ELECTRON AND SPECIES POPULATIONS BEHIND HIGH ENTHALPY SHOCK WAVES IN LOW DENSITY AIR

By

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A thesis submitted for the degree of Doctor of Philosophy of The Australian National University

June 1990
Statement of Authorship

The contents of this thesis, except where indicated by references, are entirely my own work.

P. Taloni

Paul Taloni
June 1990
Acknowledgements

Many people have assisted me over the course of my PhD research. To thank them all individually would take as many pages as I have used to describe my experiments. Those I do not mention personally know that I am sincerely grateful. At some time or another, every member of the Department of Physics has helped me in some way shape or form. Specifically I would like to thank my supervisors Professor John Sandeman and Dr Frank Houwing. Many thanks to John Sandeman who would offer advice on some aspect of the experimental technique that would invariably overcome an apparently insurmountable problem. I am also indebted to Frank Houwing whose continual encouragement and advice, not to mention his endless supply of enthusiasm, made the research program as productive as it was. Thanks are due also to Dr Don Bone for the coaching he gave me in squash as well as the many discussions we had on atomic spectroscopy. Unfortunately my squash game did not substantially improve, but my understanding of spectrophysics and spectroscopic technique certainly did. Thanks to Dr Hans-A Bachor whose expertise in this area was often utilized. I must also thank my fellow students with whom I endured the rigors of experimental physics. Thanks to Jim Taylor, with whom I have spent the last eleven years of my schooling, for his assistance in the lab and his good humour during the frustrating times. To Tim McIntyre (now Dr) and Philip Ryan (still Mr) for the many fruitful discussions concerning the areas of our research as well as the less fruitful, but equally entertaining, disputation over experimental technique. I would also like to thank the workshop staff, especially Ian Darroch and Paul Walsh, who
operated the shock tube facilities and constructed much of the equipment employed in the experiment. Somehow they always managed to have the design built “yesterday”, as per my request. Deep appreciation is held for my family, especially my father and mother who have supported me throughout my studies. Last, but by no means least, I must thank my fiancee Stephanie who has endured the difficult times with much patience and understanding. We spent many a weekend in the lab setting up “the next experiment” instead of spending the time together in more relaxing ways. Now that I have submitted we can get married, start a family, take that holiday....... and I can earn a living for a change!
Abstract

Experiments were conducted to test the validity of theoretical models which describe the behaviour of chemical and thermal relaxation processes at high temperatures and low densities. Interferometric, emission and absorption experiments were performed to measure the electron densities, rotational temperature, and emission and absorption profiles for comparison with theory.

Electron populations behind high enthalpy shock waves in low pressure air were measured with spatial and temporal resolution at conditions applicable to the flight regimes of the NASA proposed aeroassisted orbital transfer vehicle using an infrared interferometric technique. Measurements using this technique were confirmed by observing the Stark broadening of the hydrogen β transition. It was observed that the electron populations plateau to a level that is significantly less than that predicted by a one-temperature model, but are in excellent agreement with values predicted by a two-temperature model. The measured rate of ionisation agreed favourably with the rate predicted by the two-temperature model, but was again significantly less than that predicted by the one-temperature model.

The broadband temporal emission characteristics of the plasma were studied in order to determine characteristic relaxation times. The emission profiles were in excellent accord with the predictions of the two-temperature model. No measure of the emissive power was made however, and therefore no comment is made as to the reliability of the model at predicting the power spectrum.
Temporally resolved emission measurements were conducted on specific rotational transitions in the N$_2^+$ molecule in the region behind the shock to determine the rotational temperature. This temperature was found to be correctly predicted by the two-temperature model, while the one-temperature model, underestimated the temperature by a factor of about 50%.

The relative intensity of two transitions in atomic and ionic oxygen were measured and compared with theoretical predictions. It was observed that the theoretical ion-to-atom emission ratio was substantially larger when described by a single temperature than when described by two temperatures. The experimental results support the two-temperature description and lend support to the conclusion of the electron number density studies, which suggest that the observed decrease in these populations was due to a lowering of the electron temperature.

An infrared CW diode laser absorption experiment was carried out in oxygen on the same transition as in the emission studies. The measured absorption was compared with that predicted by the two-temperature model, and found to be in fair agreement, although the uncertainty in the measurements is high.

The experimental results lend support to current theoretical work, which proposes that it is necessary to characterize the flow by different temperatures to accurately model conditions at the high shock enthalpy, low density regime.
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ACRONYMS AND NOTATIONS

This thesis is written in, and adheres to, the SI units system. On occasion however, certain equations contain dimensioned constants. In these instances, the equations are detailing either cross sectional or spectroscopic parameters. It is common practice to employ the cgs units system in these cases. For example, practically all spectroscopic data is given in cgs units. The thesis therefore follows this convention for those specific equations, namely, equations 2.3, 2.6, 2.7, 2.17, 2.19, 3.12, 3.16, 3.23, 4.7, 5.48 and 5.49.

The following acronyms and notations are presented in the order in which they appear in the given chapter.

AOTV : aeroassisted orbital transfer vehicle
CW : continuous wave
FWHM: full-width-half-maximum
HEO : high earth orbit
LEO : low earth orbit
OTV : orbital transfer vehicle
TT_v : pertaining to the two-temperature kinetic model of Park (1989)

Chapter 2

a_o : first Bohr radius
A_i(T) : forward rate constant for collisional ionisation
c : speed of light
c_i : wavenumber of the i^{th} band system
\( \bar{C}_X \) : mean thermal velocity of species X

d : distance between the atomic or molecular fields of two particles

\( \Delta E \) : total internal energy of a system

\( \Delta E_i^0 \) : energy of reaction

E : impact energy

\( E^* \) : energy difference between two electronic states of a molecule

\( E_X \) : activation energy for ionisation

\( E_o \) : lowest vibrational level of an upper state

f : oscillator strength

f(\( \varepsilon \)) : local electron energy distribution function

\( f_i \) : characteristic oscillator strength of the \( i^{th} \) band system

g : ratio of the statistical weights

h : Plank's constant

I : total radiation intensity

k : Boltzmann's constant

L : effective thickness of the reaction region

\( m_e \) : electron mass

n(\( \nu \)) : number density of photons with frequency \( \nu \)

\( n_e \) : local electron number density

\( \bar{n}_{N_2} \) : averaged number density of \( N_2 \) molecules

\( n_X \) : local density of species X (atom or molecule)

Q : Total cross section for electron impact with atoms or ions

\( \bar{Q} \) : velocity averaged cross section

\( Q_E \) : cross section for ionising collisions

\( Q_{fx} \) : photoionisation cross section for X type species

\( Q^i \) : ionisation cross section
\( Q_{ix}(\varepsilon) \) : cross section for electron collisional ionisation
\( Q_o \) : elastic cross section
\( Q_s \) : excitation cross section
\( R \) : internal separation for collisional ionisation
\( R_{ao} \) : centre of mass distance
\( T \) : translational temperature
\( t \) : time
\( T^* \) : characteristic temperature for the electronic state
\( T_e \) : electron temperature
\( T_i \) : characteristic temperature for the \( i^{th} \) band system
\( v \) : relative velocity of two particles
\( v_e \) : electron velocity
\( w_{ix} \) : threshold energy for species \( X \)
\( X \) : species type (atom or molecule)

**Greek symbols**

\( \delta \) : plasma thickness
\( \varepsilon \) : electron energy
\( \varepsilon_{\text{eff}} \) : effective emission
\( \kappa_i \) : forward rate coefficient for collisional ionisation
\( \lambda_i \) : characteristic wavelength of the \( i^{th} \) band system
\( \mu \) : reduced mass of a system
\( \nu \) : radiation frequency
\( \rho \) : density
\( \rho_o \) : density at STP
\( \tau_{\text{AI}} \) : autoionisation lifetime
\( \tau \) : mean lifetime before autoionisation occurs
\( \tau_c \) : collisional lifetime
\( \tau_r \) : radiative lifetime
Chapter 3

\( \omega_0 \) : \( = E_0/hc \)

\( \Psi \) : number of NO molecules

\( A_i \) : i=1, 2, ..., 5 rate controlling constants

\( A \) : parameter dependent on the molecule type

\( C \) : reaction rate constant for vibrational excitation

\( c \) : average molecular speed

\( c_m \) : pitching moment coefficient

\( C_p \) : specific heat at constant pressure

\( C_V \) : specific heat at constant volume

\( D_X \) : dissociation energy of molecule X

\( \bar{D}_s \) : average vibrational energy per unit mass of molecule s

\( D_s \) : effective diffusive coefficient for species s

\( e \) : electron charge

\( E \) : total energy per unit mass

\( E_e \) : sum of the electronic excitation energy and kinetic energy of the electrons

\( E_r \) : activation energy of the reaction

\( e_{v,s}^{**} \) : vibrational energy per unit mass of species s at temperature \( T_e \)

\( E_{v}^{*} \) : vibrational energy at the electron temperature

\( e_{v,s}^{*} \) : vibrational energy per unit mass of species s at temperature T

\( e_e \) : total electronic energy per unit mass of molecule s

\( E_v \) : vibrational energy

\( e_v \) : total vibrational energy per unit mass

\( E_{v,0} \) : vibrational energy at time t=0
\( e_{v,s} \) : vibrational energy per unit mass of species \( s \)

\( E_{\text{Vib}} \) : average vibrational excitation energy per molecule

\( E_{\text{Vib,Eq}} \) : average vibrational excitation energy per molecule at equilibrium

\( f \) : electron gas heat transfer

\( H \) : total enthalpy per unit mass

\( h_{es} \) : electronic enthalpy per unit mass of species \( s \)

\( h_{v,s} \) : vibrational enthalpy per unit mass of species \( s \)

\( \hat{I}_s \) : first ionisation potential for species \( s \)

\( k \) : Boltzmann's constant

\( k_e \) : thermal conductivity by the electron gas

\( K_{\text{eq}} \) : equilibrium constant for the reaction

\( k_f \) : forward reaction rate for vibrational excitation

\( k_{vv'} \) : rate coefficient for a transition from state \( v \) to \( v' \)

\( M \) : mach number

\( M_s \) : molecular weight of species \( s \)

\( N_X \) : number density of the \( X \)th state

\( n_e \) : number density of free electrons

\( \dot{n}_{\text{ies}} \) : molar rate of production of species \( s \) by electron impact ionisation

\( n_v \) : number density of the \( v \)th vibrational state

\( N_X \) : number density of the \( x \)th state

\( p \) : pressure

\( p_e \) : electron pressure

\( q_r \) : radiative power loss

\( Q_{\text{rad}} \) : radiative energy transfer rate

\( \bar{R} \) : universal gas constant

\( T \) : translational temperature
\( t \) : time

\( T_a \) : atom temperature

\( T_{av} \) : \( = \sqrt{T_Tv} \) = geometrically averaged temperature

\( T_e \) : electron-electronic excitation temperature

\( T_r \) : rotational temperature

\( T_{RC} \) : reaction dependent rate controlling temperature

\( T_s \) : heavy particle translational temperature immediately behind the shock front

\( T_v \) : Vibrational-electron-electronic temperature

\( u^i, u^j, u^k \) : velocity vector in 3-D space i, j, k=1, 2, 3

\( V_i \) : diffusion velocity for species i

\( w \) : flow velocity

\( \dot{w}_s \) : mass rate of production of species s

\( x^i, x^j, x^k \) : vector in 3-D space i, j, k=1, 2, 3

\( y_s \) : mole fraction of species s

Greek Symbols

\( \Delta \) : moment of energy transfer

\( \delta^{ij} \) : Kronecker delta

\( \varepsilon_{vib}^{\text{Diss}} \) : average vibrational excitation energy

\( \varepsilon_{vE} \) : average vibrational excitation energy per molecule at equilibrium

\( \varepsilon_{ei} \) : average vibrational excitation energy per particle i

\( \varepsilon_v \) : average vibrational excitation energy per molecule

\( \gamma \) : ratio of specific heats \( (C_p/C_v) \)

\( \eta \) : frozen thermal conductivity for translational-rotational energy of heavy particles

\( \eta_e \) : frozen thermal conductivity for electron energy due to electron collisions
\( \eta_v \) : frozen thermal conductivity for vibrational energy due to molecular collisions

\( \kappa \) : equivalent thermal conductivity

\( \mu \) : total viscosity

\( \mu_m \) : reduced molecular mass of the colliding species

\( \nu_{es} \) : effective collision frequency for electrons and heavy particles

\( \nu_i \) : collision frequency of species i

\( \rho \) : total density

\( \rho_e \) : electron density

\( \rho_s \) : density of species s

\( \sigma_v \) : limiting cross section for vibrational excitation at infinite temperature

\( \tau' \) : vibrational relaxation time corrected for the limiting cross section

\( \tau_D \) : vibrational excitation time by heavy particle impact

\( \tau_e \) : vibrational relaxation time for excitation by electron collisions

\( \tau_{es} \) : electronic vibrational relaxation time for species s

\( \tau_s \) : translational vibrational relaxation time for species s

\( \tau_{Vib} \) : vibrational relaxation time for excitation by heavy particle collisions

\( \Theta \) : trim angle of attack

**Chapter 4**

\( a \) : speed of sound

\( C(N_e,T) \) : Stark broadening coefficient

\( D \) : shock tube diameter
\( \Delta l_s \): Stark width

\( I_o \): initial radiation intensity

\( k_{ff,w}^{i} \): absorption coefficient for the inverse Bremsstrahlung process

\( k \): spectral absorption coefficient

\( L \): optical path length

\( M \): mach number

\( m \): molecular mass

\( N_e \): electron number density

\( P \): pressure

\( R \): universal gas constant

\( r \): distance from shock tube axis to the Mach cone

\( r' \): distance from the Mach cone to the expansion fan

\( T \): temperature

\( u \): shock velocity

\( z \): distance from the shock tube exit

Subscripts

1: undisturbed test gas

5: compressed driver gas

D: undisturbed driver gas

s: shock wave

R: reservoir

Greek Symbols

\( \alpha \): microwave attenuation factor

\( \gamma \): ratio of specific heats \((C_p/C_V)\)

\( \lambda \): compression ratio
$\Delta \lambda_s$ : Stark broadened wavelength

$\mu$ : Mach angle

$\omega_p$ : plasma frequency

**Chapter 5**

A : constant times the inverse moment of inertia of the electrons

$A_{nm}$ : Einstein A coefficient

$A_{\text{max}}$ : maximum fringe amplitude

$A_{\text{min}}$ : minimum fringe amplitude

B : rotational constant

C : constant depending on the change of dipole moment of a molecule

c : speed of light

$C_{\text{abs}}$ & $C_{\text{em}}$ : constants depending on the change of dipole moment

$D_V$ : centrifugal distortion constant

d : line shift

$\Delta g$ : FWHM

e : electric charge

$E_{e,v,r}$ : energies of electronic, vibration and rotation respectively

F : term values of rotational transitions for the nonrigid rotator

$f_i$ : oscillator strength

G : term values of vibrational transitions

$g_i$ : degeneracy of level i

$G_s$ : Gladstone dale coefficient for species s

$H(\alpha,v)$ : Voigt profile

h : Planks constant

$I_A$ : moment of inertia of the electrons about the internuclear
axis

$I_B$ : moment of inertia of the molecule about an axis 
perpendicular to the internuclear axis

$I_{a,j}$ : transition intensity of the $j^{th}$ level of an atom

$I_{i,k}$ : transition intensity of the $k^{th}$ level of an ion

$I_o$ : initial intensity

$J$ : rotational quantum number

$J$ : total angular momentum vector

$K$ : total angular momentum apart from spin

$k_{\nu}$ : frequency dependent absorption coefficient

$L$ : angular momentum of the electrons

$L$ : optical path length

$m_a$ : atomic mass

$m_e$ : electron mass

$n$ : refractive index

$N$ : angular momentum of nuclear rotation

$N_e$ : electron number density

$N_j$ : population of the $j^{th}$ level

$p$ : fringe order number

$P(\Delta \nu)$ : line profile as a function of detuning

$\text{Pha}$ : phase

$Q(T)$ : partition function

$Q_r$ : partition function

$S$ : spin vector of the electrons

$S_J$ : Honl-London formulae

$T_e$ : term values for the electronic states

$v$ : vibrational quantum number

$w$ : half-half width due to electron impacts
y : vertical fringe position at the image plane
Z : effective nuclear charge

Greek Symbols

α : angle of two beams at the spectrometer
α : ion broadening parameter
α_E : ionisation fraction at equilibrium
Δλ_D : Doppler width
γ : FWHM
Δν : detuning from line centre
Λ : angular momentum of the electrons along the internuclear axis
ε_o : permittivity of free space
κ_v : spectral absorption coefficient
λ : radiation wavelength
λ_c : Compton wavelength = h/mc
ν_{nm} : line centre frequency of the transition from state n to m
ν : radiation frequency
ν_o : band origin
ρ : density
ρ_s : density of species s
Σ : projection of the spin vector S along the internuclear axis
τ_i : lifetime of level i
ω : wavenumber = 1/λ
ω_1x_e : measure of the anharmonicity of the oscillator
Ω : vector sum of Λ and Σ
θ_I : ionisation temperature (θ_I=I/k)
ρ_I : characteristic plasma density
Chapter 1

INTRODUCTION

1.1 Background

In recent years with the advent of the space shuttle, much activity has taken place in the low earth orbit (LEO). This activity has included scientific exploration as well as commercial enterprise. Much of the commercial activity has included the deployment of satellites into various orbits ranging from LEO's, up to 400 km, to high earth orbits, HEO's, with deployment altitudes as high as 35,900 km for the geosynchronous sites.

To date, the satellite deployment vehicles have been multistage rocket systems, consisting of a lower stage which transports the payload from ground to a LEO, and an upper stage booster continuing from the LEO to the HEO. These upper stage rockets, which are of course expendable, are expensive and of relatively low reliability. The servicing of both geostationary and equatorial satellites, the establishment of permanently manned space stations and space manufacturing, all require a transportation system more flexible than the shuttle, or upper stage rocket, capable of travel between the LEO and the HEO.

A considerable commercial advantage would be achieved if the upper stage vehicle could be made reusable. This premise leads to the concept
of an orbital transfer vehicle, OTV, which employs rockets for its ascent and descent stages. A high price is paid in fuel however, for the ability to reuse the vehicle, as the fuel required for the descent burn is carried at the expense of cargo. To overcome this problem the aeroassisted orbital transfer vehicle, AOTV, has been proposed. (For a review see Park 1985a and 1987a). Such a vehicle has an aerodynamic surface, capable of producing drag and a small amount of lift. It is envisaged that such a vehicle, on return to the LEO from a HEO would carry out aerobraking and aeromaneuvering procedures and decelerate by drag, removing the need for a decelerating rocket burn.

The AOTV has a well defined flight regime. This vehicle is expected to have a perigee altitude of approximately 80 km, where the air pressure is approximately 13 Pa, and, at this point, travel at near escape velocities of approximately 10 kms$^{-1}$. Certainly, at these altitudes, the atmosphere is very tenuous but proves to be highly reactive. The shock waves associated with such an environment are expected to produce flow fields that are in a state of chemical and thermal nonequilibrium. The air in these flow fields will undergo vibrational excitation, dissociation and significant ionisation. The study of reentry physics is becoming of significant importance, and the development of such a vehicle is set to become a major technological challenge in the coming decades.

In order to develop the AOTV, it will be necessary to obtain an understanding of the chemical kinetics at the flight regimes where these processes are important. The nonequilibrium chemistry affects both the heat transfer to the vehicle as well as its aerodynamic
capabilities. Unlike chemical kinetic models applied to the study of shock heated monatomic gases such as argon, modelling the chemistry of shock heated air is inherently difficult due to the large number of species in the plasma, their type and the number of possible reactions in which they may participate. Eleven species, namely, N\textsubscript{2}, O\textsubscript{2}, N, O, NO, N\textsuperscript{+}, O\textsuperscript{+}, N\textsubscript{2}\textsuperscript{+}, O\textsubscript{2}\textsuperscript{+}, NO\textsuperscript{+} and e\textsuperscript{-} may be involved in some fifty reactions, many of which have rate constants that are currently unknown. Furthermore, molecular species introduce other temperatures with which the flow may be characterized. Any chemical kinetic model therefore, must address the problems of large species numbers, multiple reactions and be capable of accounting for vibrational, rotational, electronic excitation, electron translational and heavy particle translational temperatures; not a trivial exercise. These are problems faced by the theorist. The experimentalist too has certain limitations that hamper the study of shock heated air at high enthalpy conditions, a consequence of the nature of the plasma and the difficulties associated with the generation of such flows in the laboratory.

Studying the chemical kinetics involves an investigation of the various species, their population histories and their role in reaction sequences. Laser absorption and emission spectroscopy are non-intrusive experimental techniques that lend themselves to such a study. There are problems however associated with spectroscopy in an air plasma. Emission measurements may be made, for example, in order to determine rotational and vibrational temperatures of excited states of N\textsubscript{2}\textsuperscript{+}. However this does not result in any information on the populations of the ground electronic states. Absorption techniques can employ either a narrowband or broadband background source.
Narrowband absorption is difficult to reduce however, because a knowledge of the widths, shifts and shapes of absorbing transitions is essential and these line shape parameters are presently unknown for many species in the environments of interest.

Useful absorption measurements for molecular nitrogen must take place in the ultraviolet. The strongest absorption bands in the $O_2$ molecule are also in the ultraviolet (the Schumann-Runge transitions). The $\beta$ and $\gamma$ transitions in the NO molecule lie in the range 200 to 400 nm. Strong atomic absorbers in an air plasma have transitions approaching the infrared. The spectral positions of these strong transitions place severe restrictions on the experimental diagnostic.

