MODELING OF NO RADIATIVE EMISSION IN NON-EQUILIBRIUM HYPERSONIC FLOW

BY

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THESIS

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ABSTRACT

The thermochemistry of supersonic flows has been studied thoroughly in the context of military aircraft development. Similarly, High speed hypersonic flight has been studied by both defence and civilian entities in the context of re-entry vehicles and spaceflight more generally. Hypersonic flight in regimes which causes little to no ionisation, on the other hand, are still the subject of ongoing studies. The renewed interest by high-tech nations in hypersonic weapons and vehicles has highlighted the general lack of knowledge, as well as the challenge that complex hypersonic flow thermochemistry represents.

Because of compressible flow effects, the chemical reactions and non equilibrium conditions found in the shock regions of hypersonic flows have to be measured using non-invasive optical diagnostic techniques. The creation of Nitric Oxide in hypersonic shocks can be measured both by radiative emission and absorption measurements. NO is an ideal optical diagnostic tool because it has a significant absorption cross section, and is a strong emitter in the IR and the UV. The ability to model radiative emission from NO is therefore crucial to the interpretation of optical diagnostics of hypersonic air flow.

This work focuses on modeling NO radiation in the UV, as well as vibrationally and electronically excited populations of NO. The conditions used for the simulations are a shock tube and a cylinder in a Hypervelocity Expansion Tube (HET) experiment. The simulated
HET conditions present a 2D flow field moving around the cylinder and presents several regions of interest including the bow shock and the expansion region. Overlay techniques are applied to DSMC flow solutions in order to compute radiative emission and transport. Self normalized integrated intensity profiles are computed using the NO $\gamma$, $\beta$, and $\delta$ bands in the 210 nm - 250 nm region for the HET conditions for the HET case. Absolute spectra radiance measurement from a shock tube is simulated, using 1D solutions from several DSMC chemistry sets. Normalized spectra in the 210 nm - 250 nm region are used to extract nonequilibrium temperature by fitting the measurements with synthetic spectra.

The number density of excited species in a flow are one of the challenging parameters to compute when modeling radiative emission. A Quasi Steady state (QSS) overlay method offers an alternative to a Boltzmann calculation for the population of electronically excited species. The prediction of these electronically excited populations are necessary for the modeling of UV radiative emission. The existing collisional-radiative model is expanded with a set of reactions which provide new population mechanisms for electronically excited states of NO and N$_2$. Although not a contributor in terms of radiation in the spectral region of interest, N$_2$ serves as an energy reservoir capable of re-excited quenched NO molecules. The resulting population calculations are compared with Boltzmann calculations for the HET at full density and in rarefied conditions.

A collisional-radiative model for vibrationally excited population analogous to the QSS model is presented. This model uses experimentally determined quenching rates for the first three vibrationally excited states of NO and the first vibrationally excited state of N$_2$ to compute the population of these states. The computation of these states is used for modeling
IR radiative emission and inform absorption experiments. The vibrational collision model is applied as an overlay to the HET DSMC solution, similarly to the QSS computation. Time resolved vibrational calculations are performed at points in the wake region of the HET domain where the residence time of the flow allows for the collisional mechanisms to produce non-Boltzmann populations. Finally, this collisional-radiative model is added to a mass transport solver to determine the first three steady state vibrational populations of NO.
ACKNOWLEDGMENTS

I would like to thank Professor Levin for her continued support and role as a mentor. The progress I made in my understanding of the field of non-equilibrium hypersonics, as well as in academic rigor in general would not have been possible without her. I would also like to thank Dr. Tumuklu and Irmak Karpuzcu for their invaluable work, providing DSMC solutions of great quality without which this work would not be possible. My work with these individuals has been a tremendous source of growth for me and I hope many people will have the chance to benefit from the quality of their character.

I want to acknowledge the essential contribution of Dr. Yanes who, in addition to liberally sharing experimental data, was always willing to discuss the cases studied and share his expertise. In addition, I want to thank Dr. Yanes’ Ph.D advisor, Professor Austin for helping Professor Levin and I interpret and understand the HET experiment data. This work was also facilitated by Dr. Wysong and Dr. Gimelshein who, although not directly involved with the radiation simulations in this work, provided their expertise with DSMC.

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Although there is no discrete boundary between supersonic and hypersonic flow, Hypersonic air flow typically involves chemical reactions. This is because the flow, in regions such as bow shocks, has enough enthalpy to overcome the energy barrier posed by endothermic reactions such as molecular dissociation and recombination. These chemical reactions are responsible for the formation of new species such as atomic oxygen and Nitric Oxide (NO). In addition to these chemical reactions, hypersonic shock layers produce non-equilibrium conditions where the various internal energy modes of molecular species are populated independently. These non-equilibrium effects are particularly important in rarefied conditions where the collision rate between particles is small. Understanding the thermochemistry of hypersonic flow is necessary to the accurate modeling of properties such as heat loads, lift, drag, shock layer interactions, all of which are essential to the design of hypersonic vehicles.

Some measurements of hypersonic flow can be taken by placing pressure transducers and thermocouples on the surfaces of a geometry in an expansion tube or a test vehicle. These direct measurement techniques are powerless to produce information about the physics and chemistry involved in the shock layers however. Optical diagnostics are a powerful method of extracting information such as temperature, pressure, and chemical composition of a gas layer. Among the species present in hypersonic air shock layers, NO is a strong emitter in
the UV. The NO γ bands, caused by the $A^2\Sigma^+ - X^2\Pi$ transition in particular can be easily detected, and produce regular progressions which are sensitive to changes in vibrational and rotational temperatures, making them ideal for diagnosing non-equilibrium environment. In order to use emission measurement, proper modeling of the radiation is required.

Radiation modeling is a mature field, with most of the foundational work done in the 1950’s and 1960’s. Some parameters necessary for the accurate modeling of radiation remain a challenge today, particularly when it comes to predicting electronically excited species populations in non-equilibrium conditions. This work presents the radiation modeling of two sets of experiments, along with new and improved overlay techniques to compute the population of excited species, using the flow field solutions produced by a DSMC code. The first experiment is a cylinder exposed to Mach 7 conditions using air and gas mixtures where the O$_2$ content is changed. DSMC code allows for some flexibility in the free stream conditions, which this work uses to analyse the formation of excited species in ten and a hundred times less dense free stream condition. Radiation simulations for this experiment are modeling UV emission in the 210 nm - 250 nm range. The second experiment is a shock tube where the emission intensity through a band-pass filter centered at 235 ± 7 nm is modeled. The intensity through the band pass is modeled as a function of the effective shock velocity which ranges from 4 to 5.5 km/s.

This work addresses the challenge posed by predicting excited populations by presenting a Collisional-Radiative (CR) population model. More specifically, this work expands the existing CR model to include, in addition to the $A^2\Sigma^+$ state of NO and the $A^3\Sigma_u^+$ state of N$_2$, the $B^2\Pi$, $C^2\Pi$, and $D^2\Sigma$ states of NO, and the $B^3\Pi_g$ and $C^3\Pi_u$ states of N$_2$. The addition
of the NO states allows to better model the NO spectra at wavelengths below 230 nm where these upper states become major contributors. Although the upper states of N\textsubscript{2} included in the expanded CR model do not contribute to the radiation in the UV region of interest to this work, the addition of these states allow for better fidelity in predicting the population of the A\textsuperscript{2}Σ\textsuperscript{u}\textsuperscript{+} state of N\textsubscript{2} which has a long lifetime and acts as an energy reservoir capable of exciting NO. Finally, the formation of NO in hypersonic shocks occurs from reactions which favor high vibrational excitation of the reactants, leading to high vibrational temperature of NO when it is formed. A model is presented which incorporates quenching and excitation rates for the first three vibrationally excited states of NO and the first vibrationally excited state of N\textsubscript{2} and offers insight into the vibrational relaxation process in hypersonic flows.
CHAPTER 2

EMISSION SIMULATION OF HYPersonic FLOW

2.1 Hypersonic Flow Solutions

2.1.1 DSMC parameters

High-Mach number chemically reacting flows are modeled using direct simulation Monte Carlo (DSMC) [1], which is a powerful tool used for the study of complex thermochemical environments involving thermal non-equilibrium and rarefied gas conditions. The Statistical Modeling In Low-density Environment (SMILE) [2] computational solver is used with several different thermochemical models. SMILE employs the majorant frequency scheme [3] for collision modeling. To accurately and efficiently model viscosity-temperature dependence, the Variable Hard Sphere (VHS) [1] model is used in SMILE and the VHS model parameters for the chemical species are given in Table 2.1 at a reference temperature of 1,000K.

In order to understanding the impact of different thermochemical molecular processes on the flowfield parameters and ultraviolet NO spectra, two different thermochemical sets are used. The first model, will be referred to as the $TCE-LB$ model which employs the Larsen-Borgnakke (LB) [4] approach to model rotational-translational (R-T) and vibrational-translational (V-T) energy transfer. More specifically, Millikan and White (MW) [5] and Parker’s rates [6] with the DSMC correction factors [7, 8] were used to model (V-T) and (R-T)
Table 2.1: Constants for the evaluation of cross-sectional and rotational and vibrational relaxation

<table>
<thead>
<tr>
<th>Species</th>
<th>Diameters</th>
<th>Viscosity</th>
<th>$Z_{r,\infty}$</th>
<th>$T^\ast$</th>
<th>$\theta$</th>
<th>Viscosity coefficient, [Nsm$^{-2}$]</th>
</tr>
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<tbody>
<tr>
<td>$N_2$</td>
<td>3.58</td>
<td>0.68</td>
<td>15.70</td>
<td>80</td>
<td>3371</td>
<td>$4.075 \times 10^{-5}$</td>
</tr>
<tr>
<td>$O_2$</td>
<td>3.37</td>
<td>0.68</td>
<td>14.40</td>
<td>90</td>
<td>2256</td>
<td>$4.915 \times 10^{-5}$</td>
</tr>
<tr>
<td>NO</td>
<td>3.41</td>
<td>0.65</td>
<td>5</td>
<td>117</td>
<td>2719</td>
<td>$4.525 \times 10^{-5}$</td>
</tr>
<tr>
<td>N</td>
<td>3.11</td>
<td>0.65</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$3.724 \times 10^{-5}$</td>
</tr>
<tr>
<td>O</td>
<td>2.96</td>
<td>0.65</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$4.391 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

$^a$ at a reference temperature, $T_{\text{ref}} = 1000$ K.

relaxation rates, respectively. Note that this chemistry set uses a continuous internal energy
distribution, the rotational collision number, $Z_r$, determining the probability of rotational
inelastic collision, and the vibrational characteristic temperatures, $\theta$, for each species, are
presented in Table 2.1. On the other hand, the discrete-energy LB model is applied for the
V-T, R-T, and vibration-vibration (V-V) energy transfer in the second thermochemical set
which will be referred to as the *Bias-LB* model. The near-resonant V-V energy transfer
model, although mostly neglected in DSMC, was recently developed by Gimelshein et al. [9]
to study the vibrationally favored dissociation reactions in detail. A high-fidelity extended
Bias-LB model which results in higher dissociation rates when the colliding pair has higher
vibrational energy, often referred to as vibrationally favored dissociation is used in the Bias-
LB model [9]. On the other hand, the TCE-LB model uses the total collision energy (TCE-
LB) where the reaction probability depends upon the total energy of particles, regardless of
their vibrational energy contribution. In the TCE-LB model, the reaction rate, $k$, presented
in the Arrhenius form is given in the following relationship

$$k(T) = AT^n \exp(-E_a/kT) \quad (2.1)$$

where $A$ is the pre-exponential factor, $n$ stands for the temperature-dependence, and $E_a$ is the activation energy. The values for the dissociation and exchange reactions are given in Table 2.2 and are taken from Ref. [9] and Ref. [10] for reaction set A and reaction set B respectively. For the study of the effect of $O_2$ content in the free stream on radiation in the HET experiment, the Bias-LB model with reaction rate set A is used. For the study of the effect of free stream density on radiation, set B (TCE-LB) is used. The Shock tube experiment modeling uses both thermochemical sets A and B in order to compare the two sets.

