Arcjets operating on molecular propellants such as ammonia or hydrazine are expected to produce significant amounts of diatomic species such as \( \text{N}_2 \), \( \text{NH} \), and \( \text{H}_2 \) in the discharge [1]. Internal mode energy exchange (Vibration-Vibration, Vibration-Electronic, Electronic-Electronic, and Vibration-Translation) between these molecules can result in highly non-Maxwellian distribution of energies within their internal modes of vibration, electronic excitation, and rotation. These diatomic species are also extremely effective in moderating electron energies via inelastic collisions involving their internal modes (vibration, electronic excitation, and rotation). Consequently, the electron energies in arcjets operating on such molecular propellants are strongly related to and determined by the distribution of molecules in various vibrationally and electronically excited states. Under these conditions therefore, the concept of an electron temperature loses meaning. Instead, one must refer to electron energy distribution, or an average electron energy if a meaningful average exists. The modelling of such inter-mode energy transfer is extremely complicated and presents a challenge to the areas of chemical physics and numerical analysis. In this paper, we present numerical solutions to quasi one-dimensional supersonic flows with state-specific vibrational rate kinetics. These simulations represent some of the energetics expected to occur in arcjets. This work is a necessary first step before complete modelling of the discharge including the effects of electron-impact processes (see also [2]). The numerical method used here is the Linearized Block Implicit (LBI) method of Briley & McDonald [3]. The LBI method has excellent stability properties and extends easily to multi-dimensions. Formulation of the boundary and initial conditions for this problem are discussed in detail, and these essentially carry over for similar 2-D and 3-D cases.

**Nomenclature**

\[
\begin{align*}
A & \quad \text{cross-sectional area of the nozzle (m}^2) \\
e & \quad \text{internal energy per unit volume (J/m}^3) \\
E_{i,v} & \quad \text{energy of vibrational level } v \text{ of species } i \text{ (J)} \\
k & \quad \text{Boltzmann's constant (J/K)} \\
M_{i,v} & \quad \text{molecular mass of the diatomic species (kg)} \\
M_m & \quad \text{atomic or molecular mass of the diluent species (kg)} \\
n_{i,v} & \quad \text{number density of vibrationally active species } i \text{ at level } v \text{ (m}^{-3}) \\
n_m & \quad \text{number density of diluent species} \\
N_d & \quad \text{number of vibrationally active species} \\
N^*_m & \quad \text{number of diluent species} \\
p & \quad \text{pressure (N/m}^2) \\
p_0 & \quad \text{reservoir pressure (N/m}^2) \\
t & \quad \text{time (s)} \\
T & \quad \text{temperature (K)} \\
T_0 & \quad \text{reservoir temperature (K)} \\
u & \quad \text{velocity (m/s)} \\
V_{\text{max}} & \quad \text{highest vibrational level considered in the diatomic species} \\
x & \quad \text{axial or streamwise coordinate (m)} \\
\rho & \quad \text{mass density (kg/m}^3) \\
\end{align*}
\]

1. **Introduction**

Arcjet thrusters are electrothermal devices where a propellant stream is ohmically heated and subsequently expanded to supersonic speeds. These thrusters are capable of robust operation using a variety of propellants including monatomic and polyatomic gases. The energy added into the gas is distributed into thermal heating (i.e. increase in translational mode temperature) and into various internal modes (electronic excitation, vibration, and rotation). However, it is mainly the thermal
heating which is subsequently converted into directed kinetic energy (i.e. useful thrust) in the nozzle. Thus, any energy distributed into the internal modes which is subsequently not recovered in translational motion is lost and referred to as a "frozen flow loss". This work is a first step toward predicting frozen flow losses.

The internal mode energy exchange between molecules in a discharge not only results in re-distribution of input electrical energy, but also determines, moderates, and governs electron energy distributions. Electrons which normally acquire large kinetic energies from applied electric fields in monatomic gases, are restricted from doing so in plasmas containing appreciable amounts of molecular species. This is because inelastic collisions between electrons and molecules results in transfer of electron kinetic energy to vibrational, electronic, or rotational excitation. Since energy exchange between molecules also occurs in these discharges, the well known non-Maxwellian distribution such as Treanor distribution[4] occurs among the molecules such as N\textsubscript{2}, thereby leading to highly non-Maxwellian electron energy distributions. Such distributions can occur at low pressures in molecules such as N\textsubscript{2} and CO (100 torr) [5] or supra-atmospheric pressures (20 atm.) [6]. Consequently, it is likely that the concept of an electron temperature in arcjet plasmas is meaningless and that one must resort to electron energies or a mean electron energy instead.