Due to the large number of species of both the molecular and atomic form to account for, many possible transitions of varying wavelengths from the vacuum ultraviolet to the far-infrared are possible, making the selection of a suitable light source or emission detector, difficult. Tunable dye lasers are required for CW absorption in the visible, excimer lasers may be used as light sources in the ultraviolet and tunable diode lasers are needed in the infrared. Broadband continuum sources must have an effective blackbody temperature greater than the plasma under study. These light sources and their detectors must of course be coupled with the appropriate optics.

A great deal of theoretical work in the area of ionised air has been carried out in the last thirty years. More recently, a two-temperature kinetic model for ionising air has been developed by Park (1989). His model has been the basis of a computer code which has been applied to
the flight regime of the AOTV and has made predictions on:

i) the population histories of the eleven molecular, atomic and ionic species,

ii) the rotational and vibrational temperatures characterizing the flow and

iii) the nonequilibrium radiative emission of the plasma.

This code represents perhaps the most accurate attempt to model conditions behind the shock fronts associated with the AOTV.

On the experimental front, very little data exists for the species populations at these conditions. There are difficulties (to be detailed later) associated with the production of such high enthalpy shock fronts in the laboratory. It is obvious that no single body of experimental work could possibly hope to measure all of the parameters predicted by any kinetic model for ionising air. Recognizing this fact, the present investigation looks specifically at a few parameters in an attempt to lend support to the theoretical work. In particular, the ionisation that occurs behind the high enthalpy shock waves in low pressure air at specific conditions is studied in detail. Therefore, the literature review that follows, is devoted to the experimental and theoretical work that has been carried out in the field of ionisation behind shock waves in air.

1.2 A review of relevant literature

While studying the electrical conductivity of ionised air, Lamb and Lin (1957) made the observation that the ionisation rate was considerably faster behind the shock wave than had been expected. The ionisation rate observed by Petschek and Byron (1957) for shock waves of
comparable strength in argon, was several orders of magnitude slower than Lamb and Lin had observed; even allowing for the difference in the ionisation potentials between the species of argon and those constituents of air. During their investigation, Petschek and Byron employed a shock reflection technique that determined the local electron number density by correlating it to the intensity of the visible light emitted by the shock heated gas.

Niblett and Blackman (1958) tried to employ the technique of Petschek and Byron to determine the ionisation relaxation time behind shock waves in air. A hydromagnetic shock tube was employed to produce shock waves with Mach numbers from 11 to 17 travelling into 133 Pa of air. The assumption was made that the luminous region following the shock front was due to processes involving free electrons. However, while the visible radiation in shock-heated argon is due primarily to free-free and free-bound continuum radiation, the visible radiation from shock-heated air has been found to be due to molecular band systems (Penner, 1959). As pointed out by Lin et al (1962), the point of onset of intense radiation behind the shock wave was most likely due to the arrival of the contaminated driver gas from the electrical discharge, and was not due to the ionisation as Niblett and Blackman had assumed. These luminosity measurements, perhaps wrongly interpreted, were reported as being able to demonstrate that the ionisation time decreases with increasing Mach number.

A method, based on the measurement of the attenuation of microwaves to determine the electron densities and ionisation rates in shock-heated air, was employed by Manheimer-Timnat and Low (1959). Shock waves in the Mach number range from 8.2 to 10.4 for air; and for
nitrogen/oxygen mixtures (99.75% / 0.25% by volume) in the Mach number range from 7.4 to 8.8, both in pressures ranging from 0.13 to 1.33 kPa, were studied. The authors showed there was good agreement between the experimentally determined electron number density and theoretical calculations based on a thermodynamic equilibrium model. Eight reaction sequences were considered in their model, two dissociation reactions, one formation reaction (that of NO) and five ionising reactions. Microwave techniques tend to suffer a fundamental limit, namely, poor spatial resolution, which is a consequence of the long wavelengths. This tends to make good spatial resolution within the relaxation zone difficult. Manheimer-Timnat and Low had a rather small (12.7 mm diameter) test section and as such, their microwave attenuation signal was probably related to the presence of shock waves in the waveguide than to any ionisation relaxation behind the shock wave in the test section.

Lin et al (1962) used magnetic-induction and microwave reflection probes in a 600 mm diameter shock tube to investigate the ionisation profile behind strong shock waves in air with Mach numbers ranging from 14 to 20 at initial pressures of 2.6 to 26 Pa. Using techniques similar to those used by Lin & Kivel (1959) and Manheimer-Timnat & Low (1959), they observed the power reflection coefficient of the microwave probe in order to deduce the electron number density (more precisely, the electron densities deduced from probes of different frequencies under similar experimental conditions were compared). In conjunction with this experimental technique, Lin et al employed a magnetic-induction process similar to that used by Lamb and Lin (1957) to measure the electrical conductivity distribution behind shock waves
in air with a spatial resolution comparable to the effective width of the applied magnetic field. The main result of this work was the observation that for the range of shock strengths covered (shock velocities from 4.5 km s\(^{-1}\) to 7 km s\(^{-1}\)), the ionisation distance was approximately 10 to 40 times the mean free path of the undisturbed gas ahead of the shock front and that the electron number density appeared to overshoot the equilibrium value, by a factor of between 2 and 3, for some distance behind the shock front before relaxing back towards equilibrium.

In a complementary paper to that of Lin, Neal and Fyfe (1962), an extensive theoretical interpretation was made of the experimental results obtained in the aforementioned work by Lin and Teare (1963). A critical examination was made of the various ionising reaction sequences. Electron impact and ion impact ionisation, photoionisation, charge exchange, electron attachment and ionisation by neutral atom and molecular impact were the ionisation processes considered. Rate equations were derived for these reactions and solved by numerical integration. Since the low ionisation regime was studied, Lin and Teare use a ‘one-way coupling’ approximation between dissociation, ionisation and radiative excitation. One-way coupling refers to the technique whereby the temperature, density and species concentrations are initially calculated independent of ionisation and radiative excitation, and then used to determine the rates for these processes. Upon numerical integration, they produced, as a function of distance behind the shock front, an instantaneous electron production rate plus electron and positive ion densities. As a result, a detailed breakdown of specific ionisation rates for the various ionisation processes was
compiled. The dominant ionisation reactions in their analysis were the atom-atom reactions followed by photoionisation, electron-impact, atom-molecule and molecule-molecule collisional ionisation; the importance of each reaction being a function of shock velocity. Lin and Teare stressed that the electron impact reactions contribute little to the ionisation at shock velocities below about 5 kms\(^{-1}\) but may become the dominant ionising reaction at velocities greater than 9 kms\(^{-1}\). The dominant atom-atom process in the low velocity regime was considered to be the associative ionisation reaction

\[
N + O \leftrightarrow NO^+ + e^-.
\]  

\(\text{...(R1)}\)

The net energy required for this ionising reaction is considerably less than the full ionisation potential of NO, as chemical energy is released by the association of the N and O. On comparing their theoretical model with the experiments of Lin et al., Lin and Teare demonstrated that there was reasonably close agreement between theory and experiment. The conclusion was made that for shock velocities up to 9 kms\(^{-1}\), the dominant electron producing reaction sequences were the atom-atom ionising collisions, whereas electron impact processes may become predominant at shock velocities in excess of 10 kms\(^{-1}\). Furthermore, according to their calculations, the overshoot of the electron number density would be expected to disappear at shock velocities less than 4 kms\(^{-1}\) and greater than 9 kms\(^{-1}\). Their desire to extend the model to shock velocities greater than 9 kms\(^{-1}\) was hampered on two fronts. Firstly, a greater knowledge of the electron impact ionisation rates at higher velocities was required and secondly, the ‘one-way coupling’ must give way to a ‘two-way coupling’ between dissociation and ionisation. Two-way coupling required that the
ionisation and radiative processes occurred simultaneously with the chemical processes and as such, their iterative technique was unsatisfactory.

Wilson (1966) extended the experimental work of Lin et al and the theoretical work of Lin and Teare. Firstly, Wilson conducted experiments at shock velocities from 9 to 12 kms$^{-1}$ and observed the infrared emission of the shock-heated air at wavelengths greater than 5 μm. Above 5 μm the continuum radiation consists mainly of free-free Bremsstrahlung radiation, the intensity of which is proportional to the square of the electron number density. Wilson presents a ‘simple’ model for air in which ‘infinitely fast dissociation’ is assumed. Here Wilson makes the assumption that at shock speeds greater than 8 kms$^{-1}$ in air, dissociation rates are infinite and the gas instantaneously jumps to a state of thermodynamic equilibrium across the shock. This model differs from that of Lin and Teare in that their model assumed finite dissociation and one-way coupling. Wilson's infrared results show some correlation with both the proposed simple model and the model of Lin and Teare. However the radiation intensity in the continuum showed a tendency to be lower than that predicted by certain models. The conclusion was made that below velocities of 9 kms$^{-1}$, the associative ionisation reaction (R1) was the dominant ionisation process (as suggested by Lin and Teare) and furthermore confirmed that at velocities greater than 9.5 kms$^{-1}$, the electron impact processes begin to dominate. The reaction (R1) however, is still thought to be an important ionising reaction beyond 9.5 kms$^{-1}$. The reactions,

\[ N + N \rightleftharpoons N_2^+ + e^- \quad \text{(R2)} \]
and
\[ O + O \leftrightarrow O_2^+ + e^- \]  
...(R3)

are also suggested as becoming important at higher temperatures. Wilson observed that, above 9.5 kms\(^{-1}\), ionisation lengths decrease with shock velocity. This result lends support to the assumption that, for velocities greater than 9.5 kms\(^{-1}\), electron impact ionisation becomes a process that will start to compete with reaction (R1). In the theoretical analysis of Lin and Teare, it was assumed that the energy invested in ionisation was small compared to the enthalpy of the shock heated air and was thus neglected in the energy conservation equation. Wilson, wishing to extend the velocity regime beyond 9.0 kms\(^{-1}\), was not able to make this assumption. Above 9.0 kms\(^{-1}\), the energy invested in ionisation was no longer small compared to the enthalpy of the shock heated air and had to be included in the energy conservation equations when calculating the temperature. Hence a coupling had to be made between the rate equations for ionic and neutral species\(^1\).

Calculations were made and modelling techniques discussed, for the determination of the electron number density in the shock layer surrounding an upper atmosphere reentry vehicle by Evans, Schexnayder and Huber (1970). The authors considered 54 reaction sequences involving 11 reactants. However a reduced set of 18 sequences and 7 reactants was shown to produce almost indistinguishable predictions for intermediate velocities. It was demonstrated that the electron number density profiles are extremely sensitive to finite rate chemistry and that the profiles can be

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1 As dissociation tends to proceed faster than ionisation at higher shock speeds, the ionisation rate equations were decoupled from the dissociation reactions.
significantly changed by finely adjusting the reaction rate constants.

It has been experimentally observed (Lin et al, 1962 and Allen et al, 1962) that at shock velocities below 9.5 kms\(^{-1}\), the nonequilibrium radiation behind the shock front is elevated considerably above the equilibrium value. Zhelesnyak et al (1970) undertook a theoretical analysis of relaxation and nonequilibrium radiation behind shock waves in air. A calculation was made as to the expected populations of atomic and molecular radiators. Their analysis predicted the intensity of radiation from certain spectral regions to pass through a maximum exceeding an equilibrium level. This nonequilibrium radiation overshoot was explained as follows. As had been demonstrated by Appleton et al (1968), a decrease in the dissociation of N\(_2\) results in an increase in the population of N\(_2\) together with a subsequent increase in the atom temperature T\(_a\). In a complementary paper Appleton (1967) also showed that an increase in the vibrational relaxation time \(\tau_v\) increases the vibrational temperature T\(_v\) and so T\(_v\) rapidly approaches T\(_a\). This occurs at the beginning of the relaxation process. Zhelesnyak et al propose that the situation will change as the electron population increases, as there is now a strong interaction between the vibrational transitions and the free electrons. As such the vibrations are intensely “cooled” by electron collisions with the result that T\(_v\) departs from T\(_a\) and approaches T\(_e\). At higher values of T\(_a\) and T\(_v\), the electrons are further heated by the interactions with the vibrational levels of N\(_2\) and T\(_e\) considerably exceeds its local equilibrium value. This local overheating of the electrons takes place in the relaxation zone causing the emission from the molecular transitions to overshoot their equilibrium value. As the shock velocity increases however,
dissociation of $N_2$ increases, resulting in a less pronounced heating of the electrons. This should result in the disappearance of the nonequilibrium radiation overshoot at shock velocities in excess of 9.5 kms$^{-1}$.

An investigation of the ionisation occurring behind shock waves in binary mixes of nitrogen and oxygen was undertaken by Schafer and Frohn (1972). The theoretical study considered a reduced set of species, 9 in total, together with a reduced set of chemical reactions. In the Mach number regime of interest, $M=7$ to $17$, the $NO^+$ ion is considered to be the predominant carrier of positive charge. For reactions involving the dissociation-recombination of NO, the rate constants of Hansen (1968) were employed. The reaction constants of Lin and Teare (1963) were used for the remaining reactions. Schafer and Frohn used hollow total collector and Langmuir probes to determine the ion density behind the shock front. Their theoretical results were confirmed by the experiment and the numerical solutions showed a strong dependence of the relaxation time on the initial oxygen concentration. A change in the relaxation time of an order of magnitude was possible with only a 10% change in the oxygen concentration.

Chan and Glass (1974) presented further results on the radiative relaxation behind high velocity shock waves in air. Photodiode and photomultiplier detectors were used to monitor the luminous emission from the shock heated air at 530 nm. The nonequilibrium radiation overshoot was shown to disappear for shock waves travelling greater than 9.5 kms$^{-1}$, supporting the view that the dissociation of $N_2$ occurs more rapidly, resulting in less overheating of the electrons. The
relaxation times were shown to be a function of molecular processes below 9.5 kms\(^{-1}\) and due to atomic ionisation beyond that velocity.

Zalolin et al (1980) undertook an experimental and theoretical analysis of ionisation behind shock waves in air. They postulated that for shock waves of velocity greater than 9.5 kms\(^{-1}\), the population of the excited states of atoms may be lower than the local-equilibrium value. Because of this, the electron population, \(n_e\), will be smaller than the value calculated by the Saha equation. It was suggested that this phenomenon may have an effect on the ionisation rate since at the high velocity regime, ionisation of atomic species is the dominant ionisation process. Plots of their numerical calculations, together with the experimental results of Wilson (1966) show satisfactory, though not conclusive, agreement. Their hypothesis is somewhat supported by the experimental determination of the population of excited atomic states of nitrogen and oxygen using emission spectroscopy. The intensity of the transitions \(\lambda=745.2\) nm in nitrogen and \(\lambda=777.3\) nm in oxygen were monitored with a spectrometer equipped with several radiation detector channels. They observed that the intensity of emission from these excited atomic states was some 40 times lower than expected from the equilibrium intensity of radiation. The electron population was established via infrared interferometry. These results are among the small amount of experimental data that exists for the electron number density at the low pressure, high shock velocity regime.

Ionisation was measured behind intense shock waves in air by Gorelov et al (1983) using thin disposable electrostatic probes. The shock velocity ranged from 4 to 16 kms\(^{-1}\). In order to calibrate the probes, test measurements of the electron densities were conducted
using a microwave reflectometer operating at 39 GHz for shock velocities from 5 to 7 kms\(^{-1}\) and by observing the Stark broadening of the hydrogen beta line at the wavelength of 486.1 nm for velocities in excess of 10 kms\(^{-1}\). These results confirmed the proposal of Zalogin \textit{et al} (1980) that a deviation from local thermodynamic equilibrium occurs due to the depletion of excited states at velocities exceeding 9 kms\(^{-1}\) when test pressures are low.

Vardavas (1984) developed an iterative method for modelling reactive gas flows within shock tunnels. The model overcomes the problems associated with the solution of "stiff" equations that are a result of specific chemical reactions proceeding at substantially faster rates than those of the bulk flow properties. The essence of the nonequilibrium model involves the solution of a system of equations. This system contains the equation of state, the gasdynamic equations (conservation of mass, momentum and energy), and rate equations. The solution of this system yields the concentration of gas species \(i\), \(q_i\), in mol g\(^{-1}\) of the mixture, at any given point in the flow.

The model described uses a single temperature to characterise the flow. It makes predictions as to the species mole concentrations of the 11 constituents of shock heated air. At the conditions of interest for the AOTV, the model predicts equilibrium electron number densities approximating \(3.5 \times 10^{15}\) cm\(^{-3}\). These populations are rapidly reached, the peak in the concentration occurring approximately 0.5 cm behind the shock front. The induction time for ionisation is very short. These results compare favourably with the theoretical work of Lin and Teare (1963) and the experimental work of Wilson (1966) and suggest
that, at the shock velocities considered, the electron-atom ionisation processes dominate.

Park (1985) calculated the dissociating and ionising nonequilibrium flows behind normal shock waves at conditions appropriate to the AOTV. This calculation characterized the flow by two temperatures. The departure of the vibrational and electron temperatures from the heavy particle temperature was addressed and the viscous transport properties were accounted for. The chemical rate parameters were varied to determine their effect on the radiative behavior of the plasma. This model makes predictions for the species populations behind a shock wave travelling at a velocity of 10 kms$^{-1}$ into air at a pressure of 13 Pa. Eleven species were considered as participating in 18 reaction sequences. Park concluded that calculations of the vibrational relaxation times, based on the formula of Millikan and White (1963), underestimate the relaxation times at high temperatures and thus affects the predicted population of species. The usual expression for the chemical rate coefficients, characterized by one temperature, were deemed inadequate. The dissociation rates have typically been dependent on the vibrational temperature. Park showed that the rotational ladder climbing processes can occur together with vibrational ladder climbing and, as the rotational temperature exceeds the vibrational temperature, rotational processes will significantly affect the dissociation rate. Finally, Park acknowledged that data for the nonequilibrium radiation, to which the theory could be compared, is inadequate and the best data are scattered by a factor of 4.
Park (1986) refined the analysis discussed in the 1985 paper to account for its various limitations and produced numerical results for shock wave velocities up to 6.4 kms\(^{-1}\) in nitrogen. A limiting value for the cross section for vibrational excitation was introduced to remove the unrealistically large value predicted by the Millikan and White formula for temperatures in excess of 40,000 K. This limiting value was calculated by adjusting the computed radiative behaviour to match that observed in shock tube experiments. Corrections were also made to the vibrational excitation rates shown by Lee (1985) to become smaller than those predicted by classical Landau-Teller theory for higher temperatures. This departure from the Landau-Teller theory occurs at these temperatures because the excitation process displays a diffusive characteristic similar to that discussed by Keck and Carrier (1965) rather than the single step excitation assumed in the classical theory. On this basis Park used the vibrational relaxation time derived by Lee. Reaction rates based on a geometric average temperature \(T_{av}\) given by \(T_{av} = \sqrt{TT_v}\), were also adopted in the revised model. Caution needs to be exercised however in extending the model to higher velocities. At higher velocities, the electron impact dissociation and ionisation processes becomes important. The rate coefficients for the electron impact dissociation processes are unknown, but are thought to be 100 times faster than the heavy particle impact dissociation.

Park (1989\(^2\)) applied the two-temperature model to the investigation of chemical nonequilibrium in the shock layer at conditions applicable to that of the reentry environment of the AOTV corresponding to a shock wave velocity of 10 kms\(^{-1}\). The electron impact dissociation rate, which

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\(^2\) It is noted at this point that the original paper "Assessment of two-temperature kinetic model for ionising air", appeared in AIAA in 1987. It was reprinted in The Journal of Thermophysics in 1989. The 1989 paper is referred to from here on in.
has a large rate constant, was dictated by the geometric average temperature $T_{av}$ (as are all the dissociation rates). Park's model is discussed in detail in chapter 3.

Considerable experimental and theoretical work has been undertaken which aims to measure and model the ionisation processes, rates and electron populations behind shock waves in air. It is considered that the major unresolved questions concern the specific reaction processes that dominate at the high shock velocity regime. These processes will have a significant bearing on the ionisation distances.

To date, very little experimental data exists for the ionising reaction kinetics that occur behind the high enthalpy shock waves under consideration in this study. The current consensus is that the reactions R1, R2 and R3 are the dominant reaction processes leading to ionisation, although the reactions dominate according to the shock velocity. There is a need however for experimental data to support the predictions at high velocities. Furthermore, the rate controlling temperatures are presently unknown at this regime. Indeed, it is unclear as to whether more than one temperature is characterising the flow. The reaction processes and the rate controlling temperatures will affect the net production of free electrons. Hence a precise theoretical prediction of the expected population of electrons is difficult, especially in the absence of experimental data which can be used for code validation.

The major question that this thesis attempts to address is: is the flow at conditions characteristic of AOTV reentry in thermal equilibrium or
not and, if not, is the two-temperature model proposed by Park (1989) consistent with experimental data?

To answer this question, electron number densities will be measured in order to provide the much needed experimental data at the high shock enthalpy regimes. These results will yield data on the ionisation distances which can be used to infer information on the reaction processes. The characteristic temperatures will also be measured in order to determine whether or not multitemperature processes are occurring. Furthermore since the electron number density predicted by theory is sensitively dependent on whether or not the flow is in thermal equilibrium, measurement of this density will provide a basis for testing the validity of assuming thermal equilibrium.

