v1})] \, [Q_1(T_{v2})/Q_2(T_{v2})]e^{-h(\nu-\nu_{oo})/kT_{v2}} \tag{34}$$

where $\nu_{oo} = \epsilon_{12}/h$.

Combining Eqs. (34 and 32), we find that

$$\delta_\nu = [(\Phi_1 Q_1)'/(\Phi_1 Q_1)''] \, R \, \exp \, (-h\nu/kT_{v2}) \tag{35a}$$

where the double prime indicates the functions are evaluated at T_{v1} and the single prime indicates the functions are evaluated at T_{v2} and

$$R = \exp \, (-\epsilon_{12}/kT_t)/\exp \, (-\epsilon_{12}/kT_{v2}) \tag{35b}$$

where T_t, the transition temperature is

$$T_t = T_{E2}/[1 + (\epsilon_1/\epsilon_{12}) (T_{E1}-T_{E2}) / T_{E1}] \qquad (35c)$$

Note first that for equilibrium R = 1 and the partition function and line shape function ratio is unity so we find $\delta_\nu = \exp(-\epsilon_{12}/kT)$, the familiar Planck exponential. Next, note that in general, for nonequilibrium δ_ν is a function of 4 temperatures, i.e. a vibrational and electronic state temperature for both the upper and lower states of the radiative transition. If the transition is to a ground state, $\epsilon_1 = 0$ and the transition temperature reduces to the upper state electronic temperature; however, both upper and lower vibrational state temperatures are required. Next, note if all upper and lower states share a common value of vibrational state temperature then the line shape and partition function ratio terms reduce to unity. Clearly, under most nonequilibrium conditions, the δ_ν term does not reduce to the Planck exponential; however, it can be re-written as a frequency shifted Planck term evaluated at the upper state vibrational temperature.

$$\delta_\nu^{(i)} = \exp(-h(\nu + \Delta^{(i)})/kT_{v2}^{(i)}) \qquad (36a)$$

where the extent of the frequency shift is:

$$\Delta^{(i)} = \nu_{oo}[(T_{v2}-T_t)/T_t] + kT_{v2} \ln[(Q_1\Phi_1)''/(Q_1\Phi_1)'] \qquad (36b)$$

Thus, the algorithm for the standard form for the radiative transfer equation, Eq. (27a) consisting of the absorption coefficient Eq. (26 a and c) and the source function by Eq. (30) with $\delta_\nu^{(i)}$ given by Eq. (36).

In adapting this algorithm to existing programs, the absorption coefficient could be taken care of by an equilibrium code provided the T_{v1} is used in its evaluation. Note T_{E1} is also necessary if the lower level is not a ground electronic state. The $\delta_{\nu}^{(i)}$ would have to be evaluated by using the upper vibrational state temperature and computing the frequency shift which is a function of all four temperatures associated with the transition.

Note that the shift in the Planck exponential terms are positive for $T_{v2} > T_{v1}$ and $T_{v2} > T_t$. This shift would attenuate UV and increase the potential contributions in the IR. High electronic state temperatures would reverse this pattern.

The reduction of the above to the optically thin approximate, such as discussed in earlier sections, would indicate the dependence upon T_{v1} and T_{v2} is not as strong as the above expressions seem to indicate.

CONCLUSION

The objective of this study has been to develop the algorithm which will allow nonequilibrium flowfield codes to be coupled to radiative transfer codes which are currently limited to equilibrium applications. The algorithm consists of Eq. (22) for the prediction of electronic state population fractions (electronic state temperature) and Eqs. (35c), (36), (26c), (26a) and (30) for the compution of spectral absorption coefficients and source functions for use in Eq. (27a). These expressions represent a thorough treatment in the context of the bandless model which in the past has proven adequate for equilibrium radiative transfer predictions. Perhaps the approach is more than adequate as the current algorithm requires four temperatures for each transition. Clearly, a more sophisticated model can be developed; however, it would require more information ie. rotational temperatures of the electronic levels.

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