Table 2.2: Arrhenius rate coefficients for dissociation and exchange reactions used in DSMC simulations

<table>
<thead>
<tr>
<th>Indices</th>
<th>Reaction</th>
<th>$A(m^3/s)$</th>
<th>$n$</th>
<th>$E_a(J)$</th>
<th>$A(m^3/s)$</th>
<th>$n$</th>
<th>$E_a(J)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N+N$_2$ → N+N+N</td>
<td>$6.900 \times 10^{-8}$</td>
<td>-0.50</td>
<td>15.64</td>
<td>$4.981 \times 10^{-8}$</td>
<td>-1.00</td>
<td>15.63</td>
</tr>
<tr>
<td>2</td>
<td>O+N$_2$ → O+N+N</td>
<td>$3.178 \times 10^{-13}$</td>
<td>-0.50</td>
<td>15.61</td>
<td>$4.981 \times 10^{-8}$</td>
<td>-1.60</td>
<td>15.63</td>
</tr>
<tr>
<td>3</td>
<td>N$_2$+N$_2$ → N$_2$+N+N</td>
<td>$7.908 \times 10^{-13}$</td>
<td>-0.50</td>
<td>15.61</td>
<td>$1.162 \times 10^{-8}$</td>
<td>-1.60</td>
<td>15.63</td>
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<td>4</td>
<td>N$_2$+O$_2$ → O$_2$+N+N</td>
<td>$3.178 \times 10^{-13}$</td>
<td>-0.50</td>
<td>15.61</td>
<td>$4.981 \times 10^{-8}$</td>
<td>-1.60</td>
<td>15.63</td>
</tr>
<tr>
<td>5</td>
<td>N$_2$+NO → NO+N+N+N</td>
<td>$3.178 \times 10^{-13}$</td>
<td>-0.50</td>
<td>15.61</td>
<td>$4.981 \times 10^{-8}$</td>
<td>-1.60</td>
<td>15.63</td>
</tr>
<tr>
<td>6</td>
<td>N+O$_2$ → N+O+O</td>
<td>$5.993 \times 10^{-12}$</td>
<td>-1.00</td>
<td>8.197</td>
<td>$3.320 \times 10^{-9}$</td>
<td>-1.50</td>
<td>8.214</td>
</tr>
<tr>
<td>7</td>
<td>O+O$_2$ → O+O+O</td>
<td>$1.498 \times 10^{-10}$</td>
<td>-1.00</td>
<td>8.197</td>
<td>$3.320 \times 10^{-9}$</td>
<td>-1.50</td>
<td>8.214</td>
</tr>
<tr>
<td>8</td>
<td>N$_2$+O$_2$ → N$_2$+O+O</td>
<td>$1.498 \times 10^{-11}$</td>
<td>-1.00</td>
<td>8.197</td>
<td>$3.320 \times 10^{-9}$</td>
<td>-1.50</td>
<td>8.214</td>
</tr>
<tr>
<td>9</td>
<td>O$_2$+O$_2$ → O$_2$+O+O</td>
<td>$5.393 \times 10^{-11}$</td>
<td>-1.00</td>
<td>8.197</td>
<td>$3.320 \times 10^{-9}$</td>
<td>-1.50</td>
<td>8.214</td>
</tr>
<tr>
<td>10</td>
<td>NO+O$_2$ → NO+O+O</td>
<td>$5.993 \times 10^{-12}$</td>
<td>-1.00</td>
<td>8.197</td>
<td>$3.320 \times 10^{-9}$</td>
<td>-1.50</td>
<td>8.214</td>
</tr>
<tr>
<td>11</td>
<td>N+NO → N+N+O</td>
<td>$1.318 \times 10^{-8}$</td>
<td>-1.50</td>
<td>10.43</td>
<td>$8.382 \times 10^{-15}$</td>
<td>0.00</td>
<td>10.42</td>
</tr>
<tr>
<td>12</td>
<td>O+NO → O+N+O</td>
<td>$1.318 \times 10^{-8}$</td>
<td>-1.50</td>
<td>10.43</td>
<td>$8.382 \times 10^{-15}$</td>
<td>0.00</td>
<td>10.42</td>
</tr>
<tr>
<td>13</td>
<td>N$_2$+NO → N$_2$+N+O</td>
<td>$6.590 \times 10^{-10}$</td>
<td>-1.50</td>
<td>10.43</td>
<td>$8.382 \times 10^{-15}$</td>
<td>0.00</td>
<td>10.42</td>
</tr>
<tr>
<td>14</td>
<td>O$_2$+NO → O$_2$+N+O</td>
<td>$6.590 \times 10^{-10}$</td>
<td>-1.50</td>
<td>10.43</td>
<td>$8.382 \times 10^{-15}$</td>
<td>0.00</td>
<td>10.42</td>
</tr>
<tr>
<td>15</td>
<td>NO+NO → NO+N+O</td>
<td>$1.318 \times 10^{-8}$</td>
<td>-1.50</td>
<td>10.43</td>
<td>$8.382 \times 10^{-15}$</td>
<td>0.00</td>
<td>10.42</td>
</tr>
<tr>
<td>16</td>
<td>N+O+O → O+O+O</td>
<td>$4.001 \times 10^{-10}$</td>
<td>0.25</td>
<td>5.288</td>
<td>$9.447 \times 10^{-18}$</td>
<td>0.42</td>
<td>5.928</td>
</tr>
<tr>
<td>17</td>
<td>O+O+O → NO+O</td>
<td>$1.598 \times 10^{-18}$</td>
<td>0.50</td>
<td>0.497</td>
<td>$4.134 \times 10^{-21}$</td>
<td>1.18</td>
<td>0.553</td>
</tr>
<tr>
<td>18</td>
<td>NO+N → N+O</td>
<td>$8.890 \times 10^{-18}$</td>
<td>0.25</td>
<td>0.000</td>
<td>$2.020 \times 10^{-17}$</td>
<td>0.10</td>
<td>0.000</td>
</tr>
<tr>
<td>19</td>
<td>NO+O → O$_2$+N</td>
<td>$5.279 \times 10^{-21}$</td>
<td>1.00</td>
<td>2.719</td>
<td>$1.395 \times 10^{-17}$</td>
<td>0.00</td>
<td>2.653</td>
</tr>
</tbody>
</table>
2.1.2 HET

The cases referred to as Hypersonic Expansion Tube or ”HET” are modeled after an experiment conducted at Caltech by Yanes [11] where a cylinder with a diameter of 31.75 mm and a span of 76.2 mm is placed perpendicular to the free stream path. The free stream conditions for the HET simulation are Mach 7.18, a temperature of 752 K, a static pressure of 824.5 Pa, a density of 3.8 g/m$^3$, a stagnation enthalpy of 8.3 MJ/kg, and a mean free path of 1.86$\times$10$^{-5}$ m. The 2D DSMC solution for the case is presented in Fig. 2.1 and shows the regions of interest around the cylinder. The free stream moves from left to right in the figure as well as in future line plots and contours representing the HET cases. The bow shock is the first region of interest, along with the stagnation region, where the temperatures are the highest (with translational temperature of 6000 - 10000 K) and the most radiation is produced. The flow moves from the shock layer to the expansion region, also referred to as the shoulder of the cylinder in this work, before moving in the wake region where the gas density and temperatures are very low (less than 2000 K). close to the cylinder wall, to the right of the cylinder is a recirculation region which is also characterised by low temperatures and pressure.

For all cases considered in this study the free stream velocity is 3950 m/s in x direction. To see the effect of O$_2$ dissociation on the overall flow field and NO ultraviolet radiation characteristics, four cases with different free stream O$_2$ mole fractions are considered, and the conditions are given in Table 2.3. These simulations are performed using the Bias-LB chemistry set and are referred to in this case as high O$_2$, air, medium O$_2$, and low O$_2$.

The same conditions used in the Bias-LB air case are simulated using the TCE-LB chem-
Figure 2.1: General flowfield characteristics for a hypersonic flow over a cylinder

Table 2.3: Free Stream parameters for the cases [11]

<table>
<thead>
<tr>
<th>Case name</th>
<th>$N_2$ mole fraction</th>
<th>$O_2$ mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low $O_2$</td>
<td>0.937</td>
<td>0.063</td>
</tr>
<tr>
<td>Medium $O_2$</td>
<td>0.895</td>
<td>0.105</td>
</tr>
<tr>
<td>Air</td>
<td>0.790</td>
<td>0.210</td>
</tr>
<tr>
<td>High $O_2$</td>
<td>0.727</td>
<td>0.273</td>
</tr>
</tbody>
</table>

istry set. In addition to the standard air case with a free stream number density of $7.233 \times 10^{22}$ m$^{-3}$, lower density flows with number densities of $7.233 \times 10^{21}$ m$^{-3}$ and $7.233 \times 10^{20}$ m$^{-3}$ are also simulated. These cases are referred to as high density, medium density, and low density cases respectively.

2.1.3 Shock Tube

Both TCE-LB and Bias-LB are used to model the shock tube experiment conducted by Gorelov et al [12]. To model one-dimensional unsteady normal shock simulations for chemically reacting flows [13], a two-dimensional setup taking advantage of the symmetry is used, as can be seen in Fig. 2.2. In particular, the top, bottom, and right boundaries are treated as a specular wall and DSMC particles enter the domain from the left boundary (i.e. inlet),
as shown in Fig. 2.2(a). After the simulation starts, a normal shock starts forming at the right boundary when the particles collide with the right specular boundary. With the march of time, the normal shock moves to the left, and gas downstream of the shock comes into thermal equilibrium, as shown in Fig. 2.2(b).

The conditions inside the shock are time dependent. To understand the time dependency of the shock conditions, the N$_2$ translational temperatures at different times are shown in Fig. 2.3 for V$_\infty$ of 4.0 and 5.4 kms$^{-1}$. The shock positions, x$_1$, x$_2$,..x$_n$, are also given in order to estimate the shock speed for different time intervals. Although the maximum value of the translational temperature does not change significantly at different times, the shock speed tends to decrease in time for both cases because of unsteady conditions downstream of the shock, as can be seen in Fig. 2.3. In particular, the shock speed is estimated as 466 ms$^{-1}$.
between 0.2 and 0.3 ms and it decreases to 446 ms$^{-1}$ between 0.8 and 0.9 ms for the $V_\infty = 4.0$ kms$^{-1}$ case. As expected, the shock speed increases with $V_\infty$, which, in turn, increases the effective Mach number. As shown in Fig. 2.3, the shock speeds between 0.2 and 0.4 ms for the $V_\infty = 4.0$ kms$^{-1}$ and $V_\infty = 5.4$ kms$^{-1}$ cases are 462 ms$^{-1}$ and 506 ms$^{-1}$, respectively. The TCE-LB and Bias-LB models are used to see the effects of different thermochemical models on the shock speeds for the $V_\infty = 5.4$ kms$^{-1}$ case but there is no discernible difference.

![Figure 2.3](image_url)

(a) $V_\infty = 4.0$ km/s  
(b) $V_\infty = 5.4$ km/s

Figure 2.3: Time variation of N$_2$ translational temperatures using the TCE-LB model.
2.2 Modeling Radiative Emission

2.2.1 Diatomic Molecule Spontaneous Emission

The generation of synthetic spectra is essential to the interpretation of emission diagnostics. For an atomic species, the spontaneous spectral emission coefficient can be defined as[14]

\[ \varepsilon_\lambda = g_U N_U A_{UL} h c \phi_\lambda \frac{1}{\lambda^4} \frac{1}{4\pi} \]  

(2.2)

where \( N_U \) is the number density of a nondegenerate upper level, \( g_U \) is the degeneracy of an energy level, \( h \) is the Plank constant, \( c \) is the speed of light, \( \lambda \) is the wavelength of the emitted photon, and \( \phi_\lambda \) is a line shape function. The probability of spontaneous emission of a particle per second from an upper energy of \( E_U \) to a lower energy level, \( E_L \), is known as the Einstein \( A \) coefficient. For a molecular transitions, in addition to electronic transitions, rotational and vibrational transitions must also be considered. Therefore, \( A_{UL} \) is given by[14]

\[ A_{UL} = \left( \frac{64\pi^4 \nu^3_{UL}}{3h} \right) (ea_0)^2 Re q_{V_U V_L} S_{J_U J_L} / (2J_U + 1) \]  

(2.3)

where \( e \) is the electron charge, and \( a_0 \) is the Bohr radius. The line strength factor, \( S_{J_U J_L} \), which is known as the dimensionless H"onl-London factor between the rotational levels of upper, \( J_U \), and lower, \( J_L \), depends on the type of electronic transition and the spin multiplicity as well as rotational quantum number. Likewise, \( q_{V_U V_L} \) is the Franck-Condon factor, which defines the likelihood of a transition between a vibrational energy level in an electronically excited state to another vibrational energy level in another electronic state. Since an electronic transition in a molecule takes place much more rapidly than a vibrational
transition, in a vibronic transition, the nuclei have very nearly the same position and velocity before and after the transition.[15] A transition moment between two vibrational quantum numbers, \( V_U \) and \( V_L \) of different electronic states can, therefore, be approximated by[15]

\[
R_{V_U V_L} = \text{Re} \int \Psi_{V_U} \Psi_{V_L} dr_c
\] (2.4)

where \( \text{Re} \) is an averaged value of the electronic transition moment for a given vibrational transition band. The transition probability is directly proportional to \( R_{V_U V_L}^2 \) or \( |\int \Psi_{V_U} \Psi_{V_L} dr_c|^2 \), where the vibrational overlap integral, \( q_{V_U V_L} = |\int \Psi_{V_U} \Psi_{V_L} dr_c|^2 \). Note that the Franck Condon factor does not depend on species concentrations or temperatures[15].