1.3 An overview of the current experiments

The aim of the experiments described in this thesis are five-fold:

i) To obtain measurements of the electron populations behind high enthalpy shock waves at conditions applicable to the flight regime of the AOTV approaching perigee and to make comparisons of these results to the predictions of both one and two-temperature models for ionising air.

ii) To study the time resolved emission behaviour of the plasma at the same condition.

iii) To determine the rotational temperature of the $\text{N}_2^+$ molecule at a point behind the shock front, and to make comparisons of this result to the predictions of both one and two-temperature models for ionising air.
iv) To measure the relative emission intensity of two transitions in atomic and ionic oxygen, in order to make a comparison with the ion-to-atom intensity ratio predicted by the two-temperature model.

v) Finally, using laser spectroscopic techniques, to measure the time resolved absorption by atomic oxygen and to compare this with the predictions of the two-temperature model for ionising air.

The major portion of this thesis is devoted to fulfilling the first aim outlined above. This aspect of the experiment was considered the most important and challenging. This is in view of the fact that so little experimental data exists on ionisation at the conditions of interest, coupled with the experimental difficulties associated with the production of high enthalpy shock waves and the subsequent measurement of electrons densities in the shock tube environment. The measurement of the electron densities required the development of an accurate, non-intrusive diagnostic system, capable of measuring relatively low electron populations with a high degree of spatial and temporal resolution.

1.4 The structure of this thesis

Following this chapter, which has given a broad overview of the work that has been conducted into ionisation behind shock waves in air, chapter 2 discusses the ionisation processes and the emissive behaviour of shock heated air, an understanding of which is of considerable importance in the analysis of data from the emission spectroscopic experiments. Chapter 3 addresses in detail the two-temperature kinetic model for ionising air developed by Park (1989). Chapter 4 outlines the objectives of the present work and details
the experimental techniques employed to achieve those aims. Chapter 5 details the data reduction process, that is, the manner in which the raw experimental data was reduced to meaningful numbers and the determination of the experimental error. Chapter 6 presents the results, and highlights some of the experimental limitations encountered during the work. Chapter 7 discusses these results in relation to the validity of the theoretical codes and the possible nature of the chemical kinetics occurring. The conclusions of the work are summarised in chapter 8, together with suggestions for the directions of further research.
Chapter 2
IONISATION PROCESSES AND THE EMISSIVE PROPERTIES OF SHOCK HEATED AIR

2.1 Introduction

This chapter details the various chemical kinetic processes that contribute to the ionisation of species in a shock heated flow. Ionisation by atomic and molecular collisions, by electron and ion impact, as well as photoionisation are discussed. Charge exchange and electron attachment are two reaction processes that are also detailed, not so much for their effect on the overall ionisation, but because of their possible influence on the electron number density profile via the continuous reshuffling of the relative populations among the different positive ions. A non-complete, but certainly sufficient, list of ionising reaction sequences is presented and the relative importance of various reactions is discussed. Cross sections and rate coefficients for these reactions are also detailed.

The radiative properties of high temperature air are also discussed, although in somewhat less detail. Due to the great number of constituent species that compose a shock heated air plasma, there are many atomic and molecular emitters over the entire spectrum. It is necessary to obtain a knowledge of the most dominant radiators and determine in which part of the spectrum they lie in order to
successfully conduct the spectroscopic emission experiments.

### 2.2 Ionisation processes

#### 2.2.1 Ionisation by atomic and molecular collision

A comprehensive, but not complete, list of ionising reactions by atomic and molecular collisions is given in appendix A. Ionisation by atomic and molecular collisions is, in general, not a dominant ionisation process. As long as the mean kinetic energy per collision partner \((3/2 \, kT)\) is small in comparison with the ionisation potential of the atomic or molecular species undergoing ionisation, reactions of the type presented in appendix A are not important. Energetic collisions between two particles in which the energy of relative motion exceeds the ionisation potential are relatively rare. The probability of an inelastic collision resulting in an ionising transition depends on the duration of time for which the two particles are within a distance \(d\) of each other. This time is of the order \(d/v\) where \(v\) is the relative velocity of the two particles. \(\hbar/\Delta E\), where \(\Delta E\) is the total internal energy change in the system and \(\hbar\) is Plank's constant divided by \(2\pi\), is the time taken by an electronic transition within an atom and should be compared with \(d/v\). For \(d/v \gg \hbar/\Delta E\), transitions to ionising levels are unlikely to occur as the electrons have ample time to adjust themselves to the changes resulting from the slowly approaching particles. Hence the cross section for ionisation via this process is small, its magnitude being dependent on a simple test of the so called near-adiabatic condition (Massey and Burhop, 1952),

\[
\frac{d\Delta E}{\hbar v} \gg 1 \quad \text{(2.1)}
\]
In the case of Ar (and all the noble gases), this condition holds true for a very large velocity range. However, in general the near-adiabatic condition may be violated when chemical energy is available in the collision process. Should the amount of energy required to produce the ion-electron pair be much less than the ionisation potential of the molecular complex formed, ionising reactions of the type in appendix A could proceed very rapidly.

Bates and Massey (1954) detail a general treatment of atomic and molecular excitation processes using the so called crossing-point method. Should crossing (or near crossing) of the potential curves for atomic collisions or potential surfaces for molecular collisions, occur, these ionisation processes will dominate. They consider the collisions between atoms or molecules A and B that approach each other along potential curves which, at a separation of R, intersects one of the potential curves of the complex molecules formed $A^+B^+$ and an electron of zero energy. Under such a situation, if separations less than R occur, the collision product may be put into an excited state with an energy above the ionisation potential. Instead of decaying by the emission of a photon, it is more likely to make a transition to the continuum state, that is, an ion plus a free electron with kinetic energy (autoionisation). Bates and Massey write the following expression,

$$Q^i = \pi R^2 (1 - e^{-R/v\tau})$$ ...

(2.2)

for the ionisation cross section, where $\tau$ is the mean lifetime before autoionisation occurs with $v$ being the relative velocity with which the atoms or molecules approach. This is expressed by Lin and Teare
where $g$ is the ratio between the statistical weights associated with the initial potential energy curve. This leads to a crossing and the sum of the statistical weights associated with all the other possible initial curves. $R_\times a_0$ is the distance between the two centers of mass of the colliding system where the crossing occurs, $a_0$ is the first Bohr radius; $\mu$ is the reduced mass of the system; $\tau_{AI}$ is the autoionisation lifetime and $E$ is the impact energy. This energy must of course be larger than the activation energy, $E_\times$, hence the condition $E > E_\times$ in equation 2.3.

The dominant ionisation process at low shock velocities is the associative ionisation reaction $R_1$. Lin (1958) observed the ionisation rate behind shock waves in gas mixtures at low pressures, containing small percentages of $N_2$ in $O_2$. From those measurements, the Maxwell-averaged cross section for reaction $R_1$ was deduced. There exist many possible crossing points for reaction $R_1$ and Lin therefore assumed that the velocity averaged results were due to such curve crossings. Hence for this reaction, with $R_\times a_0 = 10^{-8}$ cm, $\mu = 7.5$ amu, $E = 3$ eV (the energy of the reaction) and assuming $\tau_{AI} < 10^{-14}$ sec (which is an estimate based on the observation that the auto-ionisation times, unknown for $N$ and $O$, lies in the range from $10^{-15} < \tau_{AI} < 10^{-11}$ sec for the excited states of helium), Lin and Teare derive an approximate expression for the ionising collision cross section for reaction $R_1$ as

$$Q_{E > E_\times} \equiv g \pi (R_\times a_0)^2 \equiv 3 \times 10^{-17} \text{cm}^2.$$ 

... (2.4)
For the collisional ionisation processes to proceed, it is assumed that
the kinetic energy (available in the centre of mass reference frame)
exceeds the activation energy $E_x$. Hence, the cross section of equation
2.3 is velocity-averaged to ensure this criteria. The velocity averaged
cross section $\overline{Q}$ of equation 2.4 is given as

$$\overline{Q} \equiv 3 \times 10^{-17} \frac{E_x}{kT} \exp \left( -\frac{E_x}{kT} \right) \text{cm}^2$$  \hspace{1cm} (2.5)

where $k$ is Boltzmann's constant and $T$ is the temperature, under the
assumption that the velocity distribution was approximately
Maxwellian behind the shock front. For $\tau_{Al} > 10^{-14}$ sec, Lin and Teare
arrive at the corresponding expression for the ionising collision cross
section and the velocity averaged cross section

$$Q_{E > E_x} \equiv 6 \times 10^{-31} \frac{1}{E^{1/2} \tau_{Al}} \text{cm}^2 \hspace{1cm} \text{...(2.6)}$$

$$\overline{Q} \equiv 3 \times 10^{-31} \frac{1}{E^{1/2} \tau_{Al}} \left( \frac{E_x}{kT} \right) \exp \left( -\frac{E_x}{kT} \right) \text{cm}^2 . \hspace{1cm} \text{...(2.7)}$$

As the temperature range of Lin and Teare's experimental results
were very narrow, they were unable to obtain an accurate value for the
cross section between the limits of the highest (4.8 eV) and lowest
(2.8 eV) activation energies for reaction R1. To enable a determination
of the temperature dependence of the cross section for reaction R1,
forward and backward rate coefficients were obtained for the atomic
and molecular collisional ionisation reactions. The fact, that
atom–molecule or molecule–molecule collisional interactions are
strongly dependent on the molecular orientation at impact, introduces
great complexity in the calculation of the collisional cross section. For
the molecule-molecule collisional reactions, the rate constants for the
forward reactions were obtained from the molecular beam experiments
of Utterback & Miller (1961) and Utterback (1963). Utterback & Miller
experimentally determined the ionisation cross section for \( \text{N}_2 \)
molecules in collision with \( \text{N}_2 \) molecules over the energy range from 2
to 1000 eV. The observed cross sections ranged from \( 10^{-20} \) to \( 10^{-16} \) cm\(^2\).
The ionisation cross section versus energy curve exhibited structure at
around 20 eV indicative of competing reaction processes. At these
energies, dissociation effects are suggested as possibly contributing to
the observed structure as well as the ionisation of both colliding
molecules which occurs at 31.3 eV. In a complementary paper,
Utterback (1963) determined the ionisation cross section for collisions
between \( \text{N}_2 \) and \( \text{O}_2 \) molecules over an energy range from 2 to 1000 eV,
employing the same low pressure, parallel plate ionisation chamber.
The observed cross section ranged from \( 10^{-20} \) to \( 5 \times 10^{-16} \) cm\(^2\). After
correcting for the centre of mass energy, agreement was obtained for
the result of \( \text{N}_2 - \text{O}_2 \) and \( \text{O}_2 - \text{N}_2 \) experiments. Lin and Teare concluded
that it is reasonable to express the forward rate constants for the atomic
and molecular collisional ionising processes in the Arrhenius form,

\[
\kappa_i = A_i(T) \exp\left(-\frac{\Delta E_i^0}{kT}\right),
\]

...(2.8)

where \( A_i(T) \) is the forward rate constant for collisional ionisation for
the \( i \)th reaction sequence and \( \Delta E_i^0 \) is the energy of the reaction.

For \( T < 30,000 \) K, the values of \( A_i(T) \) for molecule-molecule ionising
collisions are smaller than those for atom-atom collisions. For
\( T > 30,000 \) K, the different values of \( A_i(T) \) become comparable.
2.2.2 Electron and ion impact Ionisation

Ionising reactions by electron and ion impact are of the form

\[ e^- + X \leftrightarrow X^+ + e^- + e^- \quad \text{...(R4)} \]

and

\[ X^+ + Y \leftrightarrow X^+ + Y^+ + e^- \quad \text{...(R5)} \]

where X and Y represent any neutral atom or molecule and e^- represents free electrons. For electron impact ionisation to proceed, incident electrons must have energies at least equal to the first ionisation potential E_I. The cross section for this reaction rapidly increases above threshold to a maximum where it falls off approximately linearly with high energies. If the atom in the collision has more than one subshell, more than one threshold occurs at high energies resulting in some structure in the ionisation function. The electron impact ionisation process is an endothermic reaction and hence there exists a threshold value for the electron energy below which the reaction will not proceed. The cross section for electron collisional ionisation varies as \( E^{-1} \log E \) at high energies as predicted by the Bethe-Born approximation. There is an \( (E-E_I)^n \) dependence on the cross section near threshold. Wannier (1953) observed the dependence of the yield on the electron energy just above threshold. A value for n of 1.127 was obtained by Wannier using a semi-classical treatment (for ions the exponent lies between 1.127 and 1.0), while various quantum mechanical calculations have given values for n of 1.0, 1.13 and 1.5 (Rudd, 1981).
For electrons with energies less than the energy difference between the lowest excited state and the ground state, the total collision cross section is simply equal to the elastic collision cross section (Massey and Burhop, 1952). However as the electron energies increase beyond this difference, excitation and ionisation of atoms will proceed and the total cross section will now become equal to the sum of the cross section for elastic collisions together with those for excitation and ionisation. Massey and Burhop give

\[ Q = Q_o + \sum Q_s + \int_{0}^{E_{max}} Q_E \, dE \] 

for the total cross section for electron impact with atoms or ions. \( Q_o \) is the elastic cross section, \( Q_s \) is the cross section for excitation and \( Q_E \, dE \) is the cross section for ionising collisions for which the energy of the liberated electron lies between \( E \) and \( E+dE \).

Lin and Teare (1963) reproduce the total ionisation cross section \( Q_{iX}(\varepsilon) \) for collisions between electrons with energy \( \varepsilon \) and atoms or molecules of type \( X \), in terms of the local electron energy distribution function \( f(\varepsilon) \). The rate of ion pair production per unit volume by electron impact behind a shock front is given as

\[ \frac{dn_{e}}{dt} = n_{e} \sum_{X} n_{X} \int_{w_{iX}}^{\infty} Q_{iX}(\varepsilon) f(\varepsilon) \, d\varepsilon \] 

where \( n_{e} \) is the local electron number density; \( n_{X} \) is the number density of molecules of type \( X \); \( w_{iX} \) is the threshold energy; and \( v \) is the electron
velocity with an energy $\varepsilon$. The electron velocity distribution will approximate the Maxwellian function at the electron temperature $T_e$ which is stated as being comparable to, but not identical with, the heavy particle translational temperature $T$. As a first approximation, the temperatures $T$ and $T_e$ are assumed by Lin and Teare to be equal when estimating the electron impact ionisation rate. With this assumption equation 2.10 is re-written as

$$\frac{dn_e}{dt} = n_e \left( \frac{8}{\pi m_e} \right)^{1/2} \left( \frac{1}{kT} \right)^{3/2} \sum X \int \frac{\exp(-\varepsilon/kT)}{\varepsilon} Q_{iX}(\varepsilon) \varepsilon \, d\varepsilon , \quad \text{(2.11)}$$

where $m_e$ is the electron mass.

Tate and Smith (1932) measured the ionisation cross sections of electron impact with the diatomic molecules $N_2$, $O_2$, and NO. Their measured cross sections exhibit the rapid rise to threshold followed by a monotonic decrease with increasing electron energy. The electron ionisation cross sections for atomic N and O are not as well known as their molecular counterparts. The cross section versus electron energy curve for diatomic molecules and noble gases are shown to be quite similar except for the differing threshold energies in each case. Massey and Burhop have compiled the available data on collisional ionisation by neutral atoms, ions and molecules. Looking for correlations in this data, it is evident that, with the exception of the ionisation potential, there is no threshold energy below which ionisation is not possible, and for positive ions, the cross section is exceedingly small up to energies considerably greater than the ionisation potential. In comparison with the electron impact ionisation processes, ion impact ionisation will be insignificant. Since the cross
section versus electron energy curve for diatomic molecules and noble
gases are shown to be similar, Lin and Teare state that it is reasonable
to assume that the cross section for ionisation by electron impact for N
and O follow this pattern and exhibits similar curves but with different
threshold energies.

2.2.3 Photoionisation

Ionising reactions by photoionisation are of the form

\[ h\nu + X \leftrightarrow X^+ + e^- . \] ...

\( \text{(R6)} \)

A radiation field of sufficiently short wavelength will produce ionisation. The energy of an incident photon \( h\nu \) must of course be equal to, or exceed, the first ionisation potential. Most atomic systems have their thresholds in the ultraviolet. The cross section for photoionisation rises asymptotically at threshold and as with the electron collisional ionisation, falls off with increasing photon energies. Multiphoton ionisation is possible although the intense radiation fields required to cause ionisation from a real or virtual excited state before decay are usually obtained only with lasers and are not found in the shock tube. Photoionisation studies have been carried out in air by Weissler et al (1952) and Po Lee (1955).

Lin and Teare (1963) express the rate of ion pair production per unit volume due to photoionisation (reaction R6) behind a shock front by

\[ \frac{dn_e}{dt} = c \sum_X n_X \int \frac{w_{iX}}{h} Q_{iX}(\nu) n(\nu) \, d\nu , \] ...

\( \text{(2.12)} \)
where \( c \) is the speed of light; \( Q_{fx}(v) \) is the photoionisation cross section for type X molecules at a radiation frequency \( v \); and \( n(v)\,dv \) is the number density of photons with frequencies between the interval \( v \) and \( v+dv \).

The photoionisation cross section deduced from ultraviolet absorption studies of \( \text{N}_2 \), \( \text{O}_2 \) and NO by Weissler and Po Lee (1952) and Po Lee (1955) have shown that the cross section rises sharply from threshold and attains a peak at approximately \( 2 \times 10^{-17} \text{ cm}^2 \) and, as with the electron impact ionisation process, decreases with increasing photon energy. The functional form of the photoionisation cross sections for the atomic species are similar to their molecular counterparts apart from the different threshold energies. This conclusion is drawn from the observed cross section of monatomic gases.

Camm et al (1962), Hammerling (1960) and Penner (1959) have undertaken experimental and theoretical investigations of the ultraviolet radiation emitted behind strong shock waves in air. They conclude that most of the far ultraviolet radiation emitted comes from the \( b'1\Sigma_u^+ \rightarrow X^1\Sigma_g^+ \) transition in \( \text{N}_2 \). Green and Barth (1965) use experimental data on electron inelastic collisions in the atmosphere, together with a generalization of the Born approximation, in order to model the excitation and ionisation cross sections in \( \text{N}_2 \). A result of these calculations, is that a large fraction of the collision energy ends up in ultraviolet emitting states. They suggest that the dominant radiation emitter in the far ultraviolet is the large cross section \( (2.2 \times 10^{-16} \text{ cm}^2) \) \( b^1\Pi_u \rightarrow X^1\Sigma_g^+ \) transition (the Birge-Hopfield bands) in \( \text{N}_2 \) observed by Huffmann et al (1963) which is coincident with the
transition in N\textsubscript{2} at 12.9 eV. Lin and Teare (1963) express the total intensity of this radiation per unit area of the shock front in the form

\[
I \equiv \frac{\bar{n}_{N_2} \exp\left(-E^*/kT^*\right)}{2(\tau_r + \tau_c)} \frac{E^*L}{E_L}, \quad \ldots \quad (2.13)
\]

where \( \bar{n}_{N_2} \) is an averaged number density of N\textsubscript{2} in the shock front reaction region; \( E^* = 12.9 \) eV is the energy difference between the two electronic states of N\textsubscript{2} (the Worley bands); \( L \) is the effective thickness of the reaction region; \( \tau_r \) and \( \tau_c \) are the radiative lifetime and the collisional de-excitation time, respectively, of the \( b^1\Sigma_u^+ \) state of N\textsubscript{2}; and \( T^* \) is the excitation temperature for the electronic state of N\textsubscript{2}. (Equation 2.13 neglects absorption and re-emission, that is, the plasma is assumed to be optically thin.) By putting \( Q_\text{fx}(\nu) = 2 \times 10^{-17} \text{ cm}^2 \) (which is the peak photoionisation cross section observed by Po Lee, 1955) for all photon energies above threshold they obtain from equations 2.12 and 2.13

\[
\frac{dn_e}{dt} = \frac{\pi a_o^2 (n_{O_2} + n_{NO}) \bar{n}_{N_2}}{8(\tau_r + \tau_c)} L \exp\left(-E^*/kT^*\right), \quad \ldots \quad (2.14)
\]

\( \Sigma n_X \) in equation 2.12 has now been replaced by \( (n_{O_2} + n_{NO}) \) since only photons of energy 12.9 eV have sufficient energy to ionise the O\textsubscript{2} and NO molecules. All other species (and the reactant products) have ionisation potentials beyond 12.9 eV. See table 2.1 for the relevant ionisation potentials.
<table>
<thead>
<tr>
<th>Species</th>
<th>Ionization potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>14.53</td>
</tr>
<tr>
<td>O</td>
<td>13.614</td>
</tr>
<tr>
<td>N⁺</td>
<td>29.593</td>
</tr>
<tr>
<td>O⁺</td>
<td>35.108</td>
</tr>
<tr>
<td>N₂</td>
<td>15.576</td>
</tr>
<tr>
<td>O₂</td>
<td>12.20</td>
</tr>
<tr>
<td>NO</td>
<td>9.26</td>
</tr>
<tr>
<td>Ar</td>
<td>15.755</td>
</tr>
<tr>
<td>Ar⁺</td>
<td>27.62</td>
</tr>
<tr>
<td>H</td>
<td>13.595</td>
</tr>
<tr>
<td>H₂</td>
<td>15.422</td>
</tr>
<tr>
<td>Na</td>
<td>5.138</td>
</tr>
<tr>
<td>Fe</td>
<td>7.87</td>
</tr>
<tr>
<td>Cr</td>
<td>6.764</td>
</tr>
<tr>
<td>Ni</td>
<td>7.635</td>
</tr>
</tbody>
</table>

Table 2.1
Ionisation potentials for the atoms, molecules and ions present in shock heated air in the experiment. Hydrogen is included as it is used in the Stark broadening experiments and Na, Fe, Ni and Cr since they are the dominant impurities.
In order to arrive at an estimation for the ionisation rate from equation 2.14, Lin and Teare take from Hammerling (1960) the suggested values for \( \tau_r \) and \( \tau_c \) as

\[
\tau_r = 4 \times 10^{-9} \text{ sec} \quad \text{(2.15)}
\]

and

\[
\tau_c = \left( \bar{n}_{N_2}, \bar{C}_{N_2}, \bar{Q}_{N_2} \right)^{-1}, \quad \text{(2.16)}
\]

where \( \bar{C}_{N_2} = (8kT/\pi m_{N_2})^{1/2} \) is the mean thermal velocity of \( N_2 \) molecules, and \( m_{N_2} \) is the mass of the nitrogen molecule.