Arcjet thrusters operating at low or moderate powers in the range of 1 KW to 30 KW on ammonia (NH\textsubscript{3}) or hydrazine (H\textsubscript{4}N\textsubscript{2}) are expected to produce significant amounts of N\textsubscript{2}, NH, and H\textsubscript{2}. The pressure varies from 100 torr in the nozzle to an atmosphere or several atmospheres in the constrictor or upstream of the constrictor. Typically, the E/N in these thrusters vary over a wide range: 10^{-23} V - m^2 \leq E/N \leq 10^{-16} V - m^2 (or 10^{-19} V - cm^2 \leq E/N \leq 10^{-12} V - cm^2). Molecular discharges in N\textsubscript{2} have been studied extensively in the past (for instance see [5]) over a range that is partially applicable to arcjet flows. Such studies offer valuable insight into the nature of the electron energy distribution function. For instance, Fig. 1 from [5] shows the calculated Electron Energy Distribution Functions (EEDFs) in N\textsubscript{2} discharges for a variety of E/N ratios. It is to be emphasized that this figure is a semi-log plot so that a Maxwell-Boltzmann distribution would be shown as a sloping, straight line on such a plot. As can be seen from Fig.1, the EEDFs are markedly non-Maxwellian. This has dramatic consequences for evaluation of transport properties since cross-sections for collisional processes are averaged over energy distributions (usually taken to be Maxwellian).

It is also instructive to examine the "fractional power transfer" versus E/N for N\textsubscript{2} discharges as given by Nighan [5], shown here in Fig. 2. With respect to the arcjet, this figure may be interpreted as follows. At low powers characterized by the lower E/N values displayed in Fig. 2, it can be seen that much of the energy added to the discharge goes into the vibrational modes of N\textsubscript{2}. Electronic excitation gains prominence as E/N is increased, with ionization only begining to consume input power at E/Ns approaching 10^{-15} V - cm^2. Note the conspicuous absence of dissociation, which is understandable since the dissociation energy of N\textsubscript{2} is 9.76 eV and the E/Ns in Fig. 2 are lower than those corresponding to average electron energies less than 3 eV. It is therefore clear from this example that scaling up in power for arcjets operating on nitrogen, ammonia, or hydrazine is strongly dependent on the degree of dis-equilibria between the various internal modes. Frozen flow losses and losses in efficiency are therefore related to vibrational, electronic, and rotational mode non-equilibrium. Several recent works have already pointed to striking differences between rotational, vibrational, and translational energies in the plumes.
of arcjet thrusters[1, 7].

Flows with high degree of vibrational, electronic, and chemical non-equilibrium occur in many other engineering applications. These include flow in gas dynamic lasers, rocket thrusters (chemical and electrical) and chemical vapor deposition (CVD) processes. A typical feature of these non-equilibrium flows is the large variation in characteristic times for internal processes which can vary by as much as thirty to forty orders of magnitude or more in various regions of a flow. In applications where the effects of state-specific kinetics or large number of elementary reactions have to be incorporated, there is a need for a robust, efficient, reliable, and accurate numerical method to simulate such flows.

Recently, numerical solutions to supersonic nozzle flows with high degree of vibrational non-equilibrium and state-specific kinetics have been presented [8]. These quasi 1-D solutions were obtained by integrating the steady forms of the governing equations using the stiff equation integrator LSODE [9]. While it is possible to obtain solutions to 1-D problems using this strategy, it does not extend to multi-dimensions. This is a serious drawback if one wants to study such flows in two- and three-dimensions, while including the effects of heat conduction and viscosity. Our interest in these multi-dimensional flows arises from the need to quantify the frozen flow losses and redistribution of input electrical energy in arcjet thrusters. Hence, it is desirable to have an efficient method that can handle such stiff problems and extend from 1-D all the way to 3-D.

The Linearized Block Implicit (LBI) scheme of Briley & McDonald [3] is such a method. As we show in a recent work [2], this method is very well suited for studying viscous, internal flows in geometries with high exit to throat area ratios. Our ultimate goal is to be able to study these internal flows after including the effects of vibrational and chemical non-equilibrium with state-specific kinetics.

In this paper, we tackle the first steps in calculating vibrational mode non-equilibrium, simulating the energy loading in the arcjet thruster. It must be pointed out at the outset that the results we present here do not account for the electric discharge in the arcjet unlike [2]. Rather, we simulate the energy loading of the arc as an initial total temperature to which the propellant stream is heated before expansion through the nozzle. Work incorporating vibrational/electronic mode disequilibrium together with the discharge phenomena is presently underway, and will be reported later. We focus here on flows of pure N\textsubscript{2}, N\textsubscript{2}/H\textsubscript{2}, N\textsubscript{2}/Ar, and N\textsubscript{2}/CO/Ar mixtures to illustrate the effects of inter-molecular and intra-molecular V-V (Vibration-to-Vibration) and V-T (Vibration-to-Translation) energy transfer. Our present work thus differs in approach and scope from previous or ongoing work [10, 11, 12, 13, 14, 15, 16, 17].