In Eq. 2.3, \( \tilde{\nu}_{UL} \) is given by

\[
\tilde{\nu}_{UL} = \frac{1}{\lambda_c} = T_{eU} - T_{eL} + [G(V_U) - G(V_L)] + [F(J_U) - F(J_L)]
\] (2.5)

where \( T_e \) is the minimum electronic energy of the potential energy curve for each electronic state, \( G_v \) is the measured vibrational energy with respect to \( T_e \). Similarly, \( F_j \) is the rotational energy measured from \( G_v \). Combining Eqs. 2.2 and 2.3 results in the spontaneous emission coefficient which can be written as[16]

\[
\varepsilon_{\lambda} = \frac{16\pi^3 \tilde{\nu}_{UL}^4 c}{3(2J_U + 1)} (ea_0)^2 N_U g_U \text{Re} q_{V_U V_L} S_{J_U J_L} \phi_{\lambda}
\] (2.6)

The upper state population \( N_U \), is typically computed using a Boltzmann distribution as Eq. 2.7, however this work will present alternative models to predict this upper state population.
\[ N_U = \frac{N_U^c}{(Q_{VR})_U} (2J_U + 1) \exp \left[ -\frac{hc}{k_B} \left( \frac{G(V_U)}{T_{vib}} + \frac{F(J_U)}{T_{rot}} \right) \right] \]  

(2.7)

\[ \frac{N_L}{N_U} = \frac{N_L^c (Q_{VR})_U}{N_U^c (Q_{VR})_L} \left( \frac{2J_L + 1}{2J_U + 1} \right) \exp \left[ \frac{hc}{k_B} \left( \frac{G(V_U) - G(V_L)}{T_{vib}} + \frac{F(J_U) - F(J_L)}{T_{rot}} \right) \right] \]  

(2.8)

where the upper state total partition function, \( Q_{VR} \), is given as [16]

\[ (Q_{VR})_U = \max_{V_U=0} \left[ \max_{J_U=0} (2J_U + 1) \exp \left( -B_{V_U} J_U (J_U + 1) \frac{hc}{k_B T_{rot}} \right) \right] \exp \left( -G(V_U) \frac{hc}{k_B T_{vib}} \right) \]  

(2.9)

where \( T_{rot} \) and \( T_{vib} \) are the rotational and vibrational temperatures, respectively. When fitting synthetic spectra to a measurement, a Root Mean Square (RMS) error function is used to evaluate the fit and is given by

\[ RMS = \sqrt{\frac{\sum_{i=1}^{n} (y'_i - y_i)^2}{n}} \]  

(2.10)

Where \( n \) is the number of points evaluated along the wavelength axis, \( y' \) is the measured data, and \( y \) is the synthetic data. The average intensity through a band-pass filter is calculated using
\[ I_{\text{ave}} = \frac{\int \varepsilon \lambda f(\lambda) d\lambda}{\int f(\lambda) d\lambda} \]  \hspace{1cm} (2.11)

Where \( f(\lambda) \) is a band-pass function centered on the band-pass wavelength.

Figure 2.4 Shows the contributions of different electronically excited states of NO to the UV spectral region of interest, between 210 nm and 250 nm. The electronic states considered for NO are \( A^2\Sigma^+, B^2\Pi, C^2\Pi, \) and \( D^2\Sigma, \) which will be abbreviated in this work to the A, B, C, and D states of NO. Similarly, the electronic states \( A^3\Sigma^+_u, B^3\Pi_g \) and \( C^3\Pi_u \) of \( N_2 \) are abbreviated to the A, B, and C states of \( N_2. \) As expected, the main contributor in this spectral region is NO(\( \gamma \)) which is produced by the NO(A) population. The other bands contributing to the spectra, are produced by higher electronic levels which are less populated. the NO(\( \beta \)) bands produced by the NO(B) population produce a weak signal with no distinguishing spectra features. the NO(\( \delta \)) and NO(\( \varepsilon \)) bands, caused by NO(C) and NO(D) populations respectively, contribute somewhat to the NO(\( \gamma \)) peaks in wavelengths below 227 nm and become significant contributors of the (1,0) peak. NO(\( \gamma \)) is responsible for the major features of the spectra and can be used to estimate rotational and vibrational temperatures, especially when using the (0,1) and (0,2) vibrational peaks which see less emission from other excited states of NO. For this reason, the radiation modeling and analysis for HET cases will also focus on the normalized integrated intensity of NO(\( \gamma \)).
2.2.2 Quasi Steady State Modeling of Electronically Excited NO and N$_2$

The assumption of a Boltzmann distribution for the electronically excited state population fractions given in Eq. 2.8 may fail under nonequilibrium conditions. Therefore, a set of excitation, quenching, and radiative decay mechanisms (see Table 2.4 for details) based on previous comparisons with experiments[17, 18] is solved to obtain more accurate UV emission spectra based on the NO(A) and N$_2$(A) electronically excited state population. The master equations governing the coupled NO(A) and N$_2$(A) excitation are:

$$
\begin{cases}
\frac{d[NO(A)]}{dt} \\
\frac{d[N_2(A)]}{dt}
\end{cases}
= 
\begin{bmatrix}
b_{11} & b_{12} \\
b_{21} & b_{22}
\end{bmatrix}
\begin{bmatrix}
[NO(A)] \\
[N_2(A)]
\end{bmatrix}
+ 
\begin{bmatrix}
a_1 \\
a_2
\end{bmatrix}
$$

(2.12)

where

(a) Contributions of different bands to UV spectra (Tr=Te=5900 K, Tv=6300 K)

(b) Effect of the temperature on NO(γ) spectra

Figure 2.4: Contribution of different NO bands to UV spectra and effect of Tv and Tr temperature changes on molecular emission spectra using Boltzmann statistics.
\[ a_1 = [N \cdot O] (k_{1f} + k_{2f} [M]) + \sum_{i=1}^{5} k_{8,ir} [NO][M]_i \]  
\[ a_2 = [N \cdot N] (k_{3f} + k_{4f} [M]) + \sum_{i=1}^{2} k_{6,if} [N_2][M]_i + \sum_{i=2}^{3} k_{7,ir} [N_2][M]_i \]  
\[ b_{11} = - \left\{ k_{1r} + k_{2r} [M] + k_{5r} [N_2] + \sum_{i=1}^{5} k_{8,if} [M]_i + k_9 \right\} \]

\[ b_{12} = k_{5f} [NO] \]
\[ b_{21} = k_{5r} [N_2] \]
\[ b_{22} = - \left\{ k_{3r} + k_{4r} [M] + k_{5f} [NO] + k_{6,2r} [N_2][M] + \sum_{i=1}^{3} k_{7,if} [M]_i + k_{10} \right\} \]

The square brackets represent number densities, \( k_{if} \) and \( k_{ir} \) are the forward and backward rates of the \( i \)-th reaction (see Table 2.4), \( k_{if,j} \) and \( k_{ir,j} \) are the forward and backward rates of the \( (i,j) \)-th reaction, \([M]\) is the number density of all the heavy-particles, and \([M]_i\) are the number densities of the quencher species associated with the \((6,j),(7,j)\) or \((8,j)\)-th reaction. From these recombination rates determined experimentally, [19], the principle of detailed balance [20] given in eq. 2.19 is used to compute the reverse rate coefficients.

\[ k_{\text{back}} = \frac{k_{\text{forward}}}{K} \]

where \( K \) is the equilibrium constant given by the ratio of the total partition functions involved in an exchange reaction. For an exchange reaction
\[ AB + C \leftrightarrow AC + B \] (2.20)

where molecule AB reacts with atom C to form molecule AC and atom B, the equilibrium constant K is computed as

\[
K = \frac{N_{AC}N_B}{N_{AB}N_C} = \frac{Q_{tAC}Q_{AC}Q_{tB}Q_B}{Q_{tAB}Q_{AB}Q_{tC}Q_C} \exp \left( -\frac{D_0}{k_bT} \right) \quad (2.21)
\]

where, for molecular and atomic species, \( N \) is the number density, \( Q_t \) is the translational partition function, \( Q \) is the internal partition function, \( D_0 \) is the dissociation energy of the reactant molecule, and \( k_b \) is Boltzmann’s constant. Translational and internal partition functions as well as dissociation energies are computed using NEQAIR [21] [14]. For a simple quenching reactions of species B from electronic states A to X by a bystander species, eq. 2.21 simplifies to

\[
K = \frac{N_{B(X)}}{N_{B(A)}} = \frac{Q_{B(X)}}{Q_{B(A)}} \quad (2.22)
\]

where \( Q_{B(X)} \) is the internal partition function of species B in the electronic state X. The translational and internal partition functions are computed respectively as

\[
Q_t = \left( \frac{2\pi mk_bT}{\hbar^2} \right)^{2/3} \quad (2.23)
\]
\[ Q = \sum_e g_e \exp \left( -\frac{E_e}{k_B T} \right) \left[ \sum_v \exp \left( -\frac{G_v}{k_B T} \right) \left( \sum_J (2J + 1) \exp \left( -\frac{F_J}{k_B T} \right) \right) \right] \] (2.24)

where \( m \) is the mass of the spices, \( h \) is Planck’s constant, \( e, v, \) and \( J \) are the electronic, vibrational, and rotational quantum numbers respectively, \( g_e \) is the electronic level degeneracy, and \( E_e \) is the electronic energy level. \( G_v \) and \( F_J \) are the Dunham expressions for the vibrational and rotational energy respectively, as found in Herzberg [22]. When computing the equilibrium constant for simple quenching reactions, the internal partition function for a single electronic state simplifies to

\[ Q = g_e \exp \left( -\frac{E_e}{k_B T} \right) \left[ \sum_v \exp \left( -\frac{G_v}{k_B T} \right) \left( \sum_J (2J + 1) \exp \left( -\frac{F_J}{k_B T} \right) \right) \right] \] (2.25)

The calculated reverse rate constants for each reaction was fitted in the Arrhenius form (Eq. 2.1) and the corresponding rate coefficients are tabulated in Table 2.4.

Under the QSS assumption, the left hand side of Eq. 2.12 is set to zero and the quasi-steady-state number density of NO(A) is solved by

\[ [\text{NO}(A)]_{\text{qss}} = \frac{a_1 b_{22} - a_2 b_{12}}{b_{12} b_{21} - b_{11} b_{22}}. \] (2.26)

Table 2.4 summarizes the values of the rate coefficients used in Eqs. 2.13-2.18 and the mechanisms considered including dissociation/recombination (reactions 1-4), simultaneous excitation/de-excitation (reaction 5), excitation/de-excitation [23] by heavy-particles impact (reactions 6-8), and radiative decays of NO(A) and N\(_2\)(A) (reactions 9 and 10, respectively).
Table 2.4: QSS Excitation, Quenching, and Radiative Decay Rate Coefficients [19].

<table>
<thead>
<tr>
<th>Indices</th>
<th>Reaction</th>
<th>$A^\dagger$</th>
<th>$E_a$ (J)</th>
<th>$A^\ddagger$</th>
<th>$E_a$ (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N+O+NO(A)</td>
<td>8.64×10^{-12}</td>
<td>-0.35</td>
<td>0.00</td>
<td>2.09×10^{-9}</td>
</tr>
<tr>
<td>2</td>
<td>N+O+NO+NO(A)+M</td>
<td>2.48×10^{-13}</td>
<td>-1.24</td>
<td>0.00</td>
<td>5.86×10^{-7}</td>
</tr>
<tr>
<td>3</td>
<td>N+O+NO(A)</td>
<td>8.14×10^{-17}</td>
<td>-0.35</td>
<td>0.00</td>
<td>2.33×10^{-9}</td>
</tr>
<tr>
<td>4</td>
<td>N+O+NO(A)</td>
<td>1.27×10^{-17}</td>
<td>-1.60</td>
<td>0.00</td>
<td>3.64×10^{-2}</td>
</tr>
<tr>
<td>5</td>
<td>N+O+NO(A)+N2</td>
<td>6.64×10^{-11}</td>
<td>0.00</td>
<td>0.00</td>
<td>1.84×10^{-11}</td>
</tr>
<tr>
<td>6.1</td>
<td>N2+NO+NO(A)+N</td>
<td>1.53×10^{-13}</td>
<td>-2.23</td>
<td>1.00×10^{18}</td>
<td>1.31×10^{-13}</td>
</tr>
<tr>
<td>6.2</td>
<td>N2+NO+NO(A)+N</td>
<td>1.83×10^{-13}</td>
<td>-0.50</td>
<td>9.88×10^{18}</td>
<td>1.56×10^{-14}</td>
</tr>
<tr>
<td>7.1</td>
<td>N2(A)+N+NO(A)+N</td>
<td>4.88×10^{-11}</td>
<td>0.00</td>
<td>0.00</td>
<td>5.72×10^{-9}</td>
</tr>
<tr>
<td>7.2</td>
<td>N2(A)+N+NO(A)+O</td>
<td>2.32×10^{-12}</td>
<td>0.00</td>
<td>0.00</td>
<td>2.73×10^{-10}</td>
</tr>
<tr>
<td>7.3</td>
<td>N2(A)+N+NO(A)+O</td>
<td>2.91×10^{-11}</td>
<td>0.00</td>
<td>0.00</td>
<td>2.87×10^{-9}</td>
</tr>
<tr>
<td>8.1</td>
<td>NO(A)+N2+NO(N)</td>
<td>1.15×10^{-11}</td>
<td>0.50</td>
<td>9.70×10^{20}</td>
<td>4.98×10^{-10}</td>
</tr>
<tr>
<td>8.2</td>
<td>NO(A)+O2+NO+O2</td>
<td>9.24×10^{-13}</td>
<td>0.50</td>
<td>0.00</td>
<td>2.87×10^{-9}</td>
</tr>
<tr>
<td>8.3</td>
<td>NO(A)+O+NO+O</td>
<td>3.06×10^{-13}</td>
<td>0.50</td>
<td>0.00</td>
<td>1.30×10^{-9}</td>
</tr>
<tr>
<td>8.4</td>
<td>NO(A)+O+NO+NO</td>
<td>1.69×10^{-11}</td>
<td>0.50</td>
<td>0.00</td>
<td>5.60×10^{-9}</td>
</tr>
<tr>
<td>8.5</td>
<td>NO(A)+N+NO+O</td>
<td>8.64×10^{-12}</td>
<td>0.50</td>
<td>0.00</td>
<td>3.64×10^{-9}</td>
</tr>
<tr>
<td>9</td>
<td>NO(A)→NO+hv</td>
<td>4.70×10^{6}</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>N2(A)+N2+hv</td>
<td>7.70×10^{-2}</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
</tr>
</tbody>
</table>

*Units are in [cm^3/molecule-s] or [cm^2/molecule·s] or [/s]*

Note that the radiative decay of N₂(A) is taken into account in this work. However, as can be seen in Table 2.4, the lifetime of N₂(A) (i.e. 1/A) is about eight orders of magnitude is higher than that of NO(A). Therefore, the radiative decay of N₂(A) can be neglected when one calculates the N₂(A) populations in the vicinity of hypersonic vehicles. Although N₂ does not radiate strongly, it nevertheless plays an important role in the excitation of NO to the A state by virtue of mechanism 5 in Table 2.4. Because of the long lifetime of N₂(A), it can be transported outside of the shock region where it can repopulate the depleted NO(A) populations. With the local NO(A) state populations, the UV in the stagnation region spectra can be computed using the tangent-slab approximation and the accurate, line-by-line spectral line strength database for high temperature NO which has been validated with extensive testing in the NASA Ames Electric Arc Shock Tube (EAST) facility [24].