### 2.2.4 Charge exchange

At low energies, atomic or molecular collisions with negative ions may lead to the annihilation of the initial ion with the simultaneous production of a new negative ion via the process of electron exchange

\[
A^- + B \leftrightarrow B^- + A \quad \text{(R7)}
\]

or by the negative ion-molecule reaction

\[
A^- + BC \leftrightarrow B + AC, \quad \text{(R8)}
\]

where \( A, B \) and \( C \) can be atoms or molecules. A comprehensive, but not complete, list of charge transfer reactions are given in appendix B.

These reactions involve the transfer of a single charge from species to species and so do not affect the net free electron production rate immediately behind the shock front. However at later times (and
therefore further distances) behind the shock front, the electron-ion recombination reaction rates will become comparable to the ionisation rates. In the case where different recombination processes have differing rates (for example, radiative recombination for atomic ions versus dissociative recombination for molecular ions) the charge transfer reactions may become important. The dissimilar rates for recombination could influence the electron number density profile via the continuous reshuffling of the relative populations among the different positive ions.

Information on the rate constant for the charge exchange reactions is very limited. Christophorou (1971) has assembled a list of authors who have studied the reactions R7 and R8. The limited experimental data suggests that the cross section for these reactions with collision partner energies of around 1 eV is of the order $3 \times 10^{-16} \text{ cm}^2$, which is comparable to the momentum transfer cross section (Lin and Teare, 1963).

### 2.2.5 Electron attachment

The dominant electron attachment reactions that are likely to occur behind high enthalpy shock waves in low pressure air are listed in appendix C. These reactions specifically involve $O_2$ which has a very high electron affinity. Although these reactions have a minuscule effect on the overall ionisation history, the dissociation rates of $O_2$ and NO may be considerably influenced by these reactions (at high electron densities and temperatures). Atomic and molecular oxygen are known to have very high electron affinities (Burch, Smith & Branscomb, 1958; Pack & Phelps, 1966; Curran, 1961; Evans & Uri, 1949). It has been suggested (Christophorou, 1971) that a two step process is responsible
for the electron attachment to the O\textsubscript{2} molecule. In the initial phase of the reaction scheme, the attachment of a low energy electron to O\textsubscript{2} in the ground vibrational state (v=0) of its ground electronic state (X\textsubscript{3}Σ\textsubscript{g} \textsuperscript{-}) leads to the formation of an unstable, vibrationally excited negative ion in its v=1 vibrational state, that is,

\[
\text{O}_2(v=0) + e^- \rightarrow \text{(O}_2^*)_{(v=1)}
\]

where the asterisk indicates that the molecule is in an excited state. This vibrationally excited ion then undergoes vibrational de-excitation via a collision with a third body X, that is,

\[
\text{(O}_2^*)_{(v=1)} + X \leftrightarrow \text{(O}_2^-)_{(v=0)} + X^*
\]

If the collision does not occur, the excited state ion will autoionise as decay by radiation will not proceed preferentially. Work on the electron affinities of O\textsubscript{2} (Pack & Phelps, 1966), has shown that a two step process for electron attachment to O\textsubscript{2} may be consistent with the three body reaction

\[
\text{O}_2(v=0) + e^- + S \leftrightarrow \text{(O}_2^-)_{(v=0)} + S^*
\]

In their reaction sequence, Pack and Phelps have suggested that S may be either an atom or molecule. However when S is an atom, excess energy from the three body reaction appears as translational energy and when S is a molecule, some of the excess energy appears as internal energy of the molecule.
The reaction schemes discussed above are low energy, non-dissociative electron attachment processes. However, high energy, two body electron attachment reactions of the form

\[ e^- + NO \rightarrow O^- + N^* \]

can also proceed in the environment under consideration.

Wilson (1966) studied the ionisation rate behind high speed shock waves in air by observing the infrared emission around 6 μm, where most of the radiation is due to the free-free Bremsstrahlung processes. By measuring the slope in the infrared emission signal, Wilson was able to infer an ionisation distance. The ionisation time was defined as the time at which a line drawn through the maximum slope of the infrared signal reached peak signal. This time was multiplied by the shock velocity to give the ionisation distance. These results, together with Wilson's theoretical work and that of Lin & Teare, are presented in figure 2.1. This plot provides an indication as to the most likely reaction sequences leading to ionisation for given shock velocities.

2.3 The emissive properties of shock heated air

Kivel et al (1957) present a theoretical analysis that allows an estimate to be made of the emissivity from the constituents of shock heated air. In their analysis, they assume that the strongest transitions from the high vibrational levels of the electronic ground state go to the lower vibrational levels of the electronically excited upper state. With this
Figure 2.1
Theoretical and observed ionization distances behind shock waves in air. Figure is reproduced from Wilson (1966).
assumption, they approximate all upper vibrational energy levels by the lowest vibrational levels of the upper electronic states. They concede that this assumption is not strictly correct and indeed contradicts other assumptions used in their analysis. However, the assumption is useful in making an estimate of the emissivity.

With this assumption, Penner (1959) derives the effective emissivity $\varepsilon_{\text{eff}}$ from the NO molecule as

$$\varepsilon_{\text{eff}} = 3.6 \times 10^6 \left( \frac{hc}{kT} \right)^5 \omega_0^4 \left( \exp\left(\frac{-hc\omega_0}{kT}\right) \right) \delta \psi f \frac{\rho}{\rho_0} \quad \ldots(2.17)$$

where $E_0 = h\omega_0$ is the energy of the lowest vibrational level of the upper electronic state measured relative to the ground electronic state, $\delta$ is the thickness of the plasma; $\psi$ is the number of NO molecules; $f$ is the oscillator strength of the transition and $\rho/\rho_0$ is the normalized air density ($\rho_0$ is the density at S.T.P). Penner acknowledges that equation 2.17 may be applied to all extensive band systems; the $\beta$-bands of NO, the Schumann-Runge bands of $O_2$ etc. The spectral distribution of this emissivity is obtained by differentiating equation 2.17 with respect to $\omega_0$ and is found to be proportional to $\omega_0 = E_0/hc$. This implies that the emissivity is homogenous over the visible and UV regions of the spectrum. This analysis has been shown to be within a factor of two of a more complex treatment of the problem (Kivel et al, 1957).

For band systems (the vibration-rotation bands of NO, $N_2$, $N_2^+$ etc) Penner derives

$$\varepsilon_{\text{eff},i} = \delta i \psi_i \left( \frac{\rho}{\rho_0} \right) T^4 \left( \exp\left(\frac{-hc\omega_i}{kT}\right) \right) \quad \ldots(2.18)$$
for the effective emissivity coming from the \( i^{th} \) band system where \( c_i \) is a characteristic constant that includes all the factors that are independent of pressure and temperature. Clearly this is no longer a function uniform over the entire spectrum. Equations 2.17 and 2.18 are compared by Penner and a resultant single relation,

\[
\varepsilon_{\text{eff},i} = \delta_i \left( \frac{N_i}{5.4 \times 10^{19}} \right) \exp\left( \frac{T_i}{T} \right) \left( 10^{-4} T \right)^{n_i} \quad \text{with} \quad \varepsilon_{\text{eff}} = \sum_i \varepsilon_{\text{eff},i} , \quad \text{(2.19)}
\]

is derived for the emissivity of hot air. Table 2.2 is reproduced from Penner and gives the values for the characteristic constant \( c_i \), electronic excitation temperature \( T_i \), wavelength \( \lambda_i \) and oscillator strength \( f_i \) for the species. \( N_i \) is the number density of molecules per unit volume in the \( i^{th} \) upper state. It is clear that the strongest emitters are the first negative system of \( N_2^+ \) and the first and second positive systems of \( N_2 \). It is stated that for the \( O_2 \) Schumann-Runge bands; the \( NO \) \( \beta \) and \( \gamma \) bands; the \( N_2 \) first and second positive bands; and the \( N_2^+ \) first negative bands, that the values for \( f_i \) given in table 2.2 were correct to within their quoted error and that over the spectral interval considered, there was no significant dependence on the wavelength, temperature or density.

The strongest atomic emitters, nitrogen, oxygen and their respective ions, represent the only atomic constituents of shock heated air. The strongest transitions in nitrogen lie in the UV region of the spectrum around 120.0 nm. There are transitions throughout the visible but they are relatively weak, proving to be a little stronger in the infrared. Similarly, the strongest emitters in atomic oxygen lie in the UV.
<table>
<thead>
<tr>
<th>Specie</th>
<th>Designation</th>
<th>$c_i$ (cm$^{-1}$)</th>
<th>$T_i$ (K)</th>
<th>$n_i$</th>
<th>$f_i$</th>
<th>$\lambda_i$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$</td>
<td>Schumann Runge</td>
<td>$10^4$</td>
<td>70,500</td>
<td>5</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>$\gamma$-band</td>
<td>$10^3$</td>
<td>65,000</td>
<td>5</td>
<td>0.0025</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>$\beta$-band</td>
<td>$3.2 \times 10^3$</td>
<td>65,000</td>
<td>5</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>$N_2$</td>
<td>2nd positive</td>
<td>$2 \times 10^5$</td>
<td>129,500</td>
<td>4</td>
<td>0.1</td>
<td>0.33</td>
</tr>
<tr>
<td>$N_2$</td>
<td>1st positive</td>
<td>$1.5 \times 10^3$</td>
<td>90,000</td>
<td>4</td>
<td>0.04</td>
<td>0.8</td>
</tr>
<tr>
<td>$N_2^+$</td>
<td>1st negative</td>
<td>$1 \times 10^4$</td>
<td>36,000</td>
<td>4</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>$O_2^+$</td>
<td>2nd negative</td>
<td>$3 \times 10^4$</td>
<td>55,000</td>
<td>4</td>
<td>0.1</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**Table 2.2**

Values of $c_i$, $T_i$, $n_i$, $f_i$ and $\lambda_i$ for equation 2.19 for the predominant emitters in shock heated air. The first negative bands of $N_2^+$ and the first and second positive bands of $N_2$ have amongst the lowest characteristic temperatures and highest oscillator strengths.
However, there exist a series of strong transitions, that are highly populated at the experimental conditions of interest, in the near infrared around 777.0 nm.

Figures 2.2, 2.3 and 2.4 show the important potential wells responsible for the dominant radiation emitted by shock heated air. Figure 2.2 shows the molecular diagram for N₂ and N₂⁺. The arrows are indicative of the strongest emitting bands which are, in descending order, the first negative band of N₂⁺ and the first and second positive bands of N₂. Figure 2.3 presents the molecular diagram for the Schumann-Runge transition of O₂ and figure 2.4 shows the potential energy diagram for the NO molecule, highlighting the β and γ transitions. Together with these potential curves various repulsive potentials are drawn. These potentials can act to decrease (drain) the amount of emission via the predissociation of molecules from a given state. The Schumann-Runge transition is especially vulnerable to this process as the repulsive 3Π potential intersects the upper level of the Schumann–Runge system at a low vibrational level (v′=2). This will have a direct consequence on the emission emanating from these levels. The first positive system of N₂ has two such potentials, 5Σ and 7Σ but their effect on the overall emission is substantially less than that in O₂ as they intersect the upper levels at substantially higher vibrational states (v′>12). Similarly, the β band in NO has the 2Σ repulsive state which intersects the B²Π level, but at the intersection point at v′=7, the effects on the overall emission coming from this level is, again, comparatively small.

The conclusions drawn from the foregoing discussion on ionisation and emissivities are that the dominant ionising reactions around the
Figure 2.2
Potential wells for the $N_2^+$ and $N_2$ molecules; the dominant radiating transitions, are shown. The repulsive potentials acting as a drain via predissociation are also shown.
Figure 2.3
Potential wells for the O$_2$ molecule. The dominant radiating transition is shown. The strong repulsive potential acting as a drain via predissociation is also presented.
Figure 2.4
Potential wells for the NO molecule. The dominant radiating transitions (β & γ) are shown. The repulsive potential acting as a drain via predissociation is also presented.
velocity regime of interest in the present investigation is the associative ionisation reaction

\[ N + O \leftrightarrow NO^+ + e^- \]

which will be competing with the electron impact ionising reactions,

\[ N + e^- \leftrightarrow N^+ + e^- + e^- \]
\[ O + e^- \leftrightarrow O^+ + e^- + e^- \]

as well as the associative ionising reactions,

\[ N + N \leftrightarrow N_2^+ + e^- \]
\[ O + O \leftrightarrow O_2^+ + e^- \]

as the temperature increases. From the discussion it is apparent that the shock velocity at which there exists a change in the dominant ionising process is approximately 9.5 kms\(^{-1}\). Since the experiments in the present work are being conducted at primarily 10 kms\(^{-1}\), it is evident that no single reaction will be strongly dominant and that the three aforementioned ionising reaction sets will be in competition.

In emission, the \(N_2^+\) molecule is the strongest radiator over the spectral region of interest. The first negative band of \(N_2^+\) dominates with the first and second positive bands of \(N_2\) significantly contributing to this emission. Emission from the Schumann-Runge bands, as intense as it is, is below the wavelength of transmission through the optics employed in the experiment.
Chapter 3

THE TWO-TEMPERATURE KINETIC MODEL

3.1 Introduction

This chapter discusses in detail the two-temperature kinetic model for ionising air developed by Park (1989). The need for such a model is highlighted with specific reference to the calculation of the flow conditions at the flight regimes of the proposed aeroassisted orbital transfer vehicles. The problems suffered by one-temperature models are discussed and the corrections made to the standard vibration model are examined. The reaction kinetics that Park considers in his two-temperature model are detailed, and the ionising reaction processes Park encompasses into his model are discussed in light of the ionising reaction processes addressed in chapter 2. The reaction rate coefficients and rate controlling temperatures are examined and compared with those from a one-temperature chemical nonequilibrium model (Vardavas, 1984).

3.2 The need for a multi-temperature kinetic model

In order to develop an aeroassisted orbital transfer vehicle, a far greater understanding of the chemical kinetic processes occurring behind the high enthalpy shock waves associated with its flight
through the earths atmosphere, is required. It is proposed that such vehicles will operate at perigee altitudes of approximately 80 km. At these altitudes, the air pressure is low, of order 13 Pa. Furthermore, the AOTV's operational speed is, at perigee, of the order of 10 kms\(^{-1}\). At such conditions, the flow field associated with the shock layer are expected to be in a state of both chemical and thermal nonequilibrium.

The chemical kinetics affect both the aerodynamic characteristics of the AOTV as well as influence the heat transfer rates. The chemistry affects the aerodynamics of an AOTV in two areas. It has a bearing on the allowable location of the centre of gravity of the AOTV, and affects the trim angle of attack \((c_m = 0)\) of the vehicle.

Figure 3.1, reproduced from Park (1987b), shows the theory of Weilmuenster and Hamilton (1986), together with the experimental data of Edwards \textit{et al} (unpublished but quoted by Weilmuenster and Hamilton) for the pitching moment coefficient \(c_m\) versus the trim angle of attack \(\theta\), for the raked-off blunted elliptic cone geometry proposed for the aeroassisted orbital transfer vehicle. As is clear, there is a dependence on the pitching moment to the ratio of specific heats \(\gamma\), that is, the trim angle of attack is functionally dependent on the chemical properties of the gas. This is understood, as changes in \(\gamma\) result in changes in the local shock angle due to the increased density in the shock layer. Figure 3.2 shows the dependence of the shock layer thickness on the distance along the axis of a 45° half angle cone. The figure is taken from Spurk (1970). The circles and squares refer to the upper and lower sides of the cone, respectively. These results are compared with theoretical calculations with frozen and equilibrium
Figure 3.1
The pitching moment coefficient of the Aeroassist Flight Experiment model versus the angle of attack for three different gases. It is noted that the trim angle of attack is a sensitive function of the chemical property of the gas. The plot is reproduced from Park (1987b).
Figure 3.2
Comparison of the theoretical and experimental shock layer thickness over a 45 degree cone at zero angle of attack in O2. The plot is reproduced from Spurk (1970).
As is evident, and expected, the experimental shock layer thickness near the tip of the cone is close to the theoretical shock layer thickness based on a frozen calculation. At greater distances along the cone, the shock angle decreases and the measured shock layer thickness approaches the value predicted by an equilibrium flow calculation. Since the wall pressure is functionally dependent on the local shock angle, it too is decreasing along the cone. This effect results in a positive pitching moment (nose up) to act on a lifting body. It is clear that in order to account for such aerodynamic problems, an understanding of the flow chemistry is essential. Curve 3 was calculated via a finite rate, one-temperature analysis with vibrational excitation in equilibrium. Curves 3 and 4 (curve 4 being the equilibrium case), are sufficiently close to be taken as being equal. This implies that the shock layer thickness more readily agrees with the frozen calculation (curve 1), than a finite rate value. The conclusion is drawn that the chemical rates are slower than those derived from the finite rate calculation. Other experimental data demonstrate similar results (Park, 1987b).

The deviation of experiment from theory arises from the fact that the vibrational relaxation is slower than a one-temperature model would predict and that the dissociation rate is dependent on the vibrational temperature, that is, multi-temperature processes are occurring simultaneously, resulting in the observed disparity. As stated previously, these problems not only affect the aerodynamics of the AOTV, but also the heat transfer. Unlike the Apollo vehicle, the proposed AOTV will employ a large, non-ablative heat shield. The
nonequilibrium region behind the shock wave associated with the AOTV is expected to produce a significant radiation field. Because of this, it will be essential to obtain an understanding of the radiative heat fluxes. This again requires a knowledge of the chemical kinetics.

Until recently, most chemical nonequilibrium models for ionising air have neglected thermal nonequilibrium effects. Thermal nonequilibrium, a situation where the translational, vibrational, rotational and excitation modes cannot be characterized by a single temperature, has an affect on the chemistry of the flow. As a consequence of the greatly varying reaction rates occurring within reactive gas flows, the solution of the relevant chemical rate equations is problematic, as the equations are rendered "stiff". The stiffness is due to specific chemical reactions that proceed at rates substantially faster than those of the bulk flow properties. Under such circumstances, a large negative eigenvalue appears in the Jacobian matrix associated with the problem. Vardavas (1984) has developed an iterative method for solving the flow conditions of the gas that overcome the problem of stiffness. The model does not include effects of radiation losses, heat conduction or viscosity and the vibrational temperature of the molecular constituents are taken as being equal to the translational temperature or can be set to a given frozen value. The chemical and thermodynamic properties of the gas behind the shock front are determined in the model by solving coupled gas dynamic equations together with coupled concentration rate equations.
3.3 A three-temperature description

One-temperature models assume, by definition, that all the internal modes of energy (rotation, vibration, electronic excitation) and the translational energy, are all characterized by the same temperature. In the monatomic regime it is well known that there are two distinct temperatures, the heavy particle temperature $T_a$ and the electron temperature $T_e$, controlling the reaction kinetics. This has been well demonstrated in ionising argon by Petschek & Byron (1957) and Oettinger & Bershader (1967). Any multi-temperature model for shock heated air should address five independent temperatures:

i) the heavy particle translational;

ii) the rotational;

iii) the vibrational;

iv) the electronic excitational; and

v) the electron translational temperatures.

Lee (1985) has proposed a three temperature kinetic model for ionising air. He considers the case where the rotational temperature $T_r$ and the heavy particle translational temperature $T$ are equal, under the assumption that these temperatures rapidly converge. Rotational degrees of freedom are very rapidly excited since $T_r \sim 2K$. Appleton and Bray (1964) have shown that there is a slow rate of energy transfer between electrons and heavy particles due to their large mass disparity. Lee therefore allows the electron temperature $T_e$ and the heavy particle translational temperature $T$ to deviate in his model. The vibrational temperature $T_v$ is allowed to differ from both $T$ and $T_e$ since the time required for energy exchange between the heavy particle, electron and
vibrational modes is relatively long. The electronic levels are excited to their Boltzmann distributions based on the electron temperature. The conservation equations for this model are given by Gnoffo et al (1989) (taken from Lee, 1985) and are as follows:

**Species Conservation** :

\[
\frac{\partial}{\partial t} \rho_s + \frac{\partial}{\partial x_j} \rho_s u^j = \frac{\partial}{\partial x_j} \left( \rho D_s \frac{\partial y_s}{\partial x^j} \right) + \frac{\dot{w}_s}{4} \tag{3.1}
\]

where

1. is the rate of change of mass of species s per unit volume in a cell centred at a point \( x^i \);
2. is the flux of mass of species s convected across cell walls with velocity \( u^j \);
3. is the diffusion of species s across the cell wall;
4. is the mass production rate of species s due to chemical reactions;

\( \dot{w}_s \) is the mass rate of production of species s; \( D_s \) is the effective diffusion coefficient for species s; \( \rho \) is the total density; \( \rho_s \) is the density of species s and \( y_s \) is the mole fraction of species s.