This paper is organized as follows. Formulation of the problem which differs from [8] is discussed in the next section, followed by a discussion of the numerical method in section 3. Results are discussed in section 4, followed finally by a summary and conclusions.

2 Formulation

In the arcjet, much of the ohmic dissipation takes place in the constrictor region and upstream of the nozzle. This addition of energy to the upstream subsonic propellant can be viewed as an addition of thermal energy to the flowing propellant stream driving it to choke and accelerate to supersonic speeds. Although the following is not a completely true description of the arcjet operation, the present results serve to illustrate the role of molecular energy transfer in arcjet flows. Since the problem formulation and solution methodology that is used
in the present work is completely different from that used in [8], we present them in detail here. The governing equations are the quasi 1-D gas dynamic equations together with species conservation equations [8]. These are written as follows:

\[
\frac{\partial \rho}{\partial t} + \frac{1}{A} \frac{\partial (\rho u A)}{\partial x} = 0 ,
\]

(1)

\[
\frac{\partial (\rho u)}{\partial t} + \frac{1}{A} \frac{\partial (\rho u^2 A)}{\partial x} = - \frac{\partial p}{\partial x} ,
\]

(2)

\[
\frac{\partial}{\partial t} \left( e + \frac{\rho u^2}{2} \right) + \frac{1}{A} \frac{\partial}{\partial x} \left[ u A \left( e + p + \frac{\rho u^2}{2} \right) \right] = 0 ,
\]

(3)

\[
\frac{\partial n_{i,v}}{\partial t} + \frac{1}{A} \frac{\partial (n_{i,v} u A)}{\partial x} = VT_{i,v} + VV_{i,v} + SRD_{i,v} ,
\]

(4)

\[
1 \leq i \leq N_d , \quad 0 \leq v \leq V_{\text{max}}
\]

\[
\frac{\partial n_m}{\partial t} + \frac{1}{A} \frac{\partial (n_m u A)}{\partial x} = 0 , \quad 1 \leq m \leq N_m
\]

(5)

where the subscripts \( i, v \) refer to diatomic species \( i \) in vibrational state \( v \) and the subscript \( m \) refers to diluent species \( m \) (usually monatomic). In addition, only the diatomic species are assumed to be vibrationally active and \( V_{\text{max}} + 1 \) is the total number of vibrational levels considered in each of the diatomic species. \( E_{i,v} \) is calculated by treating the diatomic molecules as anharmonic oscillators [8]. The heat of formation of various species can be included in the energy equation. However, since chemical reactions are not considered in the examples presented here, they have been left out of Eq. (3). Also, energy of the electronic levels is neglected as we do not include electronic transitions in the examples. The radiative loss which would appear as a sink term on the right hand side of Eq. (3), is neglected here since it is expected to be small for the optically thin gases considered here. These assumptions do not indicate a loss of generality, since all these terms can be included in the formulation if applicable.

The pressure is related to the temperature and the number densities through the following equation of state:

\[
p = \left( \sum_{i=1}^{N_d} \sum_{v=0}^{V_{\text{max}}} n_{i,v} + \sum_{m=1}^{N_m} n_m \right) kT ,
\]

(6)

and the mass density is related to the number densities as follows:

\[
\rho = \sum_{i=1}^{N_d} \sum_{v=0}^{V_{\text{max}}} M_i n_{i,v} + \sum_{m=1}^{N_m} M_m n_m ,
\]

(7)

where \( M \) stands for the atomic or molecular mass of the respective species. The internal energy per unit volume is given by the following, assuming equilibrium between the translational and rotational modes:

\[
e = \frac{3}{2} kT \sum_{m=1}^{N_m} n_m + \sum_{i=1}^{N_d} \sum_{v=0}^{V_{\text{max}}} n_{i,v} \left( \frac{5}{2} kT + E_{i,v} \right) .
\]

(8)

The terms on the right hand side of Eq. (4) represent the state-specific Vibration-Translation (VT), Vibration-Vibration (VV) and Spontaneous Radiative Decay (SRD) terms as described by Dunnwald et al. [18] and the reader is referred to their work for the detailed expressions for these terms.