When looking at time resolved populations of electronically excited states, NO(A) concentration reaches the QSS limit about 0.2 μs whereas the required time to reach the QSS limit for N₂(A) species about 1.75 times longer in comparison to that for NO(A). The residence
time in compression and stagnation regions of the flow in the HET case is several orders of magnitude greater than the time it takes for the QSS reactions to reach steady-state. In these conditions the QSS assumption holds. In expansion regions, the residence times are shorter, comparable to the time it takes for NO(A) to reach steady state.
2.3 Shock tube and HET experiment radiation modeling

2.3.1 HET Normalized Integrated Intensity in the UV

Part of the HET experiment modeling effort is to understand the effect of free stream O$_2$ content on radiation signal emanating from the bow shock. There is sufficient NO in the stagnation zone, with high enough temperatures for the formation of electronically excited states. The excited populations of NO radiate strongly in the UV and are thus useful for emission diagnostics. Figure 2.5 Shows a comparison between two excited state population calculation methods. The Boltzmann population is computed using the partition function of NO summed over electronic, vibrational, and rotational levels. The QSS population, as discussed previously, is computed using a set of chemical reaction and quenching rates. There is a strong agreement between the two population models caused by the higher density found in the stagnation zone. The radiative emission profile along the stagnation streamline is expected to be strongly correlated with the excited NO population number density. Spectra calculations in the UV region of interest (211 nm - 250 nm) are performed using Boltzmann excited populations in the stagnation zone.

Emission spectra calculations are performed using the DSMC flow field Temperatures and ground species. The DSMC code uses the Bias-LB chemistry set to compute a 2D flow field solution for the low, medium, air, and high O$_2$ cases. For these calculations, three excited emission bands of NO are used: NO($\gamma$, $\beta$, $\delta$). These correspond to the most populated electronically excited states of NO and are responsible for the majority of the emission signal in the 210 nm to 250 nm range. The salient feature of the spectra profiles
Figure 2.5: Comparison between Boltzmann and QSS populations for electronically excited states of NO along the stagnation line.

is the presence of four peaks which are part of the progression typical of the NO(γ) bands. The peaks are labeled by their upper and lower vibrational quantum numbers as (1,0), (0,0), (0,1), and (0,2), centered at 215, 225, 235, and 245 nm respectively. In Fig. 2.6, the intensity under each of the four peaks in the spectra is integrated, then plotted as a function of distance to the cylinder wall. Each integrated intensity profile is normalized with respect to the (0,1) peak. The relative proportion of each integrated peak gives some information on the vibrational temperature of the flow as a stronger (1,0) peak relatively to the others indicates a high vibrational temperature. Notably, the overall shape of the profile changes drastically with the free stream O₂ mole fraction. The low and medium O₂ cases show intensity profiles flattening close to the cylinder. In contrast, the air and High O₂ cases have Gaussian-like emission profiles which peak in the midway from the shock front to the cylinder wall. These profiles are driven by the ground NO number density in the flow, which itself is driven primarily by temperature. The temperature in each case is affected by the
\( \text{O}_2 \) content because of the endothermic dissociation it undergoes in the shock region. It is important to note the change in radiation profiles between the \( \text{O}_2 \) content cases is a direct result of the DSMC solution since the upper state population is computed using a standard Boltzmann distribution.

![Normalized intensity profiles integrated over each major vibrational band (1,0), (0,0), (0,1), (0,2) using DSMC flow field and Boltzmann populations for NO(A,B,C)](image)

Figure 2.6: Normalized intensity profiles integrated over each major vibrational band (1,0), (0,0), (0,1), (0,2) using DSMC flow field and Boltzmann populations for NO(A,B,C)

The predicted sensitivity of the integrated intensity profiles to free stream \( \text{O}_2 \) content is highly dependent on the DSMC chemistry set. Although not shown in this work,
DSMC results obtained using the TCE-LB chemistry set showed noticeably different profiles as a function of free stream $O_2$ content. Future experiment results will hopefully provide some insight on the correctness of both chemistry set when simulating HET conditions. The radiation modeling effort presented here allows to rule out the effects of population excitation and optical thickness as contributors to the changing intensity profiles as a function of free stream $O_2$ content.
2.3.2 Shock Tube UV Intensity Through a Band Pass Filter

The experiment by Gorelov et al [12] is an excellent case study to test the accuracy of the two DSMC chemical sets, but also the QSS population model compared to a Boltzmann population. This comparison can be seen in Fig. 2.7 (d) where, predictably, higher effective shock velocities result in higher intensity. The radiation is calculated using flow field outputs from both Bias-LB and TCE-LB, and both Boltzmann and QSS models are used to determine NO(A) population. The radiation intensity is computed using a square band-pass function, averaging the intensity of the synthetic spectra between 228 nm and 242 nm using Eq. 2.11. Although a typical instrument profile would follow a Gaussian curve resulting is slightly lower intensity, a square band-pass function is sufficient for the needs of this study. The radiation transport equation is applied using NEQAIR where the emitting slab of gas is assumed to be homogeneous across the diameter of the shock tube (10.16 cm). The length of line of sight used for the radiation calculation is the reported diameter of the shock tube.

The higher temperatures predicted by the Bias-LB model can also be seen as the TCE-LB shows a lower peak intensity when compared Bias-LB. Figure 2.7 (d) also shows the intensity profile calculated with QSS. QSS and Boltzmann models for NO(A) population calculations predict different amounts of electronically excited emitters in the flow, with QSS’s prediction being lower. This is why the calculated intensity profile is lower when using QSS for a given flowfield.

Figure 2.8 shows the difference between the two electronic excitation calculations. There is little difference in the spectra structure for different velocities because the ratio of rotational to vibrational temperature does not vary much. In addition temperature vari-
Figure 2.7: Variation of the overall translational, the NO vibrational and number density with the streamwise velocity using the TCE-LB model.
ations below 1000 K can be difficult to notice by simple visual inspection of the spectra. Note that the spectra are taken at peak intensity and their structure could vary depending on velocity and chemical model if different spatial points are considered along the x axis at a given time. QSS calculations predict 25% to 35% lower intensity when compared to the Boltzmann calculation. Figure 2.8 (b) compares the calculated peak averaged intensity through the aforementioned band-pass filter centered at 235 ± 7 nm. The best agreement for the peak averaged intensity with the experimental data from Gorelov et al. [12] is obtained by the combination of TCE-LB and QSS models. The intensity measurement was obtained for shock velocities starting at 5 kms$^{-1}$ while this study has effective shock velocities ranging from 4.5 to 5.9 kms$^{-1}$. All models tend to over predict peak intensity, with the Boltzmann Bias-LB model over-predicting the intensity the most. These values are comparable to the predicted intensity values computed by Gorelov et al.

(a) Peak intensity spectra with free stream velocities (b) Peak intensity as a function of effective shock velocity [12]

Figure 2.8: Calculated NO($\gamma$) spectra at peak intensity in the shock tube using Boltzmann and QSS for determining NO(A) population.
2.4 Non-equilibrium Temperature Extraction Through Spectra Fitting

If accurate, synthetic spectra can be fit to a measured spectra in order to obtain the temperatures of emitters in the flow. This can be done independently from any flow simulation and serve as a validation for a flow simulation. As previously discussed, the features of molecular emission spectra are sensitive to temperatures. Figure 2.9 compares the temperatures (Tv and Tr) of NO generated by the bias-LB model to several fitting schemes. The fitting process is done by minimizing the error between measured spectra taken in the bow shock region of the HET cylinder by Yanes [11] and synthetic spectra generated using an array of vibrational (Tv) and rotational (Tr) temperatures. The fitting is done by looping over Tv and Tr in increments of 400 K and minimizing a RMS error, which is computed using Eq. 2.10. Figure 2.9 (a) shows a fit using only NO(γ) and varying Tv and Tr. Because there is only one emitting species involving a single excited state, Te is not relevant in the first fitting scheme. In order to improve the fit, the residual calculation is only computed over the (0,1) and (0,2) peaks which are less affected by bands from other electronically excited states. Figure 2.4 is helpful to understand the contribution of the different electronically excited states to the UV spectra. There are two major disagreements between the temperature profile predicted by the bias-LB model and the fit in Fig. 2.9 (a). First, the fit shows Tr greater than Tv, secondly, all temperatures are greater than those predicted by the bias-LB model. However, the fit does show the temperatures decreasing as the flow moves away from the shock and towards the geometry. Fig. 2.9 (c) shows a contour plot of the RMS values for a point situated in at 2.39 mm from the cylinder wall. There is a large region where
the RMS values are very low, and close to one another. Because of this, small changes in
the synthetic spectra can easily move the best fit temperatures by several thousand degrees
Kelvin along the Tv axis. This is due to the relatively small spectral region used in the fit,
along with the fact that the two peaks used in the fit have the same upper vibrational state,
which gives this fitting scheme a poor resolution of vibrational temperature. Figure 2.9 (c)
shows NO(γ) fitted along the (0,1) and (0,2) peaks alone might not be sufficient to determine
precise non-equilibrium temperature profiles in the shock.

In Fig. 2.9 (b), the fitting is done using NO(γ, β, δ) with a residual computed over 210
nm to 250 nm. Because this fit is computed over a larger spectral region, more emitters
must be included in the radiation model, which adds a level of complexity to the task. In
this case, two additional excited states of NO are included as they affect the region below
227 nm. Tr is set equal to Te, and Tv varies independently. The fit shows Tv greater than
Tr, and the agreement between the bias-LB model and the fitted Tr temperature is good.
Figure 2.9 (d) shows the RMS contour plot corresponding to the same spatial point as in
Figure 2.9 (c), but using the fitting scheme presented in Figure 2.9 (b). Although the over-
all RMS values are greater when using three excited states fitted over 210 - 250 nm, the
temperature fit is better resolved, especially for Tv. The region where RMS values are low
is not as wide as in Figure 2.9 (c), with steeper gradients of RMS values moving away from
the best fit region. The inclusion of the (1,0) peak of the NO(γ) band greatly ameliorates
the estimation of vibrational temperature.

Figure 2.9 shows the importance of simulating smaller contributors to the spectra when
determining temperatures by fitting a broad wavelength region. Accurate temperature mea-
(a) NO(γ) fit over (0,1) and (0,2) peaks

(b) NO(γ,β,δ) fit over 210 nm to 250 nm

(c) Contour plot of RMS values computed for the point 2.39 mm from the cylinder wall, using NO(γ) and (0,1) - (0,2) peaks

(d) Contour plot of RMS values computed for NO(γ,β,δ) over 210 nm to 250 nm

Figure 2.9: NO temperature Fitting of the HET air case (M=7) spectra measurement with a Boltzmann code
surements in non-equilibrium flow is a challenging endeavor which this study does with some success. A significant improvement to this method would involve more accurate modeling of higher electronically excited states as currently, the Boltzmann model tends to over predict their contribution. A good knowledge of contaminants in the flow is also crucial as other emitters can cause noticeable changes in spectra features which affect the fitting results. This fitting efforts show, however, the limitation of using an electronic transitions to resolve multiple temperatures, and perhaps a method involving several spectral regions and more targeted transitions would be better suited for non-equilibrium temperature extraction.
CHAPTER 3

EXPANDED COLLISIONAL-RADIATIVE MODEL FOR ELECTRONIC EXCITATION OF NO AND N2

3.1 Expanded QSS model

The CR model presented in Table 2.4 was an attempt to improve the modeling of NO(A) population and the associated UV emission bands. This CR model included a coupling mechanism between NO and N2 but did not include any of the upper states of either NO or N2. Given the importance of the coupling between between NO(X) and N2(A) as well as the long lifetime of the latter species, the question arises as to whether inclusion of additional electronic states of N2 and NO and mechanisms involving these additional states will have an effect on their steady state distribution in the flow. Even though these additional excited N2 states make only a small contribution to the UV emission spectra due to transitions to the ground state being forbidden, their presence affects the concentration of the energy pooling N2(A) state through both collisional and radiative mechanisms.