**Mixture Momentum Conservation** :

\[
\frac{\partial}{\partial t} \rho u^i + \frac{\partial}{\partial x^j} \rho u^i u^j = -\frac{\partial \rho}{\partial x^i} + \frac{\partial}{\partial x^i} \left[ \mu \left( \frac{\partial u^i}{\partial x^j} + \frac{\partial u^j}{\partial x^i} \right) - \frac{2}{3} \mu \left( \frac{\partial u^k}{\partial x^k} \right) \delta^{ij} \right] \tag{3.2}
\]

where

1. is the rate of change of the \( i \)th component of momentum

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3 In the following equations, the super/sub scripts \( i \) and \( j \) refer to components in general orthogonal components. Gnoffo et al describe the reactions as occurring within a cell of finite volume.
per unit volume in a cell centered at point \( x^j \);

(2) is the flux of mass of the \( i \)th component of momentum
convected across cell walls with velocity \( u^j \);

(3) is the pressure forces acting on cell walls in the \( i \)th
direction;

(4) is the viscous force acting on cell walls in the \( i \)th
direction;

\( p \) is the pressure; \( \mu \) is the total viscosity; and \( \delta^j_\ell \) is the Kronecker delta.

**Vibrational Energy Conservation :**

\[
\frac{\partial}{\partial t} p e_v^1 + \frac{\partial}{\partial x^j} p e_v^j u^j = \frac{\partial}{\partial x^j} \left( \eta_v \frac{\partial T_v}{\partial x^j} \right) + \frac{\partial}{\partial x^j} \left( \rho \sum_{s=1}^{H} h_{v,s} D_s \frac{\partial e_v^s}{\partial x^j} \right) \\
+ \sum_{s=\text{mol}} \rho_s \frac{(e_{v,s}^* - e_{v,s})}{\langle \tau_s \rangle} + \sum_{s=\text{mol}} \rho_s \frac{(e_{v,s}^{**} - e_{v,s})}{\langle \tau_{es} \rangle} + \sum_{s=\text{mol}} \dot{\omega}_s D_s 
\]

\( ... (3.3) \)

where

(1) is the rate of change of the vibrational energy per unit
volume in a cell centered at point \( x^j \);

(2) is the flux of vibrational energy convected across cell
walls with velocity \( u^j \);

(3) is the conduction of vibrational energy across cell walls
due to vibrational temperature gradients;

(4) is the diffusion of vibrational energy across cell walls
due to molecular concentration gradients;

(5) is the energy exchange between vibrational and
translational modes due to collisions within cells;

(6) is the energy exchange between vibrational and
electronic modes;

(7) is the vibrational energy lost or gained due to
dissociation or recombination within a cell;

\(e_v\) is the vibrational energy; \(\eta_v\) is the frozen thermal conductivity for
vibrational energy due to molecular collisions; \(T_v\) is the vibrational-ele
lectron-electronic temperature; \(h_{v,s}\) is the vibrational enthalpy per unit
mass of species \(s\); \(e_{v,s}^*\) is the vibrational energy per unit mass of species
\(s\) at temperature \(T\); \(e_{v,s}\) is the vibrational energy per unit mass of
species \(s\); \(e_{v,s}^{**}\) is the vibrational energy per unit mass of species \(s\) at
temperature \(T_e\); \(\tau_{es}\) is the electronic vibrational relaxation time for
species \(s\); \(\tau_s\) is the translational vibrational relaxation time for
species \(s\); and \(D_s\) is the average vibrational energy per unit mass of
molecule \(s\).

**Electron and Electronic Excitation Energy Conservation:**

\[
\frac{\partial}{\partial t} \rho_e \frac{\partial}{\partial x} \left[ u^j \left( \rho_e + p_e \right) \right] = \frac{u^j}{2} \frac{\partial}{\partial x} \left( \rho_e \frac{\partial e_v}{\partial x} \right) + \frac{\eta_e}{4} \frac{\partial T_e}{\partial x} + \frac{\rho}{5} \sum_{s=1}^{11} \rho_{e,s} D_s \frac{\partial e_{v,s}}{\partial x} \\
+ 2 \rho_e^3 \frac{3}{2} R(T - T_e) \sum_{s=1}^{10} \frac{v_{es}}{M_s} - \sum_{s=6}^{10} \dot{n}_{e,s} \dot{i}_s - \sum_{s=11}^{15} \rho_s \frac{e_{v,s}^{**} - e_{v,s}}{\tau_{es}} - \frac{Q_{\text{rad}}}{9}
\]

...(3.4)

where

(1) is the rate of change of the electronic energy per unit
volume in a cell centered at point \(x^j\);

(2) is the flux of electronic enthalpy convected across cell
walls with velocity \(u^j\);

(3) is the work done on electrons by an electric field induced
by the electron pressure gradient;
(4) is the conduction of electronic energy across cell walls due to the electron temperature gradient;
(5) is the diffusion of electronic energy due to concentration gradients;
(6) is the energy exchange due to elastic collisions between electrons and heavy particles;
(7) is the energy lost due to electron impact ionisation;
(8) is the energy exchange due to inelastic collisions between electrons and molecules in a cell;
(9) is the rate of energy loss due to radiative electronic transitions;

\( e_e \) is the total electronic energy per unit mass of molecule \( s \); \( p_e \) is the electron pressure; \( \eta_e \) is the frozen thermal conductivity for electron energy due to electron collisions; \( T_e \) is the electron-electronic excitation temperature; \( h_{e,s} \) is the electronic enthalpy per unit mass of species \( s \); \( \rho_e \) is the electron density; \( T \) is the translational temperature; \( R \) is the universal gas constant; \( v_{es} \) is the effective collision frequency for electrons and heavy particles; \( M_s \) is the molecular weight of species \( s \); \( n_{e,s} \) is the molar rate of production of species \( s \) by electron impact ionisation; \( \hat{I}_s \) is the first ionisation potential for species \( s \); and \( Q_{\text{rad}} \) is the radiative energy transfer rate.
Total Energy Conservation:

\[
\frac{\partial}{\partial t} \rho E + \frac{\partial}{\partial x^j} \rho Hu^j = \frac{\partial}{\partial x^j} \left( \eta \frac{\partial T}{\partial x^j} + \eta_v \frac{\partial T_v}{\partial x^j} + \eta_e \frac{\partial T_e}{\partial x^j} \right) \\
+ \frac{\partial}{\partial x^j} \left( \rho \sum_{s=1}^{11} h_s D_{ss} \frac{\partial y_s}{\partial x^j} \right) + \frac{\partial}{\partial x^j} \left( u^i \mu \left( \frac{\partial u^i}{\partial x^j} + \frac{\partial u^j}{\partial x^i} \right) - \frac{2}{3} u^i \mu \frac{\partial u^k}{\partial x^k} \delta^{ij} \right) - \frac{Q_{\text{rad}}}{6}
\]

where

1. is the rate of change of the total energy per unit volume in a cell centered at point \(x^j\);
2. is the flux of total enthalpy convected across cell walls with velocity \(u^j\);
3. is the conduction of energy across cell walls due to temperature gradients;
4. is the diffusion of enthalpy across cell walls due to concentration gradients;
5. is the work done by shear forces;
6. is the rate of energy loss due to radiative electronic transitions;

\(E\) is the total energy per unit mass and \(H\) is the total enthalpy per unit mass; \(\eta\) is the frozen thermal conductivity for translational-rotational energy of the heavy particles.

Other multi-temperature models have been proposed in which the vibrational energies of individual species are characterized by their own temperatures. Candler and MacCormack (1988) have demonstrated however, that there exists only small differences between
the vibrational temperatures of the $\text{N}_2$ and $\text{O}_2$ molecules in flows over a blunt body. The three temperature model encompassed in the foregoing discussion is very complex and requires many rate parameters presently unknown.

3.4 The two-temperature kinetic model

More recently, Park (1989) has developed a two-temperature kinetic model for ionising air, that is applicable to the flight conditions of the proposed AOTV. The two-temperature kinetic model of Park considers a reduced set of rate controlling temperatures. As for the three temperature model, the heavy particle translational and rotational temperatures are considered equal. Bird (1976) has shown that the energy exchange between rotational and translational modes is very rapid, resulting in their characteristic temperatures quickly equilibrating (as previously discussed, this is a result of the very low rotational excitation temperature).

Appleton and Bray (1964) consider an independent electron temperature as a consequence of the large ratio of the atom or ion mass to the electron mass. Due to their large mass disparity, equilibration between the electron translational temperature and heavy particle translational temperature is slow. The low-lying electronic states of atoms and molecules, which hold most of the electronic excitation energy, are readily excited, by electron impact. Hence Park assumes that the electronic excitation and electron translational temperatures equilibrate rapidly. Furthermore, the vibrational temperature is taken as being equal to the electron translational temperature. This
assumption is based on the fact that the electrons interact strongly with the vibrational motion of N₂ molecules, and therefore the populations of the vibrational and electronic levels establish themselves at their Boltzmann values based on the electron temperature.

The conservation equations for the vibrational-electron-electronic temperature $T_v$ in the two-temperature model account for the following:

1. the vibrational excitation by collisions with heavy particles;
2. the elastic energy exchange between heavy particles and electrons;
3. the loss of electron translational energy by electron impact dissociation and ionisation; and
4. gains and losses of excitation energy through dissociation.

It is known that the low-lying electronic states of both atoms and molecules are populated according to the Boltzmann distribution based on the electron temperature Park (1987b). As the greatest proportion of the electronic excitation energy is held in these low-lying states, even in a nonequilibrium flow, the distribution of these states may be calculated using the electron temperature. Park (1987b) expresses the conservation of electron and electronic excitation energy by

$$\frac{\partial E_e}{\partial t} + \nabla \cdot (\vec{w}(E_e + p_e)) = - \nabla \left[ \sum_{i=1}^{n} \epsilon_{ei}(T_e) N_i \vec{V}_i \right] + \dot{E}_e - eN_e \vec{E} \cdot \vec{w},$$  \hspace{1cm} \text{...}(3.6)

where $E_e$ is the sum of the electronic excitation energy and kinetic energy of the electrons; $\vec{w}$ is the flow velocity; $f$ is the electron gas heat
transfer; \( k_e \) is the thermal conductivity by the electron gas; \( N_i \) is the number density of species \( i \); \( V_i \) is the diffusion velocity for species \( i \) and \( e \) is the electron charge.

This equation accounts for the effects on the electron-electronic excitation energy per unit volume due to the work done on the electrons by the electric field induced by the electron pressure gradient, the conduction of electronic energy due to the electron temperature gradient and the chemical kinetic reactions. This equation is analogous to equation 3.4, the expression for the electron and electronic energy conservation in the three temperature model. The first term on the right hand side of equation 3.6, representing the conduction of electron translational energy into the electron gas, is equivalent to term (4) of equation 3.4. Term (5) of equation 3.4 accounts for the diffusion of electronic energy due to gradients in the concentration; this is accounted for in the second term on the right hand side of equation 3.6. The fourth term represents the rate of transfer of electronic excitation energy by diffusion. This is equated to term (3) of equation 3.4. The third term on the right hand side of equation 3.6 is given by Park as

\[
\dot{E}_e = - \sum_{i=ion} I_i \left( \frac{\partial N_i}{\partial t} \right) + D_{N_e} \left( \frac{\partial N_{Ne}}{\partial t} \right) + 2N_e \sum_{i=al} v_i \frac{m_e}{m_i} \frac{3}{2} k(T - T_e) \\
- N_{Ne} \frac{\varepsilon_{vE}(T_e) \cdot \varepsilon_v}{\tau_e} + \sum_{i=al} \varepsilon_{ei} \left( \frac{\partial N_i}{\partial t} \right) - q_r
\]

\( ... (3.7) \)

where \( v_i \) is the collision frequency; \( m_i \) is the mass of species \( i \); \( \varepsilon_{vE} \) is the average vibrational excitation energy per molecule at equilibrium; \( \varepsilon_{ei} \) is the average vibrational excitation energy per particle \( i \); \( N_e \) is the
electron number density; $\varepsilon_v$ is the average vibrational excitation energy per molecule; and $q_r$ is the radiative power loss.

The two-temperature model (Park, 1985) is obtained by considering the situation in which substantial ionisation (>0.01%) occurs. In this instance, the electron translational energy and the molecular vibrational energies strongly couple, with the result that $T_e$ approaches $T_v$. Park expresses the conservation of vibrational energy (of the form of equation 3.3) by

$$\frac{\partial E_v}{\partial t} + \nabla \cdot \mathbf{w} E_v = -\nabla \cdot q_v + \dot{E}_v , \quad \ldots (3.8)$$

where $E_v$ is the vibrational energy.

Under the assumption that $T_v = T_e$, the energy equation of the two-temperature model (Park, 1986) is obtained by coupling the vibrational energy conservation equation with the electron and electronic excitation energy conservation equations, to give

$$\frac{\partial (E_v + E_e)}{\partial t} + \nabla \cdot \mathbf{w} (E_v + E_e + p_e) = -\nabla \left[ q_v + f k_e \nabla T_e + \sum_i \varepsilon_{e i} N_i \nabla \right]$$

$$+ \dot{E}_v + \dot{E}_e - eN_e \nabla \cdot \mathbf{w} \quad \ldots (3.9)$$

where $\dot{E}_v$ and $\dot{E}_e$ are the excitation rates of the vibrational and electronic modes, by the kinetic processes, respectively.
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The expression for the coupling of the vibrational and the electron–electronic excitation energy conservation equations for Park’s two-temperature model in air is expressed by Gnoffo et al as

\[
\frac{\partial \rho_{\text{vib}}}{\partial t} + \frac{\partial \rho_{\text{vib}} u^j}{\partial x^j} = -p_e \frac{\partial u^j}{\partial x^j} + \frac{\partial}{\partial x^j} \left( \left( \eta_v + \eta_e \right) \frac{\partial T_v}{\partial x^j} \right) + \frac{\partial}{\partial x^j} \left( \rho \sum_{s=1}^{11} h_{V,s} D_s \frac{\partial T_e}{\partial x^j} \right)
\]

\[+ \sum_{s=mol} \rho_s \frac{(e_{v,s}^* - e_{v,s})}{\tau_s} + 2p_e \frac{3}{2} R (T - T_v) \sum_{s=1}^{10} \frac{v_{es}}{M_s} - \sum_{s=6}^{10} \frac{\dot{n}_{e,s} \dot{f}_s}{s=mol} + \sum_{s=mol} \omega_s \frac{\partial}{\partial x^j} - Q_{\text{rad}}
\]

...(3.10)

The foregoing discussion illustrates the shortcomings of one-temperature models in describing flow behaviour at conditions characterised by a significant degree of thermal nonequilibrium. A further shortcoming of the one-temperature model is their description of vibrational excitation processes. The failure of the one-temperature model to describe vibrational excitation at high temperatures, and an improved description incorporated into the two-temperature model (hereafter referred to as the TT\textsubscript{V} model) is discussed below.

### 3.5 Vibrational excitation in the TT\textsubscript{V} model

Vibrational relaxation is normally described by the Landau-Teller theory as described by the relaxation equation

\[
\tau_{\text{Vib}} \frac{dE_{\text{Vib}}}{dt} + E_{\text{Vib}} = E_{\text{Vib,EQU}}
\]

...(3.11)

where \( \tau_{\text{Vib}} \) is the vibrational relaxation time in excitation of vibration by heavy particle collisions; \( E_{\text{Vib}} \) is the average vibrational excitation
energy per molecule; and $E_{\text{Vib,Eq}}$ is the average vibrational excitation energy per molecule at equilibrium.

Millikan and White (1963) have given the vibrational relaxation time for a molecular species due to inelastic collisions by heavy particles, $\tau_{\text{Vib}}$, based on Landau–Teller theory for a temperature range of 300 to 8000 K as

$$\tau_{\text{Vib}} = \frac{1}{p} \exp\left(A \left( T^{-1/3} - 0.015 \mu_m^{1/4} \right) - 18.42 \right) \sec , \quad ...(3.12)$$

where $p$ is the pressure in atmospheres; $T$ is the heavy particle translational-rotational temperature; and $\mu_m$ is the reduced molecular mass of the colliding species. $A$ is a parameter dependent on the molecule type ($A=220$ for $N_2$ & $N_2^+$, $A=129$ for $O_2$ & $O_2^+$ and $A=168$ for NO & NO$^+$).

Equations 3.11 and 3.12 fail at high temperatures for several reasons. The reasons are as follows.

i) Park (1987b) has shown that the forward reaction rate for vibrational excitation $k_f$, given by the usual Arrhenius expression

$$k_f = C T^{-n} \exp(-D/kT) , \quad ...(3.13)$$

where $D$ is the dissociation energy and $C$ is the reaction rate constant, implies an unrealistically large cross section for vibrational relaxation at temperatures greater than 8000 K, much greater than the elastic cross section. The TT$_v$ model assumes that the effective cross section is an order of magnitude smaller than the elastic cross section and was
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set at $3 \times 10^{-16}$. This value led to satisfactory agreement between experimental results in a shock tube and the theoretical predictions.

ii) Lee (1985) has shown that at these temperatures, the vibrational relaxation rates become smaller than that predicted by the Landau–Teller equation, and that the rates resemble a diffusion process.

iii) Park (1989) has shown that dissociation will occur preferentially from highly excited vibrational states.

In order to address these problems at high temperatures, Park incorporated the following modifications into TT$_v$ model.

3.5.1 Correction to the vibrational excitation cross section

i) Corrections were made to the relaxation time of Millikan and White (1963) by denoting a limiting cross section, $\sigma_v$ at infinite temperature, and observing that the relaxation time $\tau$ must be larger than a time $\tau_{\text{min}}$ given by

$$\tau_{\text{min}} = \frac{I}{N_x \sigma_v c},$$  

...(3.14)

where $N_x$ equals the number density of the $x^{th}$ state and $c$ here is the average molecular speed. Park replaces the relaxation time of equation 3.12 with

$$\tau' = \tau_{\text{Vib}} + \tau_{\text{min}}$$  

...(3.15)

where $\tau'$ now represents the vibrational relaxation time corrected for the limiting cross section. It has been shown by Park (1985) that the
available experimental data for the vibrational relaxation time of $O_2$ over a temperature range of 5,000 to 8,000 K is in far better agreement with equation 3.15 than with the equation of Millikan and White, equation 3.12. Furthermore he found that the most appropriate value for the limiting cross section $\sigma_v$, up to 62,000 K was

$$\sigma_v = 10^{-17} \left( \frac{50,000}{T} \right)^2 \text{ cm}^2 \quad \ldots(3.16)$$

This cross section is shown to accurately reproduce the nitrogen data presented by Park (1986) as well as the air data considered in Park's 1989 paper. For low temperatures, equation 3.15 reduces to the usual Landau-Teller equation. Park employs the value for the vibrational relaxation time given in equation 3.15 in the $T_T$ model.

### 3.5.2 Vibrational excitation as a diffusion process

ii) Lee (1986) solved the system of Master equations,

$$\frac{dn_{v}}{dt} = \sum_{v'=0}^{\infty} \left( k_{v',v} n_{v'} - k_{v,v'} n_v \right) n_e \quad \ldots(3.17)$$

to obtain a multilevel electron-vibration energy transfer rate equation. In this equation $n_v$ is the number density of the $v^{th}$ vibrationally excited state; $k_{v,v'}$ is the rate coefficient for the transition from state $v$ to $v'$; and $n_e$ is the number density of electrons. Under the assumption that the vibrationally excited molecules had a Boltzmann distribution based on the vibrational temperature $T_v$, he solved equation 3.17 for the harmonic oscillator by extending the classical analysis of Keck and Carrier (1965). Keck and Carrier demonstrated that the vibrational
relaxation process had a diffusive characteristic. Lee compared the
time evolution of the vibrational energy as given by the conventional
Landau-Teller type rate equation (equation 3.11) with that of the
solution to equation 3.17. A marked difference was observed between
the two rates. The Landau-Teller relaxation time increased rapidly
(some 20 times faster) than the rate of Lee. Indeed the Landau-Teller
solution displayed an exponential form. The unexpectedly slow time
for the electron-vibrational energy exchange process was considered to
be due to the diffusion characteristic of vibrational excitation, as well as
the possibility of multi-level transitions in the high temperature
regime.

Keck and Carrier, via a classical analysis derive (by transforming the
master equation to the equivalent diffusion equation)

\[ N_e \frac{\partial X}{\partial t} = \frac{\partial}{\partial \varepsilon} \left( \frac{\Delta}{2} \frac{\partial X}{\partial \varepsilon} \right) \] \hspace{1cm} (3.18)

Here \( N_e \) is the equilibrium concentration of molecules; \( X \) is the specific
population, which is the ratio of the concentration of molecules in the
nth level to the equilibrium concentration; \( \varepsilon = E/kT \) is the energy of a level
in units of kT and \( \Delta \) is the energy transfer, \( \varepsilon' - \varepsilon \), for the transition from
a state with energy \( \varepsilon' \) to a state with energy \( \varepsilon \). This is recognized as an
ordinary one-dimensional diffusion equation that demonstrates the
diffusive character of vibrational relaxation. Park derived an
expression similar to equation 3.18 and showed that the vibrational
temperature will satisfy the following equation
\[
\frac{\partial T_v}{\partial t} = \frac{\pi k T_v (D/v_u)}{2T (\frac{D}{v_u})^2} \left(\frac{T - T_v}{k^2}\right)^3 , \quad \ldots(3.19)
\]

where \( k \) is the equivalent thermal conductivity and \( D \) is the dissociation energy. Equation 3.19 may be expressed in the form

\[
\frac{\partial T_v}{\partial t} = \frac{(T - T_v)}{\tau_D} \quad \ldots(3.20)
\]

where \( \tau_D \), the relaxation time in excitation of vibration by heavy particle impact collision given by the diffusion theory, is given by

\[
\frac{\tau_D}{\tau'} = \frac{2k T_v}{\pi E_1} \left(\frac{T^2}{(T - T_v)^2}\right) \quad \ldots(3.21)
\]

Lee (1986) obtained a modified Landau-Teller type rate equation via the numerical integration of Keck and Carrier's equation. This is given by

\[
\frac{dE_v(t)}{dt} = \frac{E_v^* - E_v}{\tau_e} \left(\frac{E_v^* - E_v}{E_v^* - E_v^0}\right)^{s-1} \quad \ldots(3.22)
\]

where \( \tau_e \) is the vibrational relaxation time for excitation by electron collisions; \( E_v \) is the vibrational energy and \( E_v^* \) is the vibrational energy at the electron temperature \( T_e \), the subscript 0 refers to time \( t=0 \). For \( s=1 \), equation 3.22 becomes the usual Landau-Teller expression. Lee (1986) demonstrated that the most suitable value for \( s \) was 3.5 for \( T_e \leq 23,200 \) K. (For \( T_e \geq 23,200 \) K, \( s \) was found to be equal to 4.0. Park (1985) has shown that the electron temperature associated with the AOTV flow field will be less than 23,200 K). An \( s \) value of 3.5 gives a
relaxation rate in agreement with equation 3.22; hence $1 \leq s \leq 3.5$. Park (1986) also proposed the "bridging" formula

$$s = 3.5 \exp \left( -\frac{5000}{T_s} \right)$$

...(3.23)

where $T_s$ is the heavy particle translational temperature immediately behind the shock front.