2.1 Boundary Conditions

We assume that a large reservoir is present upstream of the nozzle and that the conditions in the reservoir such as temperature, pressure, and volume fractions of the various species present are known. Further, it is assumed that
the diatomic species are in Boltzmann equilibrium both in the reservoir and at the nozzle inlet plane and that the mixture is compositionally frozen between these two locations. In addition, heat losses and frictional losses in going from the reservoir to the nozzle inlet are assumed to be negligible, without any loss of generality.

With the above assumptions, we can relate the conditions at the nozzle inlet to those at the reservoir by conservation of energy. This gives us an equation that involves the velocity, temperature, and total number density \( \rho \) at the inlet. Since the volume fractions of the monatomic species at the inlet are known, we can relate the individual \( n_i \)'s to the total number density. For the diatomic species, the known volume fractions at the inlet together with the fact that they are in Boltzmann equilibrium [19] allows us to relate the \( n_{i,v} \)'s to the total number density. Finally, we can relate the inlet static pressure, and hence the total number density (see Eq. (6)), and temperature to their respective values at the reservoir through the isentropic equation of state [20]. In the present case, the velocity at the inlet of the nozzle is small because of the large inlet-to-throat area ratio and thus the use of the isentropic equation of state is acceptable. These conditions allow us to eliminate all the dependent variables except the velocity at the inlet, which is determined through an implicit extrapolation [3]. At the exit to the nozzle, implicit extrapolation is used for all the variables since we are interested only in supersonic flows.

Although the governing equations and boundary conditions have been presented in their dimensional form in this section, it must be pointed out that they are non-dimensionalized before being solved numerically. This we do by using upstream reservoir conditions as reference quantities. This choice is especially convenient, since the reservoir conditions need to be specified as boundary conditions anyway as we have already seen.

### 3 Numerical Method

Equations (1)-(5) together with the boundary conditions are discretized in time and linearized implicitly using the procedure outlined by Briley & McDonald [3]. Artificial dissipation in the form of a second derivative in the axial or streamwise coordinate is added to the right hand side of equations (1)-(5) to ensure numerical stability [3]. These equations are then discretized using second order accurate central differences on a non-uniform grid with fine spacings near the throat region. After eliminating the boundary points from the resulting system of linear algebraic equations using the boundary conditions, a block tridiagonal system of equations results which can be solved by using standard block LU decomposition algorithms [21]. We must note at this point that this system is linearly dependent due to the relationship between the mass density \( \rho \) and the number densities through Eq. (7), which holds at each grid point. In order to make this system linearly independent, we arbitrarily replace one of the species equations, such as the one corresponding to \( i=1 \) and \( v=0 \) at each grid point with Eq. (7) applied at that grid point. Note that this is done implicitly so that overall stability is not lost. The system of equations is now rendered linearly independent and ready to be solved.

Since we are solving the unsteady form of the governing equations here, the frozen flow solution is prescribed as the initial guess to start the solution process. This solution is obtained by numerically solving the above system of equations with the right hand side of Eqs. (4) set identically to zero. In principle, a truly frozen flow cannot be used as an initial guess for non-equilibrium calculations. How-
ever, in practice, these solutions exhibit deviations from the truly frozen flow solution due to discretization and round-off errors normally present in such numerical solutions. Therefore, the frozen flow solution can be used as initial guess for the non-equilibrium calculations.

4 Results & Discussion

We consider the geometry of the nominal 30 kW arcjet. However, as mentioned earlier, we do not model the arc. Rather, the effect of the arc’s heating of the flow is simulated as an effective upstream total temperature. The cross-section of the nozzle as a function of the axial coordinate is shown in Fig. 3. For all the results presented here, a total of 120 grid points in the axial direction is used. The unsteady, non-equilibrium calculations are stopped when the percent change in the variables is less than or equal to 0.00001 %. The size of the dimensionless time step is about $5 \times 10^{-7}$ seconds for all the cases, even though larger values can be used for some of the cases. Since the number of grid points is the same for all the cases, the total computing time for each case depends almost entirely upon the the size of the blocks in the block tridiagonal system, which is equal to $3 + N_m + N_d V_{\text{max}}$. In the present study, block sizes as large as 84 (corresponding to $N_m=1$, $N_d=2$ and $V_{\text{max}}=40$) are considered. The total computing time (including the time taken for generating the initial guess) for this case of largest block size is about 4 minutes in uniprocessor mode on the Cray Y-MP, while it is about 8 minutes for the cases with a single diatomic species.