An expanded version of the CR mechanisms presented in Table 2.4 that includes additional electronically excited states for NO and N2 was developed. The inclusion of these excited states is necessary to correctly predict radiative emissions below 220 nm and into vacuum UV where the C and D states of NO become the major contributors. The second collisional-radiative model adds the B, C, and D states of NO [25], along with the B and C states...
of N$_2$ [26]. In Table 3.1, process 6 couples the first electronically excited states of NO and N$_2$, as was considered in the first model. The coupling of N$_2$(A) and NO(A) present in the previous model now benefits from more population mechanisms for both NO(A) and N$_2$(A): NO(A) is populated by NO(C) and NO(D) through radiative processes 37 and 38 in Table 3.1, especially in rarefied conditions where collisional mechanisms are weaker. Radiative decay between N$_2$ electronically excited states is more complex than for NO, for which most transitions between electronic states are allowed. The prevalence of forbidden transitions favors certain radiative decay paths form the upper states to the lower states in N$_2$ [26]. The N$_2$(A) to N$_2$(X) transition is forbidden leading to a very long life time of N$_2$(A) in low density flow regions, where N$_2$(A) is not rapidly quenched by other species. In those regions, N$_2$(A) can excite NO into the A state. N$_2$(A) is populated through radiative decay from N$_2$(B) via an allowed transition described by process 54. Similarly, N$_2$(B) is populated by N$_2$(C) by processes 55. These radiative decay mechanisms become significant in rarefied conditions, however, the expanded model also adds reaction coupling N$_2$(A) and N$_2$(B) through collision mechanism which help populate N$_2$(A) in high density regions as well through processes 44 to 48 in Table 3.1. As for the CR model presented before, a set of forward quenching reactions rates [25] [27] [28] [29] are used to compute reverse rates using microscopic reversibility and the detailed balance [20] given in eq. 2.19.

Forward rates are temperature dependent because of the temperature exponent in the Arrhenius expression as seen in Eq. 2.1. The equilibrium constant $K$ also depends on temperature by virtue of Eq. 2.23 and 2.24. Therefore, backward rates are computed over a range of temperatures in order to be fitted fitted to an Arrhenius form. A single temperature
is used in Eq. 2.23 and 2.24 for the fitting of $k_{\text{back}}$. Figure 3.1 shows the fit of mechanism 44b.

![Figure 3.1: backward rate fit for mechanism 44](image)

The QSS matrix is set up as shown in Eq. 3.1. As per the definition of QSS, the speed of the reactions is assumed to be very fast where population number density can be resolved for every spatial point in the flow. The left hand side terms of the equations are set to zero and the excited state species populations can be solved for directly. Equations 3.2 to 3.22 describe the entries of the matrix. the species labeled ”M” represents the total number density for atomic and molecular species. unless explicitly defined, all entries of the matrix are zero.
Table 3.1: Expanded Collisional-Radiative Model Excitation, Quenching, and Radiative Decay Rate Coefficients

<table>
<thead>
<tr>
<th>Indices</th>
<th>Reaction</th>
<th>Forward rate coefficients</th>
<th>Backward rate coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$A^m$</td>
<td>$m$</td>
</tr>
<tr>
<td>1</td>
<td>NO+M+hν+NO(A)+N+M</td>
<td>$1.28 \times 10^{-27}$</td>
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<tr>
<td>2</td>
<td>NO+M+hν+NO(A)+N+M</td>
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<tr>
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<tr>
<td>4</td>
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<td>-0.05</td>
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<tr>
<td>5</td>
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<td>$8.14 \times 10^{-17}$</td>
<td>-0.05</td>
</tr>
<tr>
<td>6</td>
<td>NO+M+hν+NO(A)+N+M</td>
<td>$3.3 \times 10^{0}$</td>
<td>-0.00</td>
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<tr>
<td>7</td>
<td>NO+M+hν+NO(A)+N+M</td>
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<tr>
<td>8</td>
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<tr>
<td>9</td>
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<tr>
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<tr>
<td>12</td>
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</tr>
<tr>
<td>13</td>
<td>NO+M+hν+NO(A)+N+M</td>
<td>$8.14 \times 10^{−17}$</td>
<td>-0.05</td>
</tr>
</tbody>
</table>

Units are in [cm²/molecule-s] or [cm²/molecule-s] or [s⁻¹].
\[
\begin{align*}
\frac{d[\text{NO}(A)]}{dt} &= \begin{bmatrix}
    b_{11} & b_{12} & b_{13} & b_{14} & b_{15} & b_{16} & b_{17} \\
    b_{21} & b_{22} & b_{23} & b_{24} & b_{25} & b_{26} & b_{27} \\
    b_{31} & b_{32} & b_{33} & b_{34} & b_{35} & b_{36} & b_{37}
\end{bmatrix} \begin{bmatrix}
    [\text{NO}(A)] \\
    [\text{N}_2(A)] \\
    [\text{NO}(B)]
\end{bmatrix} + \begin{bmatrix}
    a_1 \\
    a_2 \\
    a_3
\end{bmatrix} \\
\frac{d[\text{NO}(C)]}{dt} &= \begin{bmatrix}
    b_{41} & b_{42} & b_{43} & b_{44} & b_{45} & b_{46} & b_{47} \\
    b_{51} & b_{52} & b_{53} & b_{54} & b_{55} & b_{56} & b_{57} \\
    b_{61} & b_{62} & b_{63} & b_{64} & b_{65} & b_{66} & b_{67}
\end{bmatrix} \begin{bmatrix}
    [\text{NO}(C)] \\
    [\text{NO}(D)] \\
    [\text{N}_2(B)]
\end{bmatrix} + \begin{bmatrix}
    a_4 \\
    a_5 \\
    a_6
\end{bmatrix} \\
\frac{d[\text{N}_2(A)]}{dt} &= \begin{bmatrix}
    b_{71} & b_{72} & b_{73} & b_{74} & b_{75} & b_{76} & b_{77}
\end{bmatrix} \begin{bmatrix}
    [\text{N}_2(A)] \\
    [\text{N}_2(C)]
\end{bmatrix} + \begin{bmatrix}
    a_7
\end{bmatrix}
\end{align*}
\]

where

\[
\begin{align*}
a_1 &= - \{[\text{N}][\text{O}] (k_{4f} + k_{2f}[M]) + [\text{NO}][([\text{N}_2]k_{12b} + [\text{O}_2]k_{13b} + [\text{O}]k_{14b} \\
+ [\text{NO}]k_{15b} + [N]k_{16b}) \} \\

a_2 &= - \{[\text{N}]^2 (k_{3f} + k_{1f}[M]) + [\text{N}_2]([\text{N}_2]k_{8f} + [\text{O}_2]k_{10b} + [\text{O}]k_{11b} + [N]k_{7b}) \} \\

a_3 &= - \{[\text{NO}][([\text{NO}]k_{17b} + [\text{O}_2]k_{18b} + [\text{N}_2]k_{19b} + [N]k_{20b} + [\text{O}]k_{21b}) \} \\

a_4 &= - \{[\text{N}][\text{O}]k_{5b} + [\text{NO}][([\text{NO}]k_{22b} + [\text{O}_2]k_{23b} + [\text{N}_2]k_{24b} + [N]k_{25b} + [\text{O}]k_{26b}) \} \\

a_5 &= - \{[\text{NO}][([\text{NO}]k_{27b} + [\text{O}_2]k_{28b} + [\text{N}_2]k_{29b} + [N]k_{30b} + [\text{O}]k_{31b}) \} \\

a_6 &= - \{[\text{N}_2][([\text{NO}]k_{39b} + [\text{O}_2]k_{40b} + [\text{N}_2]k_{41b} + [N]k_{42b} + [\text{O}]k_{43b}) \} \\

a_7 &= - \{[\text{N}_2][([\text{NO}]k_{49b} + [\text{O}_2]k_{50b} + [\text{N}_2]k_{51b} + [N]k_{52b} + [\text{O}]k_{53b}) \}
\end{align*}
\]
\[ b_{11} = - \{ [M]k_{2b} + [N_2]k_{4b} + [NO]k_{15f} + [O_2]k_{13f} + [O]k_{14f} + [N]k_{16f} + k_{4b} + k_{32f} \} \quad (3.9) \]

\[ b_{12} = [NO]k_{6f} \quad (3.10) \]

\[ b_{14} = k_{37f} \quad (3.11) \]

\[ b_{15} = k_{38f} \quad (3.12) \]

\[ b_{21} = [N_2]k_{6b} \quad (3.13) \]

\[ b_{22} = - \{ k_{3b} + k_{33f} + [M]k_{1b} + [NO](k_{6f} + k_{44b}) + [N_2](k_{46b} + k_{38b}) +
\quad [O_2](k_{10f} + k_{45b}) + [N](k_{9f} + k_{47b}) + [O](k_{11f} + k_{48b}) \} \quad (3.14) \]

\[ b_{26} = - \{ [NO]k_{44f} + [N_2]k_{46f} + [O_2]k_{45f} + [N]k_{47f} + [O]k_{48f} + k_{54f} \} \quad (3.15) \]

\[ b_{33} = - \{ [NO]k_{17f} + [O_2]k_{18f} + [N_2]k_{19f} + [N]k_{20f} + [O]k_{21f} + k_{34f} \} \quad (3.16) \]

\[ b_{44} = - \{ k_{5f} + [NO]k_{22f} + [O_2]k_{23f} + [N_2]k_{24f} + [N]k_{25f} + [O]k_{26f} + k_{35f} + k_{37f} \} \quad (3.17) \]

\[ b_{55} = - \{ [NO]k_{27f} + [O_2]k_{28f} + [N_2]k_{29f} + [N]k_{30f} + [O]k_{31f} + k_{36f} + k_{38f} \} \quad (3.18) \]

\[ b_{62} = [NO]k_{44b} + [O_2]k_{45b} + [N_2]k_{46b} + [N]k_{47b} + [O]k_{48b} \quad (3.19) \]

\[ b_{66} = - \{ k_{54f} + [NO](k_{39f} + k_{44f}) + [N_2](k_{41f} + k_{46f}) + [O_2](k_{40f} + k_{45f}) +
\quad [N](k_{42f} + k_{47f}) + [O](k_{43f} + k_{48f}) \} \quad (3.20) \]

\[ b_{67} = k_{55f} \quad (3.21) \]

\[ b_{77} = - \{ [NO]k_{49f} + [O_2]k_{50f} + [N_2]k_{51f} + [N]k_{52f} + [O]k_{53f} + k_{55f} \} \quad (3.22) \]
3.2 Modeling of electronically excited populations in HET conditions

3.2.1 Comparison Between the Expanded CR and Boltzmann

Figure 3.2 shows a comparison of the NO(A) number density contour in the bow-shock region between QSS with the expanded CR mechanisms and Boltzmann populations in the low, medium, and high density cases. The expanded CR model predicts an NO(A) population in the bow-shock very close to the Boltzmann limit, which can be seen also in Fig. 3.3(a). As expected, lower free stream densities cause the excited state populations to decrease in comparison to the Boltzmann limit. Figures 3.2(b) and 3.2(c) clearly show the relative decrease in NO(A) number density for the expanded CR when compared to the Boltzmann Calculation.

The addition of the B, C, and D states of NO to the expanded CR model enables the modeling of relative contribution of their respective bands to the UV spectrum. Although the NO(A) state responsible for the $\gamma$ bands dominates the UV-C spectrum, with the $\beta$ bands from the NO(B) producing a base signal on top of which $\gamma$ bands sit, the other excited states contribute significantly to the spectrum below 220 nm and dominate in the vacuum UV region. Figures 3.3, 3.4, and 3.5 compare the expanded CR population calculation along the stagnation streamline of each excited state in the model with the Boltzmann limit for the high, medium, and low density cases. As was the case for Fig. 3.2(a), the excited state populations are close to the Boltzmann limit in Fig. 3.3. Notably, Fig. 3.3(c) and 3.4(c) show a expanded CR populations slightly higher than the Boltzmann limit. This is due to the sensitivity of the expanded CR calculation to the forward and back rates where small
Figure 3.2: Contours for QSS NO(A) Number Density
changes in the rate tied to abundant species such as $N_2$ can affect the population prediction by 0 - 5%. Practically, the populations in the bow shock region of the flow for the high and medium density cases follow a Boltzmann distribution. The profile shape difference between NO and $N_2$ species is driven by the ground state species number density and the bulk translational temperature profiles. Since $N_2$ in the ground state is already abundant in the free stream, the excited $N_2$ populations depend entirely on the translational temperature. As seen in the DSMC results, the translational temperature spikes in the shock front, leading to large populations of excited $N_2$. The excited NO populations, although also driven by the translational temperature, are limited by the small amount of NO in the ground state produced in the shock, resulting in a Gaussian-like profile in the high density case.

Similarly, the excited state populations profiles in the medium density case are also driven by the ground state populations and temperature profiles. The population profiles of NO species peak much closer to the cylinder wall because of the slower creation of ground state NO in the bow-shock. Figures 3.4(d) and 3.4(e) show a decrease in their respective excited state species populations compared to the Boltzmann populations and the high density case. This trend, which is even more prominent in the low density case as seen in Fig. 3.5, is caused by the importance of spontaneous radiative decay rates in low density cases. This is because radiative decay mechanisms are not dependent on the presence of another species to affect the population calculation, and therefore become more important in rarefied conditions when compared to collision quenching and excitation mechanisms. Although lower excited electronic energy states such as NO(A) are also depleted by a strong radiative decay, they are populated by the decay of the high states through radiative mechanisms such as 37 and
Figure 3.3: High Density Stagnation Line Number Densities
This trend also explains the sharp decrease in \( \text{N}_2(C) \) population as seen in Fig. 3.4(g) caused by the short lifetime of the C state, which has a strong allowed decay path to the B state. As a result, \( \text{N}_2(C) \) diverges more quickly from the Boltzmann limit as density decreases when compared to \( \text{N}_2(A) \) or \( \text{N}_2(B) \).