### 3.5.3 Preferential dissociation from excited states

iii) Preferential dissociation refers to the enhanced likelihood of a molecule undergoing dissociation from a vibrationally excited state. The usual "ladder climbing" process, in which molecules in lower states must initially climb to the higher states before dissociation, may not be valid at high temperatures. Park assumes that dissociation will occur preferentially from these highly excited vibrational states. Since the populations of vibrational states are characterized by the vibrational temperature $T_v$, the rate coefficient should be a function of the heavy particle translational temperature $T$ and $T_v$. A geometrically averaged temperature $T_{av} = \sqrt{TT_v}$ is used to characterize the dissociative reactions in Park's model. This averaged temperature has been shown by Park to reproduce quite closely the experimental results for nonequilibrium radiative heat fluxes obtained by Allen et al (1962). At low temperatures, equation 3.13 implies that dissociation will proceed slowly and $T = T_v$. This is because for low $T$, $D/kT$ is large and therefore the dissociation reactions do not proceed rapidly. Vibrational relaxation therefore reaches equilibrium prior to significant dissociation. At high temperatures on the other hand, the dissociation reactions will proceed rapidly and occur simultaneously with
vibrational excitation and $T \neq T_v$. Due to the preferential dissociation, the rate of change of the vibrational energy $E_{Vib}$ is governed by

$$\frac{dE_{Vib}}{dt} = \varepsilon_{Vib}^{Diss} \left( \frac{dN_m}{dt} \right), \quad \text{(3.24)}$$

where $\varepsilon_{Vib}^{Diss}$ is the average vibrational excitation energy. The TT$_v$ model does not directly account for the preferential removal of highly excited vibrational states due to the preferential dissociation, but does implicitly incorporate its effect on the chemical reaction rates through the use of $T_{av}$ rather than $T$ in the equations describing the temperature dependence of certain reaction coefficients. This is discussed in further detail below.

### 3.6 The reaction kinetics in the TT$_v$ model

The TT$_v$ model has been used to predict the plasma conditions applicable to the flight regime of the AOTV. Park has employed the TT$_v$ model at various conditions and various gas mixtures. Of interest in the present investigation, is the application of the model to free-stream gas conditions of 79% $N_2$ and 21% $O_2$ at low densities of 13 Pa and shock velocities equal to 10 kms$^{-1}$, simulating the flight environment at altitudes approaching 80 km.

#### 3.6.1 Reactions and rate controlling temperatures

Eleven species are considered as participating in 31 reactions in the TT$_v$ model. $N_2$, $O_2$, $N$, $O$, $NO$, $N^+$, $O^+$, $N_2^+$, $O_2^+$, $NO^+$ and $e^-$ are taken to describe the chemical composition of the plasma. Four types of reactions are considered in the TT$_v$ model;
i) impact dissociations via,
   ia) electrons \((A_2 + e^- \leftrightarrow A + A + e^-)\)
   ib) heavy particles \((A_2 + B \leftrightarrow A + A + B)\)

ii) exchange reactions \((X^+ + Y \leftrightarrow X + Y^+)\)

iii) associative ionisation reactions \((A + B \leftrightarrow AB^+ + e^-)\) and

iv) electron impact ionisation \((X + e^- \leftrightarrow X^+ + 2e^-)\)

The electron-impact ionisation processes are assumed to occur with the colliding partner at rest as the atoms have a small thermal velocity. As such, their reaction rates in the forward and reverse directions are dictated by the electron temperature \(T_e = T_v\).

The associative ionisation processes are dictated by the heavy particle translational temperature \(T\) in the forward direction as there are no molecular species contained in the initial state. In the reverse direction on the other hand, the reaction involves ionised molecular species and electrons and therefore the rate is dictated by the vibrational temperature of the ionised molecule \(T_v\) and the electron translational temperature \(T_e\) which are set equal in the TTV model.

Allen (1964) conducted experiments in which the radiative emission from molecular nitrogen during dissociation was studied. Park (1986) compared these results with the TTV model and demonstrated that it could predict the radiative behavior if the forward rate coefficients for the impact dissociation reactions were dictated by the geometric average temperature \(T_{av} = \sqrt{TT_v}\). Similarly, the rate coefficients for the exchange reactions were dictated by this geometric average.
The rate controlling temperature for the electron impact ionisation reactions is $T_v (= T_e)$ . All other reactions are dictated by the heavy particle translational temperature $T$ . The forward and backward reaction rate coefficients are expressed as

\begin{equation}
  k_f = CT^n \exp(-E_f/kT_{RC}) \tag{3.25}
\end{equation}

\begin{equation}
  k_b = \frac{k_f}{K_{eq}} \tag{3.26}
\end{equation}

where $E_f$ is the activation energy of the reaction; $T_{RC}$ is the reaction dependent rate controlling temperature; and $K_{eq}$ is the equilibrium constant for the reaction. Park (1985b) employed a five term expression for the computed value of $K_{eq}$ in terms of $Z$ given by

\begin{equation}
  K_{eq}(T) = \exp(A_1 + A_2 \ln Z + A_3 Z + A_4 Z^2 + A_5 Z^3) , \tag{3.27}
\end{equation}

where $Z=10,000/T$.

Thirty one reactions are considered in the $TT_v$ model. These are listed in appendix D, along with the reactions rate controlling temperature, constants and the constants $A_i$.

Park (1968) employed a spectroscopic technique in a nitrogen plasma to measure the three body recombination rate of electrons and atomic ions for the reaction

\[ N^+ + e^- + e^- \rightarrow N + e^- \]
The electron number density was measured by observing the Stark broadening of the H$_{eta}$ line at 486.1 nm, while the electron temperature was determined by measuring the intensity ratio of two atomic transitions in nitrogen at 493.5 and 561.7 nm. From these measurements a rate coefficient of $10^{-26\pm0.5} \text{ cm}^6 \text{ s}^{-1}$ was obtained for the aforementioned reaction at 10,000 K. This rate coefficient is used as the electron impact ionisation rate in the TTV model. Park made the assumption that the recombination rates for the equivalent oxygen reaction were the same and hence was able to imply a forward rate coefficient for that reaction.

The rate coefficients used in the TTV model for the three associative ionisation reactions were obtained from three papers by Dunn & Lordi (1969, 1970a and 1970b). Dunn and Lordi (1969) determined the dissociative recombination rate coefficient for the inverse of reaction R1, that is

$$NO^+ + e^- \rightarrow N + O.$$  

They employed Langmuir probes to measure the electron temperature and the electron population. Simultaneous measurements of the electron number density profile were also made using microwave interferometric techniques. The identical experimental technique was also employed to determine the rate coefficients for the reactions

$$O_2^+ + e^- \rightarrow O + O$$

and

$$N_2^+ + e^- \rightarrow N + N.$$
Again these rate coefficients are used in Park's model.

The electron impact ionisation reactions considered in the TT\textsubscript{e} model are

\[ O + e^- \rightarrow O^+ e^- e^- \]

and

\[ N + e^- \rightarrow N^+ e^- e^- . \]

The eighth term in equation 3.10 is the rate at which free electrons lose energy when they are involved in an ionising collision with a neutral particle, \( \dot{n}_a \) and \( \dot{I}_a \) are the molar rate of ionisation and the first ionisation potential respectively. The limits on the summation account for the five ionised species that should be considered. Appleton and Bray (1964) modelled the exchange of energy that occurs as a result of elastic collisions between atoms, ions and electrons. Their derivation appears as the sixth term in equation 3.10.

Bowden and Park (1970) undertook a numerical study of the nonequilibrium chemistry for a fully dissociated, partially ionised nitrogen plasma expanding into a nozzle initially in a chamber at equilibrium. The ionically recombining chemistry was studied as a function of the initial chamber pressure and temperature. Their results demonstrated that a large deviation between the heavy particle translational temperature \( T \) and the electron translational temperature \( T_e \) occurs. At small chamber pressures, there were insufficient recombination reactions, and therefore insignificant recombination energy liberated to force the temperatures \( T \) and \( T_e \) to deviate. As the pressure increased however, the recombination rate
increased, with the result that a large thermal nonequilibrium was established. At extreme pressures, elastic collisions began to dominate the recombination reactions with the result that the two temperatures were bought back together. In the flight regime of the AOTV, pressures are significant enough to establish the three modes (translational, vibrational and rotational) at Boltzmann distributions based on the relevant temperatures, but this does not ensure that these characteristic temperatures will converge.

3.7 Predictions of the TT\textsubscript{v} model

The TT\textsubscript{v} model makes predictions for the profiles of the various species populations, the translational-rotational temperature $T$, the vibrational-electron-electronic temperature $T_v$ and the radiative emission. From the radiative emission profiles, predictions concerning the characteristic relaxation time are made. All of these predictions are utilized for comparison with the experimental results obtained from the work to be detailed in the following chapter. As such, the calculated species mole fractions for the eleven species as a function of distance from the shock front, the calculated temperatures $T$ and $T_v$ and the temporal radiative emission, together with the calculated characteristic relaxation times, have been reproduced from Park (1989) and are presented as figures 3.3, 3.4 and 3.5. Also reproduced from the same reference is table 3.1, that gives the instantaneous values for the aforementioned parameters at two positions behind the shock front corresponding to the points at which peak radiation occurs and at which equilibration is reached.
Figure 3.3
Predicted species mole fractions of the TTv model, for the eleven constituents of shock heated air considered by the code. Figure is reproduced from Park (1989).
Figure 3.4
Theoretical translational-rotational temperature $T$, vibrational-electron-electronic temperature $T_v$ and emissive intensity profile as a function of distance from the shock front predicted by the $TT_v$ model. Figure is reproduced from Park (1989).
Figure 3.5
Characteristic relaxation time parameter $\tau_w$ versus the shock velocity.

- □ are from Allen et al (1962) for the peak and equilibrium points respectively.
- ■ are from Park (1989) for the peak and equilibrium points respectively. ○ is from the present experiment.

Figure is reproduced from Park (1989).
**Free-stream conditions**

- Temperature $T_0$: 300°K
- Pressure $p_0$: 0.1 Torr
- Density $\rho_0$: $1.612 \times 10^{-7}$ g/cm$^3$
- Shock velocity $V_s$: 10 km/sec

**Peak radiation point conditions**

- Location measured from shock: 0.526 cm
- Location measured from foot of luminosity: 0.240 cm
- $X_p$: 0.240 µs
- Time measured from foot of luminosity $\tau_P$: 3.28 x $10^{-5}$ µs-atm
- $T_P$: 2193°K
- $T_v$: 11618°K

**Species mole fractions**

<table>
<thead>
<tr>
<th>Species</th>
<th>Mole Fraction</th>
</tr>
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<tbody>
<tr>
<td>N</td>
<td>0.5308</td>
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<tr>
<td>O</td>
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<tr>
<td>N$_2$</td>
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</tr>
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</tr>
<tr>
<td>O$^+$</td>
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</tr>
<tr>
<td>N$_2$$^+$</td>
<td>0.00204</td>
</tr>
<tr>
<td>O$_2$$^+$</td>
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<td>NO$^+$</td>
<td>0.00058</td>
</tr>
<tr>
<td>e$^-$</td>
<td>0.00594</td>
</tr>
</tbody>
</table>

- Total number density: $4.89 \times 10^{16}$ cm$^{-3}$
- Total radiation power through Gaussian: 33.3 W/cm$^3$

**Equilibration point conditions**

- Location measured from shock: 1.45 cm
- Location measured from foot of luminosity: 1.09 cm
- $X_p$: 1.09 µs
- Time measured from foot of luminosity $\tau_P$: 1.49 x $10^{-4}$ µs-atm
- $T_P$: 13152°K
- $T_v$: 9703°K

**Species mole fractions**

<table>
<thead>
<tr>
<th>Species</th>
<th>Mole Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
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</tr>
<tr>
<td>O</td>
<td>0.2090</td>
</tr>
<tr>
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</tr>
<tr>
<td>O$_2$</td>
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<tr>
<td>NO</td>
<td>0.00143</td>
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<tr>
<td>N$^+$</td>
<td>0.01240</td>
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<tr>
<td>O$^+$</td>
<td>0.000128</td>
</tr>
<tr>
<td>N$_2$$^+$</td>
<td>0.00032</td>
</tr>
<tr>
<td>O$_2$$^+$</td>
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<tr>
<td>NO$^+$</td>
<td>0.00028</td>
</tr>
<tr>
<td>e$^-$</td>
<td>0.01420</td>
</tr>
</tbody>
</table>

- Total number density: $8.71 \times 10^{16}$ cm$^{-3}$
- Total radiation power through Gaussian: 8.53 W/cm$^3$
- Total radiative heat flux: 7.10 W/cm$^2$
- Nonequilibrium to equilibrium heat flux ratio: 2.26

**Table 3.1**

The thermodynamic conditions and species mole fractions at the peak intensity point and equilibration point predicted by the TTv model. Table is reproduced from Park (1989).
The TT\textsubscript{T} model has been developed in order to forecast the chemical nonequilibrium processes occurring within the shock layers over vehicles travelling at high altitudes and velocities. A direct analogy is made by Park for the flow properties that exist along a stagnation streamline over a body and the conditions behind a normal shock. This holds true when the assumption is made that the flow properties are merely a function of the time interval after the flow passes through the shock front. Hence, the flow parameters at a point on a stagnation streamline are the same as those behind a normal shock front where the elapsed time is the same.

One final comment remains to be made as to the comparison between the one and two-temperature models and the experimental data. Park presents the predictions of the TT\textsubscript{T} model in a form not immediately suitable for a comparison with the experimental data. The predictions for the populations are given in terms of species mole fractions whereas experimental results are obtained in terms of absolute number densities. With a total number density plot it would be possible to reduce the species mole fractions to absolute number densities. Unfortunately this plot was not presented by Park. However the temperature plots are given and with a knowledge of this it is possible to reduce the molar fractions to number densities. This process is outlined in appendix E. It should be mentioned that the one-temperature model also presents output in terms of species mole fractions. However, unlike the TT\textsubscript{T} model, access was available to the one-temperature code and could therefore be suitably adjusted.
Chapter 4

THE EXPERIMENTS

4.1 The experimental objectives

The aims of the present investigation were as follows.

1. To develop a non-intrusive diagnostic for the study of the nonequilibrium ionisation behind high enthalpy shock waves at the conditions associated with the proposed flight regime of the AOTV. Absolute number densities of electrons were to be obtained and compared directly with the predictions of one-temperature and two-temperature chemical nonequilibrium codes.

2. The temporal radiative behavior of the plasma was to be investigated and compared with previous experiment and theory.

3. Employing molecular emission spectroscopic techniques, the rotational temperature at a point behind the shock front of the $\text{N}_2^+$ molecular species was to be determined and compared with the predictions of one and two-temperature models.

4. Emission spectroscopy was to be used to investigate the relative intensities of two transitions in atomic and ionic oxygen at a point behind the shock front and compare this to the predicted ion-to-atom intensity ratio of the two-temperature model. The dependence of atomic excitation on pressure and the opacity of the plasma were also to be determined.

5. Using narrow band CW laser absorption spectroscopy, the observed absorption profile was to be measured and compared with the
predictions of the two-temperature chemical nonequilibrium code. The experimental facilities developed and employed to achieve these objectives are discussed below.

4.2 The shock tube facilities

Three of the major free piston shock tube facilities available in the aerophysics laboratories were used at various stages in the present investigation. The majority of the work was conducted on the double diaphragm tube (DDT), which was operated in single diaphragm mode only. This facility is described by Sandeman and Allen (1971). Some molecular emission work was carried out on T3, (Stalker, 1966), taking advantage of the larger optical path length that T3 offered. Some of the preliminary development and testing of the diagnostic techniques was carried out on the smaller, square bore tube T2 (Houwing, 1982). The operational characteristics of each individual shock tube will not be detailed. As their basic mode of operation is identical however, that will be discussed initially.

4.2.1 Construction and operation

All three experimental facilities are categorized as free piston shock tubes. As the name suggests, a free piston shock tube employs an untethered piston whose compression stroke is confined to a compression tube. This piston, driven by high pressure air, compresses the gas ahead of it (the driver gas) to a pressure equal to the burst pressure of a metal diaphragm that separates the compression tube from the shock tube. As this diaphragm ruptures, a shock wave is formed that propagates down the shock tube to the test section where
specific diagnostics are used to monitor the parameters of interest. A diagram, representative of all the free piston facilities is presented in figure 4.1.

Before an experimental run, the piston was placed on the launcher. This was accomplished by pushing the piston back along the compression tube by either mechanically or hand driven push rods. The launcher has two functions. Firstly it provides a seat for the piston and secondly it is the interface between the piston and high pressure reservoir. A vacuum pump kept the “piston space”, the volume between the launcher and the piston, at high vacuum. This prevented the piston launching prematurely. The diaphragm station, which houses a metal diaphragm that separates the compression tube from the shock tube, was then loaded with a diaphragm which has a previously determined burst pressure. The high pressure reservoir, compression tube, shock tube, test section and dump tank were then all evacuated. Particular attention was paid to ensure that a good vacuum (< 0.01 Pa) was obtained in the shock tube. This is necessary to insure that anomalous results due to impurities in the shock tube are minimized and was achieved using a ‘Speedivac’ silicon oil diffusion pump, capable of pumping 600 litres per second at 50 Pa and 150 litres per second at lower pressures, backed by a ‘Dynavac’ rotary roughing pump. The pressure in the shock tube was monitored via a two stage Baratron gauge able to measure from 133 to 1330 Pa in the first stage and from $1.33 \times 10^{-7}$ to 133 Pa in the second stage. Dynavac thermistor gauges on the diffusion pump monitored the back pressure of the diffusion pump as well as the shock tube pressure. These gauges could measure between $1.33 \times 10^{-7}$ to 133 Pa. Both gauges were employed during the filling of the shock tube to ensure an accurate fill pressure.
Figure 4.1 Schematic diagram of the free piston shock tube. The diagram is representative of the three facilities used in the experiment, as their general mode of operation is identical.
As the shock tube was being evacuated, it was flushed with the test gas and re-evacuated, twice before the experimental run. The shock tube was then filled with the required pressure of test gas, within one minute of launching the piston.

Typical operation of the shock tube proceeds as follows. Prior to firing, the compression tube is filled with a driver gas (typically He, Ar or a He/Ar mix) to a pressure as measured by a mercury manometer. The shock tube is then filled with the desired test gas at a pressure typically much less than that present in the compression tube. In order to conserve momentum, the shock tube recoils as the piston travels down the compression tube. It is wound forward prior to firing to compensate for this movement. All the diagnostics set up at the test section are placed so as to account for this recoil. (A high speed video camera was employed to determine an accurate measure of the recoil. An average recoil of $11 \pm 2$ mm was measured.) Air under high pressure is then allowed to fill the high pressure reservoir. At this stage the piston does not launch because 'o'-rings on the launcher prevent the high pressure acting on the piston in a direction parallel to the shock tube. To fire the tube, a small amount of air is admitted into the piston space, forcing the piston off the launcher and consequently, the high pressure then acts along the tube driving the piston forward. The piston then adiabatically compresses the driver gas ahead of it to a pressure equal to the rupture pressure of the metal diaphragm. At the time that the diaphragm bursts, the piston reaches the end of its compression stroke and is brought to rest. The high pressure, hot driver gas then rapidly flows into the shock tube which contains the low pressure test gas at room temperature. A shock wave develops and
propagates down the shock tube. Since the shock travels faster than the driver gas, two distinct interfaces form. Firstly there is the unshocked–shocked gas interface, the shock front, and secondly there is the interface between the shocked test gas and driver gas, known as the contact surface. Hence, the shock front to contact surface distance, divided by the shock speed, gives the experimental test time before the test sample becomes contaminated by the driver gas. The relative movements of these interfaces is presented in figure 4.2.

After the diaphragm bursts, an expansion wave propagates back up the compression tube towards the piston. This expansion wave reflects off the piston and travels down the shock tube, eventually catching up to and overtaking the shock front. Meanwhile, the shock front fully develops and propagates down the shock tube followed by the contact surface. When certain conditions dictate, the contact surface can accelerate and overshoot the shock front. Furthermore, contact surface instabilities (see Houwing, 1982a) can form leading to a “tongue” of driver gas that can overtake, and mix with, the shock front. In the absence of these effects, the position of the observation ports must be situated far enough down the shock tube to maximize the test time, yet not be too far downstream to avoid the reflected expansion wave overtaking the shock wave.