We first consider the flow of pure $N_2$ with the reservoir temperature at 5000 K and the reservoir pressure at 2 atm. Only the ground electronic state is modeled. The mass density, velocity and temperature along the length of the nozzle are plotted in Fig. 4. As can be seen in this figure, the gradients of these quantities are quite large near the constrictor, and the open symbols (shown only for the velocity for the sake of clarity) clearly show that the non-uniform grid is able to resolve these gradients very well. Fig. 5 shows normalized population distributions for $N_2$ at three sections, namely, inlet, throat (exit to the constrictor) and the exit. The distribution at the throat is very close to a Boltzmann distribution, while the distribution at the exit shows considerable departure from equilibrium. As is evident, the initial energy loading of the gas upstream (i.e. via a high stagnation temperature) is re-distributed into the upper vibrational levels as the gas suddenly expands and cools. This effect is well known, and referred to as anharmonic V-V (Vibration-Vibration) pumping [4]. This effect occurs when conditions are such that V-V rates are much faster than V-T rates, typical of conditions in supersonic expansions. These distributions agree well with those presented in [8].

The effects of adding diluents in the form of monatomic species was also studied. These diluents are added, depending on the application, in order to either inhibit or promote V-T relaxation downstream of the constrictor region. For the 20% $N_2$/80% Ar mixture shown in Fig. 6, the $N_2$ is seen to be less V-V pumped than for the pure $N_2$ case (Fig. 5). Evidently, the vibrational modes of $N_2$ are de-excited via V-T transfer to argon. Addition of 10% $H_2$ also results in de-excitation of the vibrational modes of $N_2$ comparable to the 20%$N_2$/80% Ar case, as can be seen from Fig. 7. The population distributions, however, are not as sensitive to small changes in the percentages of $H_2$ in the mixture as was reported in [8]. This is due to an error in the values of the constants $A_{j,k}$, $B_{j,k}$ and $C_{j,k}$ (see Table 1 in de Roany et al. [8]) used for calculating the CO-$H_2$ V-T rates. The correct values for these constants are shown in Table 1.
As an illustration of inter-molecular energy transfer, we consider a mixture of 20% CO, 20% N₂, and 60% Ar. In this mixture, both CO and N₂ are vibrationally active, but only their ground electronic manifolds are modeled. We neglect vibrational energy transfer to low-lying electronic levels, although the latter could also be included within the framework of the present method. The vibrational populations of these species at the exit plane are plotted in Fig. 8. The distributions show considerable non-equilibrium and the number densities of N₂ for vibrational levels above 5 are about 2 orders of magnitude lower than those of CO. These distributions agree qualitatively with those presented in [8]. The average vibrational energy per species, defined as \( \sum_{v=0}^{V_{max}} n_{i,v} E_{i,v} / \sum_{v=0}^{V_{max}} n_{i,v} \) is plotted in Fig. 9 for CO and N₂. Dramatic transfer of vibrational energy from N₂ which has more widely spaced energy levels, to CO which has more closely spaced levels can be seen in this figure. This is in agreement with theoretical predictions [4] as well as the numerical results presented in [8]. When ammonia or hydrazine is used, species such as N₂, H₂, and NH are produced in the discharge. Thus vibrational energy transfer can take place between these species, ultimately affecting the electron energy distribution and making it markedly non-Maxwellian. The presence of such vibrationally excited molecules will thus influence transport properties such as electrical conductivity.

5 Summary & Conclusions

Representative quasi 1-D solutions for flow in a nominal 30 KW arcjet geometry exhibiting strong vibrational non-equilibrium, are presented. Although the arc is not modeled, its presence is simulated using a high value for the inlet stagnation temperature. The results are therefore somewhat representative of the vibrational populations of the ground electronic states of the relevant diatomic molecules. Since electron energies are primarily dependent on inelastic collisions with molecules such as N₂, their distribution in non-Boltzmann or non-Maxwellian since these diatomic species exhibit significant departures from equilibrium. Hence transport properties which depend on cross sections averaged over these distributions are markedly affected. This work underscores the importance of considering inelastic electron impact processes for evaluating transport properties in arcjet flows correctly.

These solutions are obtained with the LBI scheme of Briley & McDonald [3] using state-specific kinetics. This algorithm has excellent stability properties and allows the use of quite large time steps even in such stiff systems. This feature is particularly desirable when performing such calculations in multi-dimensions. The boundary and initial conditions that are discussed here carry over to multi-dimensional problems as well. The present method is therefore well suited to studying high speed, multi-dimensional, reacting, plasma flows such as those encountered in arcjet thrusters. Incorporation of the detailed kinetic processes discussed herein into a 2-D axi-symmetric model reported in [2] is presently underway.

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APPENDIX

The detailed expressions for the VT, VV and the SRD terms are given here. Even though the expressions presented here look identical to those given in [8], there are some minor differences between the two due to typographical errors in [8].