![Graphs showing the number densities for various species](image)

**Figure 3.4: Medium Density Stagnation Line Number Densities**

In Fig. 3.5 for the low density case, there is a decrease in expanded CR populations for
all excited species compared to the Boltzmann limit and other density cases. As expected, this effect is the strongest for excited state populations of high energy states with strong radiative transitions. The A, C, and D states of NO along with the C state of N$_2$ are the most affected. Figure 3.5(g) is plotted on a log scale for the number density. Remarkably, N$_2$(A) and N$_2$(B) expanded CR populations do not decrease as much in the low density case when compared to excited NO populations. This is again due to the slow radiative decay of these states, with N$_2$(A) being a dark state because the transition to the ground state is spin forbidden. This means that in conditions of reduced quenching, such as the case for lower density flows, the N$_2$(A) state will have a very long lifetime in comparison to NO excited states. Furthermore, mechanism 6 in Table 3.1 is a coupling mechanism between N$_2$(A) and NO(A). It is therefore likely that coupling mechanisms between N$_2$(A), N$_2$(B), and to a less extent N$_2$(C), allows the population of the NO(A) state outside of the shock region due to the transport of the excited N$_2$ species created in the shock.
Figure 3.5: Low Density Stagnation Line Number Densities
3.2.2 Comparison Between expanded CR and Old CR

It is useful to compare the expanded CR model with the old CR model Shown in Table 2.4. Because The older version of the CR only models NO(A) and N$_2$(A) populations, those species are used to compare the two models. Figure 3.6 shows contour comparisons of both excited species number densities on an exponential scale for the high density case. From the contours, it is apparent there are no large differences between the models and the excited populations are similar throughout the geometry. The only exception is the N$_2$(A) population directly in the shock front, where the expanded CR predicts three times more N$_2$(A). This is more apparent in Fig 3.6 showing the line plots of the species populations, where the expanded CR predicts higher N$_2$(A) populations closer to the Boltzmann limit as seen in Fig. 3.3(b). The reason for this difference is the coupling of N$_2$(A) and N$_2$(B) through reactions 44 to 48, and to a lesser extent, the radiative decay from N$_2$(B) to N$_2$(A).

![Figure 3.6: High Density Case Comparison of CR Models for NO(A) and N$_2$(A)](image)

NO(A) population on the other hand doesn’t change noticeably in any regions of the flow which is expected as the expanded CR doesn’t introduce any new mechanisms for NO(A) apart from the radiative decay from the C and D states into the A state. The trend seen for this case is confirmed for lower density cases where the N$_2$(A) population is 5 times larger in
the stagnation region for the expanded CR compared to the old CR in the medium density case. The NO(A) population remain in good agreement at lower density, although the effects of the new radiative decay mechanisms are more pronounced at lower densities, resulting in the expanded CR predicting 10% more NO(A) compared to the old CR for the medium density case. The increased N$_2$(A) predicted by the expanded CR in the shock front region could result in more N$_2$(A) being transported to the wake region of the flow once added as a source term to the mass transport model. This increase in N$_2$(A) could in turn, and especially for lower density conditions, create NO(A) in these regions through mechanism 6 listed in Table 3.1.
Figure 3.7: High Density Case Comparison of CR Models for NO(A) and N\textsubscript{2}(A) Along the Stagnation Line and Vertical Shoulder Line at x=17mm
CHAPTER 4

COLLISIONAL-RADIATIVE MODEL FOR VIBRATIONAL EXCITATION OF NO AND N2

4.1 Time Accurate Vibrational Excitation Solver

The challenge of correctly predicting upper state populations of electronically excited species translates to other molecular excitation modes. Vibrationally excited states of diatomic molecules are typically responsible for emission and absorption bands in the infrared (IR). The fundamental vibrational transition of NO is defined by the first vibrational state transitioning to the ground vibrational state inside the ground electronic state. The resulting emission band is the IR starting at 5 microns. Transition from the second vibrational state to the first, and third to the second are responsible for overtones which can be detected with a high enough spectrometer resolution. Correctly modeling the transitions associated with the first three vibrational levels is valuable as it allows a better resolution of vibrational temperatures when performing optical diagnostics. As seen with the spectra fitting, simply relying on vibrational bands in electronic transitions may not be sufficient to resolve vibrational temperature. Thus, an accurate model for predicting vibrational populations inside the ground electronic state is desirable. For this vibrational CR model, forward reaction rates were obtained through a literature search where the quenching rate coefficients of vibrationally excited N₂ and NO are determined experimentally. In addition, the radiative
lifetimes of these vibrational states are also found in literature and are converted to Einstein A coefficients. The principle of detailed balance is used to compute the reverse rate coefficients and is given in eq. 4.1.

$$k_{\text{back}} = \frac{k_{\text{forward}}}{K}$$  \hspace{1cm} (4.1)

where $K$ is the equilibrium constant computed by the ratio of the vibrational partition functions for two states involved in the quenching reaction. Reaction 4.2 is given as a typical quenching reaction to illustrate the computation of reverse rates. In this case, the forward rate corresponds to the reaction direction indicated by the arrow. Therefore, for reaction 4.2, the equilibrium constant is given by eq. 4.3

$$A(1) + B(0) \rightarrow A(0) + B(0) \hspace{1cm} (4.2)$$

$$K = \frac{Q(0)_A}{Q(1)_A} \hspace{1cm} (4.3)$$

The vibration levels partition function are computed with the Boltzmann expression shown in eq. 4.4 using the discrete energy level $E$ for the vibrational levels of interests

$$Q(v) = exp\left(\frac{-E(v)}{k_bT}\right) \hspace{1cm} (4.4)$$

where
\[ E(v) = c \times h \times G(v) \] (4.5)

\[ G(v) = \omega_e(0.5 + v) - \omega_e \chi_e(0.5 + v)^2 \] (4.6)

These reverse rates are computed for a set of temperature values ranging from 300 K to 7000 K with steps of 100 K. The data set is then fit to a curve according to eq. 4.7

\[ k_{\text{back}}(T) = \exp\left(\frac{a}{T} + b\right) \] (4.7)

where \( a \) and \( b \) are determined in the fitting process. Figure 4.1 shows the fit of rate coefficient \( k_{1b} \).

![Figure 4.1: Fit of reverse rate from forward rate and detailed balance](image)

The forward and reverse rate coefficients and fit parameters are presented in table 4.1.

Given the ground state number densities of \( N_2 \), \( O_2 \), NO, N, and O, and the bulk translational temperature of the flow at the location of interest, a time dependent population
Table 4.1: Vibrational Excitation, Quenching, and Radiative Decay Rate Coefficients

<table>
<thead>
<tr>
<th>Indices</th>
<th>Forward rate coefficients</th>
<th>Backward rate coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO(1)+N₂(0)+NO(0)+N₂(0)</td>
<td>1.70×10⁻¹⁸</td>
</tr>
<tr>
<td>2</td>
<td>NO(1)+O₂+NO(0)+O₂</td>
<td>2.40×10⁻¹⁴</td>
</tr>
<tr>
<td>3</td>
<td>NO(1)+NO(0)+NO(0)+NO(0)</td>
<td>7.60×10⁻¹⁴</td>
</tr>
<tr>
<td>4</td>
<td>NO(1)+N+NO(0)+N</td>
<td>3.50×10⁻¹¹</td>
</tr>
<tr>
<td>5</td>
<td>NO(1)+O+NO(0)+O</td>
<td>3.50×10⁻¹¹</td>
</tr>
<tr>
<td>6</td>
<td>NO(1)+NO(1)+NO(2)+NO(0)</td>
<td>2.00×10⁻¹²</td>
</tr>
<tr>
<td>7</td>
<td>NO(2)+NO(2)+NO(3)+NO(1)</td>
<td>3.00×10⁻¹²</td>
</tr>
<tr>
<td>8</td>
<td>NO(2)+NO(1)+NO(3)+NO(0)</td>
<td>3.00×10⁻¹²</td>
</tr>
<tr>
<td>9</td>
<td>NO(2)+NO(0)+NO(1)+NO(0)</td>
<td>1.54×10⁻¹³</td>
</tr>
<tr>
<td>10</td>
<td>NO(2)+O₂+NO(0)+O₂</td>
<td>6.00×10⁻¹⁴</td>
</tr>
<tr>
<td>11</td>
<td>NO(3)+NO(0)+NO(2)+NO(0)</td>
<td>3.00×10⁻¹²</td>
</tr>
<tr>
<td>12</td>
<td>N₂(1)+O+N₂(0)+NO(0)</td>
<td>3.00×10⁻¹⁵</td>
</tr>
<tr>
<td>13</td>
<td>N₂(1)+O+N₂(0)+O</td>
<td>3.50×10⁻¹⁵</td>
</tr>
<tr>
<td>14</td>
<td>N₂(1)+N+N₂(0)+N</td>
<td>3.50×10⁻¹⁵</td>
</tr>
<tr>
<td>15</td>
<td>N₂(1)+NO(0)+NO(0)+NO(1)</td>
<td>2.00×10⁻¹²</td>
</tr>
<tr>
<td>16</td>
<td>NO(1)+NO(0)+hv</td>
<td>1.10×10⁺⁰¹</td>
</tr>
<tr>
<td>17</td>
<td>NO(2)+NO(0)+hv</td>
<td>5.00×10⁻¹</td>
</tr>
<tr>
<td>18</td>
<td>NO(2)+NO(1)+hv</td>
<td>2.00×10⁺⁰¹</td>
</tr>
<tr>
<td>19</td>
<td>NO(3)+NO(2)+hv</td>
<td>2.90×10⁺⁰¹</td>
</tr>
<tr>
<td>20</td>
<td>NO(3)+NO(1)+hv</td>
<td>1.50×10⁺⁰⁰</td>
</tr>
<tr>
<td>21</td>
<td>NO(3)+NO(0)+hv</td>
<td>5.00×10⁻⁰¹</td>
</tr>
<tr>
<td>22</td>
<td>N₂(1)+N₂(0)+hv</td>
<td>0.00×10⁺⁰⁰</td>
</tr>
</tbody>
</table>

* Units are in [cm³/molecule-s] or [cm⁶/molecule²-s] or [/s]
calculation gives the excited state populations for NO(1,2,3) and N\(_2\)(1). The integration methods used for this calculation are a first order Euler scheme as well as a Runge-Kutta 4 method, the two methods give identical results down to the fourth significant figure using a time step of 10\(^{-7}\)s over 0.1 s. Every excited state species is given a starting population value corresponding to the Boltzmann value at species specific vibrational temperature. The population for each species is updated at each time step using equations 4.8, 4.9, 4.10, and 4.11.

\[
\frac{d[NO(1)]}{dt} = [NO]\{k_{1b}[N_2] + k_{2b}[O_2] + k_{3b}[NO] + k_{4b}[N] + k_{5b}[O] + k_{15f}[N_2(1)] + k_{6b}[NO(2)] + k_{8b}[NO(3)] + k_{9f}[NO(2)]\} - [NO(1)]\{k_{1f}[N_2] + k_{2f}[O_2] + k_{3f}[NO] + k_{4f}[N] + k_{5f}[O] + k_{15b}[N_2] + k_{6f}[NO(1)] + k_{7b}[NO(3)] + k_{8f}[NO(2)] + k_{9b}[NO] + k_{16f}\} + [NO(2)](k_{18f} + k_{7f}) + k_{20f}[NO(3)]
\]

(4.8)

\[
\frac{d[NO(2)]}{dt} = -[NO(2)]\{k_{6b}[NO] + k_{7f}[NO(2)] + k_{8f}[NO(1)] + k_{9f}[NO] + k_{10f}[O_2] + k_{11b}[NO] + k_{18f} + k_{17f}\} + [NO(3)]\{k_{7b}[NO(1)] + k_{8b}[NO] + k_{11f}[NO] + k_{19f}\} + [NO(1)]\{k_{6f}[NO(1)] + k_{9b}[NO]\} + k_{10b}[NO]
\]

(4.9)
\[
\frac{d[NO(3)]}{dt} = -[NO(3)]\{k_{7b}[NO(1)] + k_{3b}[NO] - k_{11f}[NO] + k_{19f} + k_{20f} + k_{21f}\} \\
+ [NO(2)]\{k_{8f}[NO(1)] - k_{11b}[NO] + k_{7f}[NO(2)]\}
\]

\[
(4.10)
\]

\[
\frac{d[N_2(1)]}{dt} = [N_2]\{k_{12b}[NO] + k_{13b}[O] + k_{14b}[N] + k_{15b}[NO(1)]\} \\
- [N_2(1)]\{k_{12f}[NO] + k_{13f}[O] + k_{14f}[N] + k_{15f}[NO] + k_{22f}\}
\]

\[
(4.11)
\]