The operating conditions of the shock tubes, that is, reservoir fill pressure, driver gas pressure, diaphragm burst pressure and shock tube fill pressure, have a definite bearing on the propagation characteristics of the contact surface. Indeed, in the present investigation, much work was carried out in order to determine the
Figure 4.2
The relative movements of the interfaces and their interaction with the gases at various stages after diaphragm rupture.
optimal shock tube conditions that allowed the experimental regime of interest to be studied, without driver gas contamination. These conditions are discussed in 4.2.2.

### 4.2.2 Driver conditions

Free piston shock tubes are unique in their ability to produce shock waves of varying enthalpy and shock speed by merely varying the parameters of reservoir fill pressure, driver gas pressure, diaphragm burst pressure and shock tube fill pressure. Their operational characteristics are described by the following set of equations (Liepmann and Roshko, 1957)

\[
\frac{P_5}{P_1} = \gamma_1 M_s^2 \left[ 1 - \frac{\gamma_5 - 1}{2} \frac{u_s}{a_5} \right]^{-2\gamma_s}, \quad \text{...(4.1)}
\]

\[
a_5 = \sqrt{\frac{\gamma_5 R T_5}{m}}, \quad \text{...(4.2)}
\]

\[
\frac{T_5}{T_D} = \left( \frac{P_5}{P_D} \right)^{\frac{\gamma_s + 1}{\gamma_s}}, \quad \text{...(4.3)}
\]

\[
\frac{P_R \lambda}{P_5} = k \quad \text{where} \quad \lambda = \left( \frac{P_5}{P_D} \right)^{\frac{1}{\gamma_s}} \quad \text{...(4.4)}
\]

where \( P \) is the pressure; \( \gamma \) is the ratio of the specific heats; \( M \) is the mach number; \( u \) is the shock velocity; \( a \) is the sound speed; \( T \) is the temperature \( R \) is the universal gas constant and \( m \) is the molecular mass. The subscripts 5, 1, s and D refer to the compressed driver gas, the undisturbed test gas, the shock wave and the undisturbed driver gas respectively; see figure 4.2.
Equation 4.1 describe the relationship between the ideal gas parameters and is known as the “shock tube equation” (see Glass and Patterson, 1955). The pressure and sound speed of the gas require correction if the shock tube is not of constant area, that is, if there is a step down in the cross section between the compression tube and the shock tube. (These corrections can be very easily explained in terms of flow through a sonic throat at the diaphragm station.)

As the shock velocity is dependent on the sound speed $a_5$, which is in turn dependent on the temperature $T_5$, greater shock velocities are possible in free piston driven shock tubes as the driver gas is adiabatically compressed prior to shock wave formation. The sound speed is also strongly dependent on the $\gamma$ of the gas and its molecular weight. The shock velocity may be varied therefore by suitably selecting the driver gas. For a high shock velocity, a low mass driver is chosen. This is typically helium, which fits the requirements and is far safer to use than hydrogen which would otherwise be the obvious choice. When slower shock velocities are desired, higher mass gases are added to the helium (typically argon) in small amounts, resulting in a significant drop in the shock speed.

Equations 4.2, 4.3 and 4.4 dictate the shock tube fill pressure, compression tube fill pressure and diaphragm burst pressure for a given velocity. The final parameter is the reservoir fill pressure. This appears in equation 4.4 as $P_R$ (see Stalker, 1966); $\lambda$ is the volumetric compression ratio and $k$ is an empirical constant which depends on the piston mass, and the dimensions of the compression tube. When satisfied, this equation ensures that the piston has come to rest when
the diaphragm burst pressure is reached. The value of k for DDT is 3.9, for T3 it is 4.3 and for T2 it is 4.2. The reservoir fill pressure is varied to satisfy equation 4.4 and any variation in diaphragm burst pressure is compensated for by varying the reservoir pressure.

The different driver conditions used on the three facilities during the experiment are presented in table 4.1 and 4.2. DDT was operated at a volumetric compression ratio of 95. This condition is extremely harsh on the facility and causes excessive wear of the piston rings. It was found necessary to replace the piston rings every 10-15 shots (the front ring was especially prone to wear).

4.2.3 Timing and triggering

Previous experiments on the shock tubes have employed pressure transducers to indicate the arrival of the shock front at typically three stations along the shock tube. The signals from these pressure transducers were sent to a timing unit that recorded the transit time between the transducers. Knowing their separation allowed a calculation of the shock speed. It was determined at an early stage in the present work that at the experimental pressures of interest, pressure transducers were not sensitive enough. It was decided therefore to employ photodiodes in the place of the pressure transducers. These photodiodes were sensitive to the luminosity from the shock heated gas. Each photodiode was housed, with its amplifier, in a small unit that could be screwed directly into the shock tube. These units were recessed slightly from the inner wall of the shock tube and protected from the harsh environment of the plasma by perspex windows. These windows were periodically removed and cleaned. The
Reservoir fill pressure | $4.0 \times 10^6\text{ Pa air}$
Compression tube fill pressure | $2666\text{ Pa Argon }+ 3.6 \times 10^5\text{ Pa Helium}$
Diaphragm type | 10 gauge 'cold rolled' mild steel
Diaphragm burst pressure | $7.2 \times 10^7\text{ Pa}$
Shock tube fill pressure | $13\text{ Pa of air}$

This condition was optimal, for it produced the desired shock velocity (10 km s$^{-1}$ into 13 Pa of air) an adequate percentage of the time with no contamination. Any decrease in the amount of Argon being admitted into the compression tube would result in an increase in the shock velocity, but the contamination would persist 100% of the time. Any increase in the amount of Argon being admitted into the compression tube and, although the contamination would not be as severe, the shock velocity would drop to below that desired. This contamination (to be discussed at length in chapter 6) was an extremely sensitive function of the fill condition.

| Reservoir fill pressure | $1.1 \times 10^6\text{ Pa air}$
| Compression tube fill pressure | $2266\text{ Pa Argon }+ 1.7 \times 10^4\text{ He}$
| Diaphragm type | 22 gauge 'cold rolled' mild steel
| Diaphragm burst pressure | $1.7 \times 10^7\text{ Pa}$
| Shock tube fill pressure | $133 & 1333\text{ Pa of Argon}$

This condition is a standard for work in Argon. There was no contamination for a substantial distance behind the shock front (20 cm) and therefore there was a significant test time (unlike the condition above for air in which the test distance was limited to only, at best, 3 cm, although this was adequate for the experimental aims to be achieved).

**Table 4.1**
The driver conditions for DDT.
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<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td>Reservoir fill pressure</td>
<td>$2.2 \times 10^6$ Pa air</td>
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<tr>
<td>Compression tube fill pressure</td>
<td>$3.1 \times 10^4$ Pa Helium</td>
</tr>
<tr>
<td>Diaphragm type</td>
<td>14 gauge 'cold rolled' mild steel</td>
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<tr>
<td>Diaphragm burst pressure</td>
<td>$2.8 \times 10^7$ Pa (single hole)</td>
</tr>
<tr>
<td>Shock tube fill pressure</td>
<td>13 Pa of air</td>
</tr>
</tbody>
</table>

**T3 operating condition.** Once again, the contamination was an extremely sensitive function of the fill condition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir fill pressure</td>
<td>$3.7 \times 10^6$ Pa air</td>
</tr>
<tr>
<td>Compression tube fill pressure</td>
<td>$5.3 \times 10^4$ Pa Helium</td>
</tr>
<tr>
<td>Diaphragm type</td>
<td>18 gauge 'cold rolled' mild steel</td>
</tr>
<tr>
<td>Diaphragm burst pressure</td>
<td>$2.5 \times 10^7$ Pa</td>
</tr>
<tr>
<td>Shock tube fill pressure</td>
<td>13 Pa of Air</td>
</tr>
</tbody>
</table>

**T2 operating condition.** Once again, the contamination was an extremely sensitive function of the fill condition.

*Table 4.2*  
The driver conditions for T3 & T2.
output pulses from these photodiodes were sent to a digital oscilloscope capable of recording the transit times to an accuracy of ± 0.05 μs. After a trigger from the first photodiode, the digital oscilloscope was appropriately delayed so as to allow a 2 μs window around the trace of the second photodiode. This allowed the shock velocity to be accurately determined. The time resolved analogue output from the photodiodes was also recorded to give an indication of the shock front, contact surface separation, as luminosity coming from the contact surface was readily distinguished from that due to the shock front due to the formers greater amplitude. This is a result of the emission from the many atomic impurities present in the contact surface, namely iron, chromium, magnesium and sodium.

4.2.4 The test section

The emission experiments in the shock tubes DDT and T3 were conducted at these tubes' exit planes. Measurements were taken through optically flat UV grade fused silica windows 0.1 m in diameter, positioned, off centre, in aluminum plates. These plates could be mounted in the superstructure of the dump tank and were interchangeable between the three tubes DDT, T3 and T2. Quartz was chosen because of its good transmission properties over the spectrum from wavelengths of 250 nm to 2.0 μm. The infrared interferometric experiments carried out in DDT were also conducted at that tube's exit plane. The Zinc Selenide windows (see section 4.4.2) were also positioned, off centre, in aluminum plates mounted in the superstructure of the dump tank.

Measurements taken across a shock tube exit are done so in a flow that is no longer uniform, normal to the tube axis. There exists a
supersonic expansion fan at the shock tube exit, and the effects of this on the measurements must be considered. Figure 4.3a shows the test section end of DDT's shock tube. D is the diameter of the shock tube and L represents the path length of a ray from an interferometer test beam passing through the flow at a distance z from the edge of the shock tube. Figure 4.3b illustrates the expansion fan that, due to the circular symmetry of the shock tube, limits the steady flow to a Mach cone. L now consists of two components $L_A = 2r$ and $L_B = 2r'$ with $r$ and $r'$ shown. If the length AB is known, (and it is readily calculated), one can obtain a value for the Mach angle $\mu$. Hence the value of $r$ may be determined. On the other hand, an accurate determination of $r'$ is difficult, as the values of the nonequilibrium flow parameters in the unsteady expansion are not easily determined. One can obtain a value of $r'$ however, by assuming a particular shape for the diffracted shock. With this, a reasonably accurate estimation of the optical path length may be obtained. Measurements were taken as close to the shock tube exit as possible to minimize these effects on the path length.

4.3 Ionisation diagnostics and their relative merits

The development of the ionisation diagnostic was the most difficult aspect of the experiment. CW laser systems were available for the spectroscopic studies and detectors were available for the emission work. An ionisation diagnostic was not available and had to be designed and implemented from scratch. Because of this, a survey of diagnostic techniques was undertaken and their relative merits considered. The various techniques are detailed below.
Figure 4.3 (a) and (b)
(a) presents the test section end of the free piston shock tube. 
(b) shows the expansion fan developing into the Mach cone that limits the steady flow.
1. Electrostatic or Langmuir probes

Although highly spatially resolved measurements are possible with electrostatic or Langmuir probes, correlating the electron number density to the probe potential can lead to uncertain results. The probe potential is of course dependent on the net distribution of charge, and not specifically the electron population. Furthermore, probes are intrusive in their nature. (See Petschek and Byron, 1957).

2. Continuum radiation monitoring

Continuum radiation emitted from a plasma in an ionising monatomic gas, is due to free-free and free-bound electron transitions. A time resolved measurement of this radiation will yield information about the rate of ionisation within the plasma. In a diatomic gas however, such a simple correlation is not possible. To make an accurate correlation between the emitted radiation and the electron population in a diatomic gas, one must be certain that molecular band radiation can be distinguished from that due to electron free-free and free-bound continuum radiation. As intense radiation covering a considerable part of the spectrum comes from the ro-vibrational transitions of \( \text{N}_2 \) and \( \text{N}_2^+ \) this becomes extremely difficult. Furthermore, due to the large number of species present in shock heated air, there exists emission from the UV to the far infrared. (See Petschek and Byron, 1957, Niblett and Blackman, 1958 and Wilson, 1966).

3. Magnetic induction techniques

If a steady magnetic field (whose dipole axis runs parallel to the shock tube) can be applied into the shock tube, then any disturbance to the steady state field can be sensed using a secondary coil. These changes
in the field, after some calibration, can give a measure of the electrical conductivity distribution behind a shock front. To achieve high spatial resolution in a large diameter tube, it is necessary to place the induction coil inside the tube itself. The probe then becomes rather intrusive (much like the electrostatic probes). Furthermore, as the spatial resolution is a function of the width of the magnetic field, spatial resolution and sensitivity are lost in small diameter tubes.

(See Lin et al., 1962).

4. Line broadening due to the Linear Stark effect

Stark broadening, due to the electric fields associated with the plasma ions and electrons, provides a method for the measurement of charged particle densities. One may use measured line profiles to derive conditions in an emitting plasma. When considering hydrogen and hydrogen like lines, the Stark broadening $\Delta \lambda_s$, given by Griem (1964) as

$$\Delta \lambda_s = C(N_e, T)N_e^{2/3}$$

may be employed, where $N_e$ is the electron number density in (cm$^{-3}$) and $C(N_e, T)$ is a coefficient that depends weakly on $N_e$ and $T$. Values for $C(N_e, T)$ are tabulated by Griem for a range of electron densities and temperatures for Stark broadened hydrogen and hydrogenic lines. At the conditions of interest, the broadening of the $H_{\alpha}$, $H_{\beta}$ and $H_{\gamma}$ lines is of the order of 20 nm, which can be easily resolved using either laser absorption spectroscopic techniques or emission spectroscopy.

5. Microwave transmission and reflection techniques

Microwave techniques employ the way in which microwaves interact with ionised gases. The microwaves passing through an ionised media
are attenuated by a factor \( \alpha \); \( \alpha \) being a function of the electrical conductivity and the dielectric coefficient of the gas. The techniques suffer the serious disadvantage of extremely poor spatial resolution, especially within the relaxation zone in small diameter shock tubes. Another severe limitation arises when one considers the plasma frequency \( \omega_p \). An electromagnetic wave whose frequency \( \omega \) is such that \( \omega < \omega_p \), cannot propagate into the plasma. \( \omega_p \) then, represents the 'cut-off' frequency for electromagnetic wave propagation. For electron densities greater than approximately \( 10^{13} \text{ cm}^{-3} \) (equivalent to a plasma frequency \( \omega_p = 1.98 \times 10^{11} \text{ Hz} \)), microwaves of wavelength \( \lambda = 0.01 \text{ m} \) (\( \omega = 1.88 \times 10^{11} \text{ Hz} \)) fail to propagate due to their rapid attenuation. This limits the technique to the low ion and electron number density regime. (See Lin et al., 1962, Lin and Kivel, 1959, Manheimer-Timnat and Low, 1959 and Gorelov, 1983).

6. **Infrared interferometry**

The use of an interferometer with a light source in the far infrared allows the measurement of the phase shift caused by the presence of free electrons in the flow field. This technique allows highly resolved spatial and temporal measurements, is non-invasive and the change in the refractive index is purely a function of the electron number density; thereby allowing straight forward correlation between the fringe shift and the electron population per unit volume. (See Zalogin et al., 1980).

7. **CO\(_2\) Laser Absorption (Inverse Bremsstrahlung)**

When radiation passes through a plasma, the radiation will be absorbed by the inverse Bremsstrahlung (free-free electron transition) process. The amount of absorption will correspond to that given by
Lambert's law, that is, 

\[ I = I_o e^{-kx} \]  

...(4.6)

where \( k \) is the spectral absorption coefficient per unit length and \( x \) is the pathlength. The absorption coefficient associated with the inverse Bremsstrahlung process is given by (Penner, 1959)

\[ k_{ff,\omega}^{翌} = 1.646 \times 10^{-21} \frac{\lambda^3 N_e^2}{T^{1/2}} \]  

...(4.7)

where \( N_e \) is the number density of free electrons; \( \lambda \) is the wavelength of the incident radiation and \( T \) is the temperature. In the present investigation, the expected value for the electron population was of the order of \( 10^{15} \) cm\(^{-3} \) at a temperature of approximately 10,000 K. The calculated absorption for these densities was of the order of 5% (for 10.6 \( \mu \)m laser radiation), but could increase depending on the shock tube conditions. This percentage is very small and the detection of such a minute change in laser intensity (considering that the maximum voltage output by the infrared detector was only 200 mV) was deemed too inaccurate for the inverse Bremsstrahlung process to be used as the ionisation diagnostic.

Considering the foregoing then, the infrared interferometry and Stark broadening of the \( \text{H}_\beta \) line were chosen as the ionisation diagnostics. The design and implementation of these techniques is to be detailed in the following sections.
4.4 Infrared interferometry

4.4.1 The experimental arrangement

The infrared interferometric ionisation diagnostic, was chosen for several reasons. It allowed a high degree of spatial and temporal resolution, was non-intrusive and the change in the refractive index was purely a function of the electron number density. The contribution from the heavy particles to the refractive index was negligible when compared with that from the electrons. (Calculations showed the fringe shift due to heavy particles, at the experimental conditions and wavelengths, to be of the order of 1/20 of a fringe. This was not resolvable in the present experiment.) The experimental schematic employed is presented in figure 4.4. An overview of the experimental system is briefly described below. The various components that constitute the system are mentioned, but are discussed in further detail in the following sections.

A Michelson interferometer was constructed about the shock tube exit in order to determine the electron number density profile as the shock front exits the tube. As discussed in section 4.2.4, the interferometric system was constructed as close as possible to the shock tube exit to minimize the effects on the path length due to the presence of the Mach cone. To achieve the highest possible spatial resolution, it was necessary to have the smallest possible beam diameter in the test and reference arms. This was achieved by placing an aperture in the CO₂ laser beam in the form of a circular iris; diffraction effects presented no problems. The CO₂ laser beam could be seen, and therefore aligned in the optical system, using phosphorescent plates illuminated by an
Figure 4.4
The schematic diagram detailing the experimental arrangement for the infrared interferometric experiments
ultraviolet lamp. The beam diameter was sufficiently small across the shock tube exit to give the desired spatial resolution. The Michelson interferometer employed was typical except for the optics which were specific to the 10.6 μm CO₂ laser radiation.

The infrared detectors were designed specifically for pulsed applications. As such their sensitivity decreased dramatically during CW applications, as the temperature of their active area increased rapidly during exposure. To ensure optimal sensitivity during the experimental run, a mechanical shutter was placed in the infrared beam (although prior to the experiment the shock tube blocked the infrared beam in the test arm as it was in the forward recoil position, it was still necessary to shutter the reference arm). This shutter was opened by a trigger pulse received from a photodiode. The only light allowed to fall on this photodiode was a He-Ne laser which was imaged onto its active area. The alignment of this He-Ne laser and photodiode was such that a beam dump, attached to the shock tube, obstructed the He-Ne beam when in the forward recoil position before the shot, but allowed the beam to fall on the photodiode when the tube had recoiled approximately 2 mm out of its total recoil length of 11 mm. This triggering system was essential when one considers the time scales involved in the experiment. Any mechanical shutter requires milliseconds to open. The shock wave however moves in the microsecond time scale. Hence the shutter could not be opened in time by any trigger associated with the propagation of the shock front. The recoil however, occurs on a sufficiently slow time scale, such that the shutter may be opened before the shock exits the tube. The full experimental schematic of the electronics system for the infrared interferometric experiments is presented in figure 4.5.
Thermoelectric cooler current for infrared detector = 60 mA at 5V

$\text{CO}_2$ laser operating conditions = 34 psi gas pressure, 15 mA tube current

Bias voltage for infrared detector = 8.5 V at 39 mA

Figure 4.5
The schematic diagram detailing the experimental arrangement for the infrared interferometric experiments
Hetrodyning the infrared signal was contemplated in order to remove any discrepancy that may have occurred in the phase direction. This could have been achieved, for example, by piezoelectrically driving the reference mirror of the interferometer during the experimental run. The hetrodyning technique was however ruled out for several reasons. Firstly, the relatively large mirror would have had to be driven at a rate approaching 50 MHz, that is, at least an order of magnitude greater than the experimental frequency. Another restriction, is the distance that the interferometer mirror must be driven in order to maintain this frequency at a constant value during the required test time. It can be shown that for a test time of 10 μs, an interferometer wavelength of 10.6 μm and a hetrodyning frequency of 50 MHz, a mirror displacement of at least 2.5 mm is required. Furthermore, to achieve this displacement in the required test time, the mirror would need to be driven at a velocity of at least 250 ms⁻¹. The aforementioned requirements are well outside the currently available piezoelectrically driven translation devices.

At the experimental wavelength, bound-free and free-free transitions start to become important. These transitions are in the continuum and as such, there is no Sellmeier like dispersion curve which can affect the phase of the system and cause discrepancies in the reduction of the phase measurement to electron densities.

4.4.2 The Michelson interferometer
The windows and compensators of the Michelson interferometer were made of Zinc Selenide (ZnSe) with a thickness and diameter of 20 mm ± 1 mm (Janos optical corporation; model 9000-3201). These
optics had a surface flatness of $\lambda/10$ at $\lambda=632.8$ nm and a parallelism of 3 seconds of arc. They were not anti-reflection coated. The windows were mounted at $10^\circ$ to the optical axis in order to eliminate any anomalous fringes due to internal reflections. The mirrors were 20 mm diameter, gold coated, with a surface reflectivity of $> 98\%$ at $\lambda=10.6 \mu m$ and had a surface flatness of $\lambda/10$ at $\lambda=632.8$ nm.