$E_{i,v}$, the vibrational energy at level $v$ of species $i$ is given by:

$$E_{i,v} = \frac{1.6022 \times 10^{-19}}{8065.479} \left[ \omega_{ei} \left( v + \frac{1}{2} \right) \right. - \left. \omega_{ei} \chi_{ei} \left( v + \frac{1}{2} \right)^2 \right]$$

where the electronic energy has been neglected since we consider only ground electronic states here. In general, $E_{i,v}$ is also dependent on the rotational quantum number [22], but in this work we treat the rotational modes as being in equilibrium with the translational modes. $\omega_{ei}$ (in cm$^{-1}$) and $\chi_{ei}$ (dimensionless) are the spectroscopic constants for molecules of species $i$ (see Table 4).

Vibration-Translation (VT) term

The VT term in the species equation (4) can be written in form as

$$VT_{i,v} = \sum_{j=1}^{N_d+N_m} n_j \left[ P_{i,j}^{v+1,v} (n_{i,v+1} - \exp (-\Delta E_i^{v}/kT)n_{i,v}) \right. - \left. P_{i,j}^{v,v-1} (n_{i,v} - \exp (-\Delta E_i^{v-1}/kT)n_{i,v-1}) \right]$$

where

$$n_j = \sum_{w=0}^{V_{\text{max}}} n_{j,w}$$

in the case of a vibrationally active species and $n_j = n_{m}$ in the case of a diluent species.

Also, $P_{i,j}^{v,v-1}$ is the rate constant (in m$^3$/s) of the VT transition:

$$X_i(v) + X_j \rightarrow X_i(v-1) + X_j,$$

where $X_i(v)$ refers to species $i$ in vibrational state $v$. The rate constant is given by [8],

$$P_{i,j}^{v,v-1} = \frac{v}{1 - \chi_{ei} v} F(\lambda_{i,j}^{v,v-1}),$$

where

$$F(\psi) = \frac{1}{2} \left( 3 - e^{-2\psi/3} \right) e^{-2\psi/3}$$

with

$$\lambda_{i,j}^{v,v-1} = 2^{-3/2} \sqrt{\frac{\Theta_{i,j}^2 |\Delta E_i^{v-1}|}{kT}}.$$

Here $\Delta E_i^{v-1} = E_{i,v} - E_{i,v-1}$ is the difference in energy between products and reactants in the VT transition; $\Theta_i = h c \omega_{ei}/k$ (with $c$, the speed of light in cm/s) is the vibrational characteristic temperature (in K) of species $i$; $\Theta_{i,j} = 16\pi^4 \mu_{i,j} c^2 \omega_{ei}^2 I/k$ is in K where $\mu_{i,j}$ is the reduced mass in kg and $I (= 0.2 \times 10^{-10}$ m) is the range parameter [23].

In the above expression for the rate constant, $P_{i,j}$ is a coefficient that allows for fitting to the available experimental relaxation data for the 1-0 transition rate i.e $P_{i,j}^{1.0}$. It is given (in m$^3$/s) as:

$$P_{i,j} = \frac{10^{-13} \left( 1 - \chi_{ei} \right) kT}{\left( \tau p \right)_{i,j} \tau_{i,j}^{1.0} \left[ 1 - \exp ( - \Theta_i / (T) ) \right]}$$

Here $(\tau p)_{i,j}$ is the vibrational relaxation time in $\mu$s.atm and is expressed as:

$$\ln (\tau p)_{i,j} = A_{i,j} + B_{i,j} (T)^{-1/3} + C_{i,j} (T)^{-2/3}$$

where $A_{i,j}$, $B_{i,j}$ and $C_{i,j}$ are empirical constants chosen to match the experimental data. They are given in Table 1.
Vibration-Vibration (VV) term

The VV term in the species equation (4) can be written in as

\[ VV_{i,v} = \sum_{v'=v}^{N_d - 1} \sum_{v''=v'}^{N_{\text{max}}} Q_{i,j;v',v''+1} [n_{i,v'}, n_{j,v''+1}] \]

\[ - \exp \left( - \frac{( \Delta E_{i,v} - \Delta E_{j,v''} )}{kT} n_{i,v} n_{j,v''+1} \right) \]

\[ - Q_{i,j;v',v''+1} [n_{i,v}, n_{j,v''+1}] \]

\[ - \exp \left( - \frac{( \Delta E_{i,v'} - \Delta E_{j,v''} )}{kT} n_{i,v'} n_{j,v''+1} \right) \]

where \( Q_{i,j;v',v''+1} \) is the rate constant (in \( m^3/s \)) of the V-V transition:

\[ X_i(v) + X_j(w-1) \rightarrow X_i(v-1) + X_j(w). \]