Because the vibrationally exited states are populated on the same order of magnitude as
the ground vibrational state at high temperatures (greater than 5500 K), the assumption
that the ground state population is constant does not hold. Therefore is necessary to fix
the ground vibrational state populations of NO and N\textsubscript{2} using the Boltzmann population at
T=T\textsubscript{trn}. The final populations of NO and N\textsubscript{2} should not exceed the input total population
for these species, which is ensured by Eq. 4.12 and 4.13

\[
[NO] = \sum_{v=0}^{n}[NO(v)]
\]

\[
(4.12)
\]

\[
[N_2] = \sum_{v=0}^{n}[N_2(v)]
\]

\[
(4.13)
\]
Table 4.2: Flow conditions at the five points around the cylinder

<table>
<thead>
<tr>
<th>region</th>
<th>Bulk $T_{\text{trn}}$ (K)</th>
<th>$[\text{O}]^a$</th>
<th>$[\text{N}]$</th>
<th>$[\text{N}_2]$</th>
<th>$[\text{O}_2]$</th>
<th>$[\text{NO}]$</th>
<th>NO $T_v$ (K)</th>
<th>$[\text{N}_2]$ $T_v$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7398</td>
<td>1.766E+16</td>
<td>3.793E+14</td>
<td>3.496E+17</td>
<td>8.388E+1</td>
<td>1.427E+15</td>
<td>9723</td>
<td>2789</td>
</tr>
<tr>
<td>2</td>
<td>5278</td>
<td>1.271E+17</td>
<td>1.410E+15</td>
<td>4.762E+17</td>
<td>4.689E+16</td>
<td>4.448E+16</td>
<td>6235</td>
<td>5372</td>
</tr>
<tr>
<td>3</td>
<td>3280</td>
<td>2.930E+16</td>
<td>4.970E+13</td>
<td>1.323E+17</td>
<td>1.714E+16</td>
<td>9.105E+15</td>
<td>5433</td>
<td>4950</td>
</tr>
<tr>
<td>5</td>
<td>1108</td>
<td>3.311E+15</td>
<td>7.925E+11</td>
<td>1.227E+16</td>
<td>1.270E+15</td>
<td>9.267E+14</td>
<td>5135</td>
<td>5095</td>
</tr>
</tbody>
</table>

$^a$ Units are in molecules/cm$^3$

Figure 4.2 shows five spatial points from the TCE-LB simulated flowfield produced using the HET-air case at full density. Each point is a DSMC cell with dimension 0.1 mm by 0.1 mm. The vibrational populations of NO and $N_2$ are computed over time in a variety of flow conditions such as strong non-equilibrium in the shock front, to more relaxed conditions and high density in the bow shock close to the cylinder. Points in the expansion region and the wake are also used. The specific conditions at each point are given by Table 4.2.

Figure 4.2: Five regions sampled from the HET-air case
4.2 OD Vibrational Population Calculations in HET

The vibrational populations are initialized using a Boltzmann distribution and the species specific vibrational temperature for each spatial point. Because the quenching and excitation mechanisms used in this model are based on collisional energy exchanges, the bulk translational temperature is used to drive the backwards rates. Figures 4.3 through 4.7 show the time accurate change in vibrational populations for NO and \( \text{N}_2 \) for each of the five spatial points selected. Each figures shows a separate plot for NO and \( \text{N}_2 \) with a log time axis and a linear scale for the number densities. A plot showing all the species together is plotted on a log-log scale for reference.

![Figure 4.3: Populations of Vibrationally Excited States of NO and \( \text{N}_2 \) at Point 1](image)

For all spatial points, the behavior of vibrational population over time is the same. The populations move from their initialized value to the Boltzmann limit set by the bulk translational temperature. The NO vibrational populations take \( 10^{-4} \text{ s} \) to reach equilibrium and \( 10^{-2} \text{ s} \) for \( \text{N}_2 \). The change in vibrational populations over time is small and is proportional to the level of non-equilibrium at the point of interest. In Fig. 4.4, the temperatures are close to equilibrium, so the differences between the initial and final vibrational populations are very small.
Figure 4.4: Populations of Vibrationally Excited States of NO and N\textsubscript{2} at Point 2

Figure 4.5: Populations of Vibrationally Excited States of NO and N\textsubscript{2} at Point 3

Figure 4.6: Populations of Vibrationally Excited States of NO and N\textsubscript{2} at Point 4
Figures 4.8 Shows calculations for time accurate vibrational populations of points 4 starting at a Boltzmann population set by the species specific vibrational temperature and moving towards a translational temperature distribution using the collisional quenching and excitation mechanisms outlined in the model. The residence time is calculated by dividing the cell dimension (0.1 mm on a side) by the bulk flow velocity magnitude. Point 2 in particular is a point where the flow velocity is low on the order of 130 m/s) due to its proximity to the stagnation point. The time frames associated with points 1 and 2 are $10^{-7}$ s and $70^{-7}$ s respectively. These residence times are too short for the time it takes for the vibrational populations to reach equilibrium which explain why the populations after these short time frames are very close to the initial conditions set with the species specific vibrational temperatures.
Figure 4.8: Effect of atomic species and N\textsubscript{2} coupling mechanisms on NO(1) population kinetics at point 4

4.3 Non-Boltzmann vibrational populations in regions of high residence time

The recirculation region in the wake of the cylinder is characterized by very low velocities. Figure 4.9 shows a contour with 5 points where the residence time for each DSMC cell exceeds 5\times10^{-2} ms. The points in question represent very small regions of the flow. The first point is located along the axis of a vortex about 1 cm downstream of the cylinder wall, and 1 cm above the stagnation line. Points 2, 3, and 5 are located close to the cylinder wall in the recirculation region. Point 3 is located on the same vortex as point 1 but further downstream of the cylinder, on the stagnation line.

Point 1 has the highest residence time with 9.2\times10^{-2}. The residence time is long enough for the populations of all species modeled to move away from the initial conditions set at the Boltzmann limit using the species specific temperatures. The residence time is still not quite long enough however for the population to reach equilibrium close to the translational temperature Boltzmann limit. Figure 4.10 marks with a red line the residence time and corresponding vibrational population. At the red line, the population of all species are no longer described by a Boltzmann distribution regardless of the temperature of reference used.
Figure 4.9: Residence time contour in the wake region of the HET high density case from the DSMC solution.

Figure 4.10: Time resolved vibrationally excited populations at residence time for point 1

In order to better compare the different population calculation for point 1, Table 4.3 shows the vibrational populations for the NO and N\(_2\) using different methods: The vibrational temperature for each species at the Boltzmann limit which is also the number used to initialize the populations in this model, the populations as predicted by the model at residence time, the steady state population as predicted by the model, and the Boltzmann limit using the
bulk translational temperature.

Table 4.3: Population calculation at point 1 - High density case

<table>
<thead>
<tr>
<th>species</th>
<th>initial populations set with $T_v$ Boltzmann</th>
<th>population at residence time</th>
<th>population at steady state</th>
<th>population set with bulk $T_{trn}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(1)</td>
<td>2.92E+14</td>
<td>1.35E+14</td>
<td>1.11E+14</td>
<td>1.11E+14</td>
</tr>
<tr>
<td>NO(2)</td>
<td>6.48E+13</td>
<td>5.44E+13</td>
<td>7.65E+12</td>
<td>8.02E+12</td>
</tr>
<tr>
<td>NO(3)</td>
<td>1.47E+13</td>
<td>9.19E+12</td>
<td>5.49E+11</td>
<td>6.02E+11</td>
</tr>
<tr>
<td>N$_2$(1)</td>
<td>3.77E+15</td>
<td>3.10E+15</td>
<td>9.27E+14</td>
<td>9.33E+14</td>
</tr>
</tbody>
</table>

* Units are in molecules/cm$^3$

Points 2 through 5 behave in a similar fashion to point 1, although the residence times are shorter leading to less divergence form the initial population at $t=0$. Because in this model, N$_2$ does not benefit from fast reactions caused by atomic species, N$_2$(1) tends to only diverge from the initial Boltzmann $T_v$ limit in regions of very high residence time such as point 1.

In order to understand the effect of free stream density on the population predictions in high residence time regions of the flow, the medium density case is considered. The DSMC solution shows a much smaller recirculation region, and generally more diffuse flow features. A new set of three points is chosen as shown in Fig. 4.11 where points 1, 2, and 3 are analogous to points 1, 2, and 5 in the high density case discussed previously.

In addition to more diffuse wake flow structures, the medium density case produces competing conditions for non-Boltzmann populations in points with high residence time. The residence time at point 1 is comparable to that of point 1 in the high density case. Residence times in points 2 and 3 however are four times longer than their high density counterparts, with residence times of $3.38 \times 10^{-2}$ ms and $6.53 \times 10^{-2}$ ms respectively. With such long residence times, one would expect the collisional reactions would have time to move the
Figure 4.11: Residence time contour in the wake region of the HET medium density case

vibrational populations away from the $T_v$ Boltzmann limit but not quite reach the steady state values which are reached at $1 \times 10^{-2}$ s, as seen most obviously in point 1 from the high density case. The lower density of the medium density case causes the wake region to be rarefied however, slowing down the reactions taking place there. As a result, the only species which reaches a non-Boltzmann population at these points is NO(1) due to atomic collisional mechanisms 4 and 5 from Table 4.1. A comparison of various population calculation for point 2 in the medium density case is presented in Table 4.4 as this point is representative of the behavior observed in the two other points.

Table 4.4 also shows a notable result which is reminiscent of the effect of rarefied conditions on the expanded CR model results. Higher energy levels with many radiative decay paths to lower levels see their population diverge at steady state from the Boltzmann limit the
Table 4.4: Population calculation at point 2 - Medium density case

<table>
<thead>
<tr>
<th>species</th>
<th>initial populations set with T_v Boltzmann</th>
<th>population at t residence</th>
<th>population at steady state</th>
<th>population set with bulk T_{trn}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NO(1)]</td>
<td>2.37e+12</td>
<td>1.73e+12</td>
<td>9.16e+10</td>
<td>9.20e+10</td>
</tr>
<tr>
<td>[NO(2)]</td>
<td>7.32e+10</td>
<td>7.29e+10</td>
<td>9.57e+07</td>
<td>1.13e+08</td>
</tr>
<tr>
<td>[NO(3)]</td>
<td>2.39e+09</td>
<td>2.36e+09</td>
<td>1.11e+05</td>
<td>1.54e+05</td>
</tr>
<tr>
<td>[N_2(1)]</td>
<td>4.18e+13</td>
<td>4.16e+13</td>
<td>8.27e+11</td>
<td>8.32e+11</td>
</tr>
</tbody>
</table>

^a Units are in molecules/cm^3

most. NO(3) steady state population is notably lower than the Boltzmann limit for the bulk flow translational temperature. This effect is even more pronounced in the low density case. This effect is not as pronounced for the first two vibrational levels of NO because they are more accessible and are populated by the radiative decay of higher levels.
4.4 Mass Transport for Vibrationally Excited NO

The mass transport model (MassTR) uses equation (Eqn. 4.14) which, for a two dimensional case, is given as

$$\frac{\partial \rho_s}{\partial t} = -\frac{\partial \rho_s u}{\partial x} - \frac{\partial \rho_s v}{\partial y} + D_s \left( \frac{\partial^2 \rho_s}{\partial x^2} + \frac{\partial^2 \rho_s}{\partial y^2} \right) + S_s$$  \hspace{1cm} (4.14)

where s=1, 2, 3 for species NO(1), NO(2), and NO(3) respectively. This is a coupled partial differential equation system. \( u \) and \( v \) are the overall flow field velocities in \( x \) and \( y \) directions respectively. The only unknowns are the density \( \rho \) of each species and the system is coupled through the source terms \( S_s \). Diffusion coefficients for each vibrationally excited species is calculated using the Eqn. 4.15 in \( \text{cm}^2/\text{s} \) which uses Lennard-Jones potential for the collisional cross section of the species:

$$D_{AB} = 0.00188 \left[ T^3 \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{0.5} \times (P\sigma_{AB}^2\Omega_{AB})^{-1}$$  \hspace{1cm} (4.15)

where \( \sigma_{AB} \) is the rigid sphere collision diameter of particles A and B in angstrom, \( P \) is pressure in atm, \( T \) is temperature in K, \( M_A \) and \( M_B \) are the molecular weights. For the case at hand NO(1), NO(2), and NO(3) are the particles "A" and the properties of particle "B" is calculated at each cell point for the mixture according to the mole fraction of each ground species. At every cell, a diffusion coefficient for each of the vibrationally excited states is calculated for that state diffusing into the local gaseous solution. The solution is modeled by a single species with the average properties of its constituents. For the species "B" the average properties for mass and molecular diameter is calculated using Eqn. 4.16
and Eqn. 4.17 where \( x \) is the mole fraction of each ground state species. \( \sigma_{AB} \) and \( \Omega_{AB} \) are calculated with the Eqn. 4.19 and Eqn. 4.20 and for the individual \( \sigma \) and \( \epsilon \), values from Table 4.5 is used.

\[
\sigma_B = \sum_{i=1}^{5} x_i \sigma_i \tag{4.16}
\]

\[
M_B = \sum_{i=1}^{5} x_i M_i \tag{4.17}
\]

\[
\epsilon_B = \sum_{i=1}^{5} x_i \epsilon_i \tag{4.18}
\]

\[
\sigma_{AB} = 0.5 \times (\sigma_A + \sigma_B) \tag{4.19}
\]

\[
\Omega_{AB} = (1.074 T_{AB}^{-0.1604}) \tag{4.20}
\]

\[
T_{AB} = \frac{kT}{\epsilon_{AB}} \tag{4.21}
\]

\[
\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B} \tag{4.22}
\]

The source term used in Eq. 4.14 is for NO(1), NO(2), and NO(3), Eq. 4.8, 4.9, and 4.10 respectively. \( N_2(1) \) is not considered in this implementation of the MassTR model because it
Table 4.5: Molecular Diameters and Epsilon values for 5 mixture air species

<table>
<thead>
<tr>
<th>Species</th>
<th>$\sigma$ (Å)</th>
<th>$\varepsilon/k$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>3.11</td>
<td>97.5</td>
</tr>
<tr>
<td>O</td>
<td>2.96</td>
<td>71.4</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.58</td>
<td>107.4</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3.37</td>
<td>80.0</td>
</tr>
<tr>
<td>NO</td>
<td>3.41</td>
<td>131</td>
</tr>
</tbody>
</table>

would not be a trace species, making up a substantial of the mole fraction in the flow which would greatly increase the complexity of the model. Since NO is the principle radiating source of interest, and N$_2$(1) doesn’t radiate in the same region, N$_2$(1) it is left out of this model. The time step used in the simulation is $1 \times 10^{-9}$ s and the model runs until it reaches steady state. Figure 4.12 shows the solution for vibrationally excited populations to converge in the three main regions of the flow (bow shock, shoulder, wake).