The rate constant is written as a sum of a short range and a long range contribution [8] as follows:

\[ Q_{i,j;v',v''+1}^L = Z_{i,j} \left( S_{i,j;v',v''+1}^L + L_{i,j;v',v''+1}^L \right) e^{- (\Delta E_{i,v'} - \Delta E_{j,v''+1})/2kT} \]

where \( Z_{i,j} = 10^{-6} \times 400 \sigma_{i,j}^2 \sqrt{\pi kT/2\mu_{i,j}} \)

which is the collision number in \( m^3/s \) and \( \pi \sigma_{i,j}^2 \) is the collision cross-section in \( cm^2 \) with \( \sigma = 3.75 \times 10^{-8} cm \). We also have

\[ S_{i,j;v',v''+1}^L = S_{i,j} T \frac{v}{1 - \chi_{ei}v} \]

\[ \frac{w}{1 - \chi_{ei}w} F(\lambda_{i,j;v',v''+1}^L) \]

and

\[ L_{i,j;v',v''+1}^L = \frac{L_{i,j}}{T} \left( \frac{g_{i,v,v'}^0}{g_{i}^{1,0}} \right)^{2} \left( \frac{g_{j,v''+1,1}^1}{g_{j}^{1,0}} \right)^{2} \]

\[ \cdot \exp \left( - \frac{( \Delta E_{i,v'} - \Delta E_{j,v''+1} )^2}{b_{i,j} kT} \right) \]

where \( S_{i,j} \) (in \( K^{-1} \)), \( L_{i,j} \) in \( K \) and \( b_{i,j} \) in \( K \) are empirical parameters fitted to available experimental data. Their values are given in Table 2. Also, \( F(\lambda) \) is the same as before in the case of VT transfer while the expression for \( \lambda \) now becomes

\[ \lambda_{i,j;v',v''+1}^L = 2^{-3/2} \sqrt{\frac{T_\lambda}{\Theta_{i,j}}} \left| \frac{\Delta E_{i,v'} - \Delta E_{j,v''+1}}{kT} \right| \]

Finally

\[ \left( \frac{g_{i,v,v'}^{1,0}}{g_{i}^{1,0}} \right)^2 = \left( \frac{a_i + 1}{a_i + 3 - 2v} \right)^2 \]

\[ \cdot \exp \left( - \frac{v(a_i + 2 - 2v)(a_i + 4 - 2v)}{a_i(a_i + 3 - v)} \right) \]

where \( a_i = 1/\chi_{ei} \).

Spontaneous Radiative Decay term

The SRD term in the species equation (4) for radiative transition between levels of the same electronic species can be written as [8]

\[ SRD_{i,v} = \sum_{w=1}^{w'} A^{v+w,v}_{i,v} n_{i,v+w} - A^{v,v-w}_{i,v} n_{i,v} \]

where, \( A \), the Einstein A coefficients are given by

\[ \frac{A^{v,v-w}_{i,v}}{A^{1,0}^i} = \frac{1}{(a_i - 2)(a_i - 3)^w} \]

\[ \cdot \frac{v!}{(v - w)!} \frac{b_v(b_v + w)(b_v + 2w)}{\Pi_{q=1}^{w-1}(a_i - v + q)} \]

where \( b_v = a_i - 2v - 1 \) and \( w' \) and \( A^{1,0}^i \) (in \( 1/s \)) are given in Table 3.

References


### TABLE 1.

<table>
<thead>
<tr>
<th>Species</th>
<th>$A_{i,j}$</th>
<th>$B_{i,j}^* (K^{1/3})$</th>
<th>$C_{i,j}^* (K^{2/3})$</th>
<th>$\Theta_{i,j}^*/\Theta_{i}^2 (K^{-1})$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-CO</td>
<td>-15.23</td>
<td>280.5</td>
<td>-549.6</td>
<td>$45.6 \times 10^{-2}$</td>
<td>[24]</td>
</tr>
<tr>
<td>CO-Ar</td>
<td>10.38</td>
<td>0.0</td>
<td>0.0</td>
<td>$53.72 \times 10^{-2}$</td>
<td>[24]</td>
</tr>
<tr>
<td>CO-$H_2$</td>
<td>-26.22</td>
<td>-10.61</td>
<td>-12.80</td>
<td>$6.089 \times 10^{-2}$</td>
<td>[25]</td>
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<tr>
<td>$N_2-H_2$</td>
<td>-26.22</td>
<td>-10.61</td>
<td>-12.80</td>
<td>$6.089 \times 10^{-2}$</td>
<td>[25]</td>
</tr>
<tr>
<td>CO-$N_2$</td>
<td>-7.934</td>
<td>147.7</td>
<td>0.0</td>
<td>$45.6 \times 10^{-2}$</td>
<td>[8]</td>
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<tr>
<td>$N_2-N_2$</td>
<td>-12.539</td>
<td>258.9</td>
<td>-390.9</td>
<td>$45.6 \times 10^{-2}$</td>
<td>[8]</td>
</tr>
<tr>
<td>$N_2-Ar$</td>
<td>-15.62</td>
<td>168.95</td>
<td>0.0</td>
<td>$53.72 \times 10^{-2}$</td>
<td>[8]</td>
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</tbody>
</table>

### TABLE 2.

<table>
<thead>
<tr>
<th>Species</th>
<th>$S_{i,j}^* (K^{-1})$</th>
<th>$L_{i,j}^* (K)$</th>
<th>$b_{i,j}^* (K)$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-CO</td>
<td>$1.64 \times 10^{-6}$</td>
<td>1.6142</td>
<td>40.36</td>
<td>[23]</td>
</tr>
<tr>
<td>CO-$N_2$</td>
<td>$7.006 \times 10^{-8}$</td>
<td>$1.897 \times 10^{-2}$</td>
<td>191.42</td>
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</tr>
<tr>
<td>$N_2-N_2$</td>
<td>$9.37 \times 10^{-8}$</td>
<td>0.0</td>
<td>-</td>
<td>[8]</td>
</tr>
</tbody>
</table>
### TABLE 3.

<table>
<thead>
<tr>
<th>Species</th>
<th>$w'$</th>
<th>$A^{-1.0}$ (1/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-CO</td>
<td>4</td>
<td>30.3</td>
<td>[23]</td>
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<tr>
<td>$N_2-N_2$</td>
<td>-</td>
<td>0.0</td>
<td>[8]</td>
</tr>
</tbody>
</table>

### TABLE 4.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\omega_{ei}$ ($cm^{-1}$)</th>
<th>$\omega_{ei}X_{ei}$ ($cm^{-1}$)</th>
<th>$\Theta^*_e$ (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-CO</td>
<td>2169.8</td>
<td>13.288</td>
<td>3121.0</td>
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</tr>
<tr>
<td>$N_2-N_2$</td>
<td>2358.6</td>
<td>14.324</td>
<td>3396.8</td>
<td>[22]</td>
</tr>
</tbody>
</table>
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E /N

for an electric
discharge in
nitrogen (from ref.15).

A Maxwellian distribution would appear linear on
this plot.

30-kW Arcjet Geometry

Fig.1: Electron Energy Distribution Functions (EEDFs) for an electric discharge in
nitrogen (from ref.[5]). A Maxwellian distribution would appear linear on
this plot.

Fig.2: Normalized fractional power is shown here versus E/N for an electric
discharge in nitrogen (from ref.[5]).

Profiling of mass density (normalized by 0.1365 Kg/m$^3$), temperature
(normalized by 5000 K), and axial velocity (normalized by 1442 m/s) are
shown here versus the streamwise coordinate (normalized by 0.01 m).

Fig.4: Profiles of mass density (normalized by 0.1365 Kg/m$^3$), temperature
(normalized by 5000 K), and axial velocity (normalized by 1442 m/s) are
shown here versus the streamwise coordinate (normalized by 0.01 m).

Fig.3: Schematic of the 30 KW arcjet geometry used in the quasi 1-D calculations.
Fig. 5: Populations of vibrationally excited nitrogen molecules normalized by the ground vibrational populations at the respective locations is shown here versus vibrational quantum number \( v \). This is for flow of pure \( N_2 \).

Fig. 6: Populations of vibrationally excited nitrogen molecules normalized by the ground vibrational populations at the respective locations is shown here versus vibrational quantum number \( v \). This is for flow of \( N_2/Ar \).

Fig. 7: Populations of vibrationally excited nitrogen molecules normalized by the ground vibrational populations at the respective locations is shown here versus vibrational quantum number \( v \). This is for flow of \( N_2/H_2 \).

Fig. 8: Populations of vibrationally excited nitrogen molecules normalized by the ground vibrational populations at the respective locations is shown here versus vibrational quantum number \( v \). This is for flow of \( N_2/CO/Ar \).
Fig. 9: The average vibrational energy per particle (normalized by $6.903 \times 10^{-20}$ J) is plotted here versus streamwise coordinate (normalized by 0.01 m) for flow of $N_2/CO/Ar$. Note how the nitrogen up-pumps the CO via vibrational energy transfer and is de-excited in the process.