Similarly to the Collisional-radiative model for vibrational states, MassTR uses the translational temperature given by the DSMC solution as the excitation and quenching mechanisms are still driven by particle collision. The cases used are still the HET conditions for high, medium, and low density, using the TCE chemistry set. The Collisional-Radiative model presented in Table 4.1 are added as the source term of the MassTR solver. The solver adds mass transport through a diffusion and a convection term which allows greater fidelity when compared to the 0D calculation performed in each DSMC cell using the residence time as previously discussed. When using the CR model without mass transport, the excited populations in the flow must be initiated with the vibrational temperature and then marched in time according to the chemical rates available, for the duration of a given cell’s residence time. The mass transport allows for a solution at steady state independent from
Figure 4.12: Convergence of NO(1) Population Around the Cylinder
initial conditions. Line plots are taken in three regions of interests which are the stagnation line, the vertical line at the shoulder of the cylinder, and the wake line as shown in Fig. 4.13. Plots showing self normalized population distributions allow for a better understanding in the difference in flow structure between the Boltzmann and MassTR solutions.

Figure 4.13: Line plots used for MassTR result comparisons

Figure 4.14 Shows a comparison for the high density case, of NO(1) population computed using the MassTR and Boltzmann with species specific vibrational temperature (here T_v of NO). The results presented in this section will all be comparisons between the MassTR calculation and the species specific vibrational temperature Boltzmann population unless otherwise specified. Generally MassTR predicts a larger NO(1) population in the shock by 10-20% when compared with the Boltzmann calculation. This is especially true closer to the cylinder where the transport terms push the excited species, concentrating them in the stagnation region. The two models are in good agreement in the shoulder region. In the wake, MassTR predicts significantly less NO(1) than the Boltzmann calculation. This is due in part by the fact MassTR uses the Bulk translational temperature, which tends to be lower in this region compared to NO’s vibrational temperature. It is also due to the very
low densities which correlate to the rate of production of excited species whereas Boltzmann calculations only depend on temperature.

![Figure 4.14: Contour of NO(1) using MassTR and Tv-Boltzmann, High Density](image)

The results for other excited states of NO will follow a consistent pattern, regardless of the density of free stream, although this pattern will be more pronounced when considering the medium and low density cases later. Figure 4.15 shows NO(2) population predictions by MassTR are considerably lower than the Boltzmann calculation in every region of the flow including the bow shock. This is due to the CR model not having many excitation mechanisms for NO(2) (and NO(3)) outside of self excitation by NO species. NO(2) does benefit from reaction 10 which involves O$_2$ as a bystander species, but not from reaction
with N₂ or atomic species. The role of bystander species (species which are not NO and don’t undergo any changes during quenching or excitation reactions) will be discussed later.

Similarly to NO(2), NO(3) population are much lower in the MassTR model as see in Fig. 4.16. This is due to similar reasons with NO(3) not benefiting from any bystander excitation mechanisms at all. In addition, several excitation mechanisms of NO(3) rely on the presence of NO(1) and NO(2) which may be ”delayed” by transport terms pushing them downstream. Of course, in reality NO(2) and NO(3) would be populated through collisional reactions with all the species present in the flow, and a future work could add these mechanisms by simply applying the rates used with NO(1) to the other excited levels.
Nevertheless, this work focused on incorporating excitation and quenching rate explicitly found in the literature.

![Figure 4.16: Contour of NO(3) using MassTR and Tv-Boltzmann, High Density](image)

(a) MassTR NO(3)  
(b) Tv Boltzmann NO(3)

(c) Normalized, MassTR: $2.5 \times 10^{21}$, Boltzmann: $4.5 \times 10^{21}$ (m$^{-1}$)

Figure 4.16: Contour of NO(3) using MassTR and Tv-Boltzmann, High Density

A better picture for the comparison of vibrational populations by model is given in Fig. 4.17 where line plots are shown for the stagnation line, the wake line, and the vertical shoulder line. This figure better illustrates the agreement between the Boltzmann calculation and the MassTR for NO(1) in the bow shock and the shoulder, but also shows the difference present in the wake region.

The results for the medium density case follow a similar trend as the one established in the high density case. Figure 4.18 shows a good agreement between the two models
Figure 4.17: Line Plots for NO(1,2,3), High Density
in the stagnation region and the shoulder for NO(1). Once again, MassTR predicts lower populations in the wake region.

![Figure 4.18: Contour of NO(1) using MassTR and Tv-Boltzmann, Medium Density](image)

(\text{a}) \text{MassTR NO(1)} \hspace{2cm} (\text{b}) \text{Tv Boltz NO(1)}

(c) Normalized, MassTR: $4.4 \times 10^{22}$, Boltzmann: $1.4 \times 10^{21}$ (m$^{-1}$)

Figure 4.18: Contour of NO(1) using MassTR and Tv-Boltzmann, Medium Density

NO(2) predictions are lower relatively to the Boltzmann calculation as the density of the free stream decreases as shown in Fig. 4.19. This is due to the same reasons described for the high density case, however as density decreases, more mechanisms cause the decrease in population. As seen in the 0D CR calculations, the radiative mechanisms become important at lower densities. These tend to affect high energy levels with several radiative decay path to lower levels disproportionately.

NO(3) populations predicted by MassTR and very low, even in the bow shock. Figure 4.20
Figure 4.19: Contour of NO(2) using MassTR and Tv-Boltzmann, Medium Density
Shows the combined effects of the exclusively self exciting mechanisms of the source terms and the transport terms which concentrate the NO(3) population in a slim layer close to the cylinder as it produced in the bow shock.

Figure 4.20: Contour of NO(3) using MassTR and Tv-Boltzmann, Medium Density

Figure 4.21 shows the line plots for the medium density case. Similarly to the high density case, we can see the NO(1) population in the bow shock exceeds the Boltzmann calculation slightly as the flow moves closer to the cylinder. The effect of radiative decay on all the excited populations predicted by the MassTR can be seen in the medium density case.

Looking closer at the bow shock region of the medium density case, it is possible to understand the effect of various mechanism on the population distribution of vibrationally
Figure 4.21: Line Plots for NO(1,2,3) Medium Density
excited states of NO. When considering Fig. 4.21 (b), the NO(2) population in the bow shock seems to be a convolution of two functions, with the first one being dominant from \(x = -0.004 \text{ m}\) to \(-0.002\text{m}\), and the other dominating from that point to the cylinder wall. This is because further away from the cylinder, NO(2) benefits from the bystander excitation mechanism 10 which dominated in the regions of the shock closer to the free stream, where NO(1) and NO(3) have not been created in sufficient quantities to become major contributors in the population of NO(2). As the flow moves towards the cylinder, NO(1) becomes very populated and self excitation mechanisms become more dominant. Notice NO(2)’s profile is similar to NO(3) when close to the cylinder. NO(3) is populated exclusively by self excitation mechanisms.

Figure 4.22 shows a comparison between Fig. 4.21 and a similar calculation conducted with bystander excitation mechanisms for NO(1) deactivated. Notice that, in addition to the much lower NO(1) population predicted, the shape of the population profile is identical to NO(3) as both are now populated exclusively with self excitation mechanisms while NO(2) still benefits from reaction 10 involving \(O_2\). NO(1) only becomes populated close to the cylinder wall where it benefits from large NO ground populations and the other two excited state populations.

Predictably, results for the low density case confirm the trends set by the two previous cases. Figure 4.23 shows the contours with NO(1) calculations for both MassTR and Boltzmann. In the low density case, the effect of radiative decay and rarefied gas conditions on populations is even more pronounced for all excited states of NO. On thing of note which is the visible effect of the transport terms in MassTR moving excited species from the bow shock into the top right corner of the domain where the Boltzmann population are nonexis-
Figure 4.22: Effect of bystander species on NO(1,2,3) in the stagnation region, medium Density
tent.

Figures 4.24, 4.25, and 4.26 all show NO(2) and NO(3) population to be extremely low in all regions of the flow. Particularly, NO(3) is almost non-existent in the low density case. With the rarefied gas conditions of the low density case, the effect of the diffusion term of the MassTR model is clearly visible. Figure 4.23 shows the vibrationally excited NO moving upstream from the cylinder wall into the diffuse bow shock compared to the Boltzmann calculation. Although this effect is somewhat visible in the other density cases, it is always in competition with the convection term dragging the excited populations towards the cylinder wall inside the bow shock.
Figure 4.23: Contour of NO(1) using MassTR and Tv-Boltzmann, Low Density
Figure 4.24: Contour of NO(2) using MassTR and Tv-Boltzmann, Low Density

Normalized, MassTR: $2.7 \times 10^{13}$, Boltzmann: $6.5 \times 10^{16}$ (m$^{-1}$)
(a) MassTR NO(3)  
(b) Tv Boltzm NO(1)  

(c) Normalized, MassTR: $3.4 \times 10^7$, Boltzmann: $3.0 \times 10^{16}$ (m$^{-1}$)

Figure 4.25: Contour of NO(3) using MassTR and Tv-Boltzmann, Low Density

(a) Stagnation Line  
(b) Shoulder  
(c) Wake

Figure 4.26: Line Plots for NO(1,2,3), Low Density
CHAPTER 5
CONCLUSION

The modeling of Hypersonic flow UV emission in strong shocks was successful in replicating experimental results from ground based facilities. The modeling of radiative emission from the shock tube experiment yielded results on par with the experiment and similar simulation efforts. The fitting of measured spectra with synthetic spectra to extract non-equilibrium temperatures has proven to be a difficult task. Although the fitting results for the HET air case were successful in reproducing the temperature patterns predicted by DSMC solutions, the sensitivity of the fitting process to small spectral features, and its insensitivity to changes in vibrational temperatures makes those results tenuous. The modeling of normalized spectra and normalized integrated intensity profiles has revealed the sensitivity of radiation overlay methods to small changes in chemistry sets and DSMC solutions. This was particularly manifest in the effect of O$_2$ content in the intensity profiles. This sensitivity has highlighted and motivated the need for more sophisticated, non-Boltzmann excited population modeling techniques.

One such technique is presented in the form of the QSS calculations based on Collisional-Radiative models which rely on a set of forwards and backwards reaction rates for the formation, quenching, and radiative decay of excited species. The QSS CR population predictions combined with radiation modeling has produced good agreements with the shock
tube experiments by Gorelov. However, the lack of higher electronically excited states for NO has limited the usefulness of the CR model because of its inability to show the relative contribution of these higher electronic states to UV spectra, especially in wavelengths below 230 nm. A new and expanded CR model was introduced which includes the B, C, D, states of NO and the B and C states of N₂. The overlay of this expanded CR model with a QSS assumption over the HET case DSMC results has shown a Boltzmann distribution produces a good estimation for the population in the bow shock region. The expanded CR has also introduced new mechanism which strengthen the coupling mechanism between NO(A) and N₂(A) by which N₂(A) acts as an energy reservoir, re-exciting NO to the A state in regions of the flow where NO is otherwise no longer excited.

It was shown that an analogous model to the CR model for electronic states could be implemented for vibrationally excited states of NO and N₂ in the form of a time accurate vibrational excitation solver. Predictions of this model for vibrationally excited populations in the HET cases showed very little deviation from the initial prediction using the species specific vibrational temperature, provided by the DSMC solution, in a Boltzmann distribution. This is because the residence times in the flowfield are very small due to the high flow velocities, even in compression regions such as a bow shock. However, at very specific locations in the wake region where residence times were exceptionally long, the model did predict non-Boltzmann population distributions. In order to leverage the potential of both the time accurate vibrational excitation solver, an overlay methods incorporating mass transport terms is used. This method shows vibrational populations for NO only and produces results different from both a Boltzmann populations using NO vibrational temperature, as
well as the vibrational CR model in a 0D calculation. The excited NO populations predicted by the MassTR model are generally lower than the Boltzmann calculations, especially in expansion regions and for NO(2) and NO(3). This is because of the primarily because of the lack of bystander species driven excitation mechanisms for these two states of NO. The current vibrational excitation model is most sufficient for predicting NO(1) population and therefore the fundamental transition for NO in the IR. Adding more mechanisms to the model by future works will allow for an accurate modeling of the overtone emission bands in the same region by higher vibrationally excited states.
REFERENCES