The beam splitter was also made of ZnSe and had a diameter of 25.4 mm and a 2 mm thickness (Oriel corporation, model 45363). The beam splitter had a surface flatness of $\lambda/40$ at $\lambda=10.6 \mu m$ and a parallelism of 3 minutes of arc or better. The front surface had an all dielectric 50/50 coating at 10.6 $\mu m$ and 45$^\circ$ while the rear surface had an anti-reflection multi-layer dielectric at 10.6 $\mu m$ and 45$^\circ$. All optics were placed on Oriel corporation transverse mounts that were secured to a concrete table damped from external vibrations.

4.4.3 The tunable CW CO$_2$ laser
The laser employed as a light source for the Michelson interferometer was a Model TCX-5 tunable CO$_2$/CO laser system (Laser Dynamics Limited). This laser was chosen due to its versatility, compactness and high degree of beam stability. The laser typically produced 6 Watts TEM$_{00}$ on the P-20 line (10.6 $\mu m$). It has a flowing gas system that offers a wavelength range of 5-11 $\mu m$ by appropriately selecting the gas mixtures. Only CO$_2$ was used in the present investigation and therefore only the P-20 line was used. The amplitude stability of this laser was better than 1$\%$ and the frequency stability was better than 2 parts in $10^9$ over 0.1 seconds. The laser cavity underwent some change in length due to thermal expansion as soon as it was powered up and
hence it did not operate stably on the P-20 line for 5 minutes or so (at which time it had reached equilibrium), after which the stability was as quoted above.

4.4.4 The HgCdTe infrared detectors

The infrared detectors used in the present investigation were photoconductive devices. These devices are semiconductors whose resistance decreases when exposed to infrared radiation. Photoconductive devices have a mode of operation somewhat similar to that of other photon detectors, such as photomultipliers. The infrared photons however do not have sufficient energy to completely remove electrons from a surface, as with the photomultiplier. They do however have enough energy to free an electron from the crystal lattice and so increase the number of free electrons and/or holes that act as current carriers. The process has been described as an internal photoelectric effect. This effect is amplified by cooling the semiconductor and thereby reducing the number of thermally excited electrons. HgCdTe detectors were chosen for their high specific detectivity and fast response time at 10.6 μm.

Initial experiments were conducted using a Boston electronics corporation high speed uncooled infrared laser detector (model R005-2). This is a room temperature high speed HgCdTe photoconductive device, with an active area of 1 mm², a rise time of 1 ns and optimized for the 10.6 μm CO₂ laser radiation. Losses in the Michelson interferometer (reflections off the windows, compensators and beam splitter etc), resulted in approximately 250 mW of CO₂ laser radiation falling on the detector. Because of these low powers, and the responsivity of the device being only 20 mV/W at 10.6 μm, a
peak-to-peak output of only 1-4 mV was obtained (this problem was amplified as the sensitivity decreased as the temperature of the detector surface increased due to absorption of the infrared radiation). This output was unacceptably low in the electrically noisy environment in which the experiment was taking place. In an attempt to rectify this problem, a high speed amplifier was built using the integrated circuit SE/NE592. This is a wide band video amplifier with a 120 MHz bandwidth with adjustable gain from 0 to 400. The characteristics of this amplifier were studied, and it was found not to be linear over the entire frequency range of interest. Furthermore, it was found that electrical noise was readily amplified and caused considerable problems at the triggering stage, pre-triggering of the digital recording device being a common problem. Much work was undertaken with Faraday shielding in an attempt to reduce noise as seen by the amplifier, but it was not possible to reduce the noise below the experimental signal which was of order 1 mV.

To overcome the low signal and amplification problems, a second detector was obtained. This was an EG & G Judson infrared incorporated, high speed thermoelectrically cooled infrared laser detector (model J15TE4/10-MC31G-SO1M). Again this is a HgCdTe photoconductive device with an active area of 1 mm², a rise time of 1 ns and optimized for the 10.6 μm CO₂ laser radiation. The responsivity of this device however was somewhat higher at 2 V/W. Furthermore, due to the thermoelectric cooling, the inherent noise (due to thermal electrons) was greatly reduced. The Judson infrared detector, being thermoelectrically cooled, required a heat sink at the back surface of the cooler capable of dissipating at least 10 Watts with less than 2 K
temperature rise (the maximum heat sink temperature was not to exceed 323 K). Due to the high cost of the device, coupled with the fact that overheating would cause permanent damage in a short time, a water cooled copper heat sink was constructed around the detector. The design of this heat sink is presented in figure 4.6. The infrared detector was "glued" to the heat sink with a thermally conducting paste.

The coolant was a mixture of distilled water (with an anti-algae additive) and ethelyene glycol, kept by two refrigeration units at a temperature of 278 K. This was pumped through the heat sink at a rate of 5 liters/min and maintained the surface temperature of the heat sink at 278 K. To eliminate any condensation that may have occurred on the detectors optical surface, an air-tight cover was built around the detector so that nitrogen could be purged through, and subsequently sealed. A rubber "bladder" was incorporated into the nitrogen supply line to compensate for volume changes that occur as a result of the nitrogen cooling and thereby removed any undue mechanical stress on the detector. All wiring from the detector passed through a hole in the enclosure, which was sealed after fitting. A simple bias circuit was attached directly to the back of the heat sink in order to have the detector as close as possible to the bias electronics. This was done in an attempt to minimize electromagnetic pickup and earth loops. Electromagnetic noise proved to be a serious problem in the experiment. Operating with very low signal levels, several electromagnetic sources, (electrical noise from the CO₂ laser power supply, the bias electronics and two local FM radio stations operating on nearby bands), were picked up and convoluted with the infrared
Figure 4.6
The design of the infrared detector housing showing the water cooled, copper heat sink, bias electronics and N2 purge system.
signal. Faraday shielding and "true earths" were employed to eliminate these problems. The power to the thermoelectric cooler was provided by a constant current supply with less than 2% ripple. A digital multimeter was used to monitor the thermistor resistance, which was indicative of the detector temperature. The thermoelectric cooler was operated typically at a temperature of approximately 190 K. When the CW CO₂ laser was imaged onto the detector, the temperature of the detector would again rise, causing the sensitivity to decrease and indeed approached the 1 mV output of the Boston electronics uncooled infrared device. This heating process had a time constant of the order of 5 seconds, and hence appropriate millisecond shuttering of the CO₂ laser, eliminated this problem. With the heat sink operational, the thermoelectric cooler was able to cool to temperatures some 50 K lower than when the detector was air cooled, resulting in a signal increase of some 30%.

4.4.5 Data acquisition
Two high speed digital recording units were employed in the fringe counting experiments; these being a 32 MHz LeCroy high speed transient recorder and a 20 MHz Phillips Digital CRO. Both units were continuously recording devices whereby one could, in effect, gather data before the triggering event. As the final timing photodiode was 140 mm from the tube exit, this was used to trigger both recording devices. As the devices had an effective recording time after trigger of 100 μs and since the shock front took approximately 15 μs to transverse the 140 mm, no delay unit was necessary. A Macintosh Plus interfaced to the LeCroy transient recorder allowed downloading of the data via a Mac 488A IEEE Bus Controller, while the data captured on the Phillips digital CRO was photographically recorded and subsequently digitized.
4.5 Stark broadening of the $H_\beta$ line

4.5.1 Introduction

The line broadening mechanisms due to the Doppler effect and the Stark effect have attained great experimental importance in plasma diagnostics. Since these effects depend upon parameters such as temperature, pressure and the populations of electrons, atoms and ion fields, it is possible to determine these parameters experimentally by studying specific line profiles. These studies, coupled with an accurate theoretical basis, provide a convenient, non-intrusive plasma diagnostic.

As a rule of thumb, Doppler broadening increases with increasing temperature, whereas Stark broadening increases with increasing electron number density. Broadening by charged particles is due to the linear Stark effect for hydrogen and hydrogenic lines and the quadratic Stark effect for other atoms. The line profile (or more importantly, their FWHM) depends directly on the density of free electrons.

Wherever possible, the hydrogen and hydrogenic like lines are most often employed as the diagnostic. The first choice for electron population measurements was the $H_\beta$ line. This transition is strong, very well broadened (broadening can be of the order of tens of nanometers with effectively no line shift) and does not overlap with neighbouring lines which can make data reduction difficult (unlike the $H_\gamma$ and $H_\delta$ lines at high electron populations). The $H_\beta$ line ($\lambda=486.1$ nm) is in a part of the spectrum that is readily accessible, clear of molecular and atomic transitions that may have competed with it, and, since it
possesses an intensity dip at its centre due to the absence of an unshifted Stark component, it is not prone to self absorption. Furthermore the intensity dip results in a shape that is a very characteristic and easily detectable fingerprint. Most importantly however, the theory is well developed for the \( H_\beta \) transition and experiments suggest that electron densities may be determined to better than 7%.

The Stark broadening of the \( H_\beta \) line was monitored for two reasons. Firstly, it provided a check of the results obtained in the infrared interferometric experiments. Secondly it allowed a more accurate interpretation to be made of fractional fringe shifts. Due to the very low signal levels coupled with the inverse Bremsstrahlung absorption (Penner and Olfe, 1968), fractional fringe shifts (\( \Delta p < 1/2 \)) were difficult to reduce to electron populations. Without a simultaneous measure of this absorption, the magnitude of the fractional fringe shift could not be accurately determined. The Stark broadened measurements set the upper limit to the population and hence measurements from fractional fringe shifts could be confirmed. The \( H_\beta \) line was chosen specifically because of the accurate theoretical analysis that has been conducted on it, and because the broadening parameters are well documented.

4.5.2 The experimental arrangement

In the present investigation, a small percentage (0.5% by number density) of \( \text{H}_2 \) was added to the test gas prior to the experiment. The line profile of the second Balmer line, \( \text{H}_\beta \), was observed. It was calculated at an early stage in the experiment, using expected experimental values for the temperature, that at the experimental
Chapter 4: The experiments

regime of interest, the Doppler broadened profile would account for only a small percentage of the FWHM compared to the Stark broadened profile at the position behind the shock front where the measurements were to be made.

For hydrogen in the region of complete dissociation and ionisation, the potential energy per atom is 15.74 eV (the dissociation per H atom is 2.24 eV and the ionisation energy is 13.5 eV). The ionisation potential of H$_2$ is 15.442 eV. These potentials are higher than the ionisation potentials of N, O, N$_2$, O$_2$ and NO. Therefore it was not expected that electrons liberated by the possible earlier ionisation of the hydrogen would cause any significant change in the induction time. Furthermore, as the number density of the hydrogen impurity was very low, it was shown that any dissociation and subsequent ionisation of H$_2$ had a negligible effect on the total electron population. Even had the induction time changed slightly as a result of the hydrogen impurity, this would have had little effect on the results, as the Stark broadening measurements were conducted at a position behind the shock where the electron populations had fully evolved to their pseudo-equilibrium values. The experimental arrangement for the Stark broadened experiments are presented in figure 4.7.

A point close to the exit of the shock tube was imaged onto the entrance slit of a 1 m 'Spex' spectrometer, the output of which was monitored by an Optical Multichannel Analyser (OMA). The OMA has 500 channels in the horizontal and the resolution was 0.015 nm per channel. The OMA was gated for an interval of 0.5 µs.
Figure 4.7
Schematic diagram detailing the experimental arrangement for the Stark broadening experiments.
If the time evolution of the line profile was not constant during the gate time of the OMA (that is if line centre is populated more rapidly than the wings of a given transition), then the OMA will see a convolution between a shallow broad Lorentzian and a steep narrow Lorentzian, resulting in a meaningless line width. To ensure that this was not the case, the time evolution of the line was checked with a photomultiplier at different detunings and was shown to be constant to about 5%.

4.5.3 The Optical Multichannel Analyser

The OMA is an instrument designed for the simultaneous measurement of light intensity in a linear array of 500 channels. It consists of two parts. The first, the OMA head (Princeton Applied Research, model 1205 D), is a Videcon silicon intensified tube detector. This had been manufactured with a fibre optic face plate and was equipped with the option of a UV scintillator, extending the effective wavelength at which the detector may be employed. The fibre optic face plate had an aperture diameter of 12.5 mm and is of quartz construction. The detector had a rise time of 1 ns and could be operated in gated or real-time mode. The detector is linear with respect to light intensity over the range of 100 to 800 nm and one channel at a time is read with a scanning electron beam.

The second component is the OMA driver, (Princeton Applied Research, model 1205 A). Both the head and driver were matched at the time of manufacture. The OMA driver is essentially a solid state memory unit. Initially the driver digitizes signals coming from the head, and once in digital form, directs the data to either of two 500 word 21 bit memories.
There exist two ancillary units to the OMA. The first is the OMA gate pulse generator. This comprises a Marx generator that powers two krytrons, one being the on (gate open) krytron and the other being the off (gate closed) krytron. The open/close time was controlled by an RC circuit whose RC time (and hence gate time) was adjustable from 0.5 µs to 100 µs. The gate open time was essentially instantaneous. A negative going 1130 V pulse was required by the OMA head to gate. Focusing was achieved by changing the amplitude of the gate pulse. The second unit was the OMA reset controller. This device resets and holds clear the “A” memory of the driver. A trigger pulse sent to the reset controller, starts memory “A” recording and instructs the OMA gate pulse generator to open. After the experimental run, the contents of memory “B”, containing background radiation, was subtracted from memory “A”. The resultant (which holds the experimental data), located in memory “A–B”, was then downloaded to a Macintosh Plus via an RS-232 interface. A schematic diagram of the electronics system for the Stark broadened experiment is presented in figure 4.8.

4.5.4 The photomultiplier

The temporal resolution of the OMA is limited by the gating time. By virtue of its design, the OMA integrates in time any signal it is monitoring during this gate time. This will introduce errors in the extracted profile if, at various detunings from line centre, the emission is evolving at differing rates. Should the time evolution of all parts of the line profile be equivalent, and with adequately small gating times, it is possible to establish the FWHM of the line from the OMA results after deconvolution of the instrument function. To this end, it was necessary to establish the time evolution of the $H_\beta$ line at various
Photodiode analogue out sent to digital CRO so peak emission point could be compared with gate pulse

**Figure 4.8**
The electronics systems employed with the Stark broadening experiments.
detunings from line centre. The photomultiplier employed for this part of the experiment was an RCA 1P28. This photomultiplier was peaked for 400 nm with an absolute sensitivity of 50 mA/W at this wavelength. It had an anode pulse rise time of < 2 ns. The RCA 1P28 required 50 Ω termination to eliminate cable reflections at the experimental frequency.

4.5.5 Triggering and timing

The previous section described the procedure with which the time history of the Hβ line was measured at several detunings. These experiments demonstrated that the evolution across the line was essentially constant (from line centre to ± 40 nm from line centre) within the first 3 μs. It was necessary therefore to gate the OMA for this period of time for which the time evolution was a constant. As described in section 4.5.3, it was possible to gate the OMA down to an interval of 0.5 μs. A problem arose however in the timing of this gate pulse. On receiving a trigger, the OMA gate pulse generator required 1μs to open. This was due to electronic propagation delays. Hence the pulse generator had to be triggered 1μs before the arrival of the shock front. It was not possible to use some trigger upstream of the test section delayed by an appropriate time. At shock velocities of 10 kms⁻¹, the closest timing station from which a trigger could be taken was, in time, 30μs away. To delay this trigger for the appropriate period, required knowing the shock velocity to better than 1 part in 30 from shot to shot. This was not possible in the present investigation.

To allow triggering 1μs prior to the shock arriving, a special assembly was designed that allowed a pin photodiode to be flush mounted to the shock tube inner surface, 10 mm (1 μs in time at 10 kms⁻¹) from the
tube exit. The design of this photodiode trigger is presented in figure 4.9. Care was taken to ensure that the photodiode did not disturb the flow. The diode was inside the dump tank during the experiment. Signals coming from it were received, via a cable leading through a vacuum tight seal, to its amplifier.

4.6 Emission from molecular nitrogen

4.6.1 The experimental arrangement

Emission from molecular nitrogen was monitored as a means of determining the rotational temperature. Section 5.4.3 outlines the method by which the rotational temperature may be deduced by measuring the time resolved emission of two different rotational transitions in a given vibrational band. The experimental arrangement for the technique is presented in figure 4.7. The experimental arrangement for these experiments was the same as that used for the Stark broadening experiments. One particular rotational transition was chosen and the spectrometer was placed onto that line (accurate wavelength calibration is discussed in section 6.4). This technique gave one temporally resolved result per firing of the shock tube. Another rotational transition (within the same vibrational band) was chosen and the spectrometer was placed onto that line. This procedure produced the two required temporally resolved ro-vibronic transitions, and relied on good shot-to-shot repeatability.

The spectrometer could not simply be “placed” at the correct spectral position in order to monitor the emission from a specific rotational level. It was not considered accurate enough to use theoretical values
Figure 4.9
Design of the pin photodiode housing showing, diode, flush mounted, 10 mm from the tube exit. End section of tube may be removed. Power and signal are fed, via cables, to amplifiers through a vacuum tight seal.
for the wavelengths and associated rotational quantum numbers. To account for any possible shift in the lines of interest, it was necessary to obtain a spectrum of the rotational transitions at and around the vibrational bands of interest. This was done employing the same experimental technique utilized in the Stark broadening experiments, section 4.5.2.

4.6.2 The molecular transitions

Emissivity calculations for the constituents of hot air have shown (see section 2.3, chapter 2) that the strongest emitters, at temperatures applicable to hypersonic vehicles, are the first negative system of N$_2^+$ and the second positive system of N$_2$. The energy level scheme for these molecular transitions are presented figure 4.10. Park (1989) considers in the TTV model, that the radiation at wavelengths between 400 nm and 420 nm comprised mostly of the first negative band system of N$_2^+$ and that in the wavelength range 550 nm to 1000 nm contains atomic line emission from N and O atoms and the first positive system of N$_2$.

4.7 Emission from atomic and ionic oxygen

4.7.1 The experimental arrangement

Among the strongest atomic emitters in shock heated air are the atomic oxygen transitions at 777.196, 777.418 and 777.540 nm. These atomic transitions are detailed in section 4.7.2. The relative intensities of these transitions were monitored at various pressures in order to determine the dependence of the atomic excitation on density and determine the optical opacity of the plasma. The 464.914 nm transition in ionic oxygen was also monitored with the same experimental
Figure 4.10
Energy level diagram of the $N_2$ molecule showing the first and second positive groups of $N_2$ and the $^2\Sigma^+ \rightarrow ^2\Sigma^+_g$ transition in $N_2^+$, responsible for the strong emission in shock heated air. Figure is reproduced from Herzberg (1950)
technique in order to make a measurement of the relative intensity of transitions in O and O*. This transition in O* was chosen because it lay in a relatively clean part of the spectrum, free from the strong emitters of shock heated air. Furthermore, the emission was to be observed in the quasi-equilibrium region where the dissociation was essentially complete and the molecular transitions have peaked in their emission. It may have been possible to employ laser absorption spectroscopic techniques on the oxygen ion, however the population of the ionic levels was relatively low, and weak absorption lines are more difficult to measure than weak emission lines, as the signal-to-noise ratio is less favourable. It transpired that the ionic oxygen emission had to be observed over several separate accumulations of the OMA from successive experimental runs at the same condition. This of course would not have been possible with a laser absorption experiment. The experimental arrangement for the atomic and ionic oxygen emission experiments is presented in figure 4.7. The experimental setup was almost identical to that of the molecular emission experiments, section 4.6, except for the introduction into the optical system of a broadband filter (Wratten filter # 72B) which cut-off any emission below 500 nm. This filter was essential, as it was necessary to remove contributions to the spectrum from the intense emission coming from the (0,0) and (1,1) ro-vibronic transitions of N₂⁺ at 388.1 and 391.0 nm. These transitions overlap in second order, with the atomic oxygen lines of interest.

4.7.2 The oxygen transitions

There are several reasons why the aforementioned oxygen transitions were selected for investigation.

1. They are well documented in the literature (Wiese et al (1969 & 1980) and have reliable values for their oscillator strengths.
2. The atomic lines are spectrally isolated, and their intensity readily exceeds the background radiation at 777.0 nm, and simple optical filtering could remove the problem associated with emissive contributions coming from second order.

3. The upper levels of the atomic transitions are far removed from the effects of a decrease in the ionisation potential due to the broadening of the high lying Rydberg states. That is, they are not transitions to a pseudo-continuum.

4. The ionic transition is also spectrally isolated, lying in a clean part of the spectrum, and the upper level is amongst the more populated of the ionic levels.

An energy level diagram of the atomic transitions in question is presented in figure 4.11.

**4.8 Infrared CW diode laser absorption by atomic oxygen**

**4.8.1 The experimental arrangement**

The levels in atomic oxygen, studied in the emission experiments, were also selected for study with infrared CW diode laser absorption spectroscopy. The experimental schematic for this experiment is presented in figure 4.12. Typically, optogalvanic tuning would have been employed to measure the detuning from line centre in such an experiment. Unfortunately, this was not possible in the present work as one would have required an oxygen hollow cathode or discharge lamp. Such a lamp is difficult to make as oxygen is of course very reactive. It may have been possible to construct a lamp using gold or
Figure 4.11 Energy level scheme for the oxygen atom. Multiplet 5S0 - 5P studied in the emission experiments is shown. Figure is reproduced from Kuhn (1962). The transition wavelengths are given in angstrom units.
Figure 4.12
Schematic diagram detailing the experimental arrangement for the CW diode laser absorption experiment.
platinum electrodes that are not as reactive in the oxygen plasma, but in the present work, this was not possible. Furthermore, it was considered that such a lamp may contribute considerably to the line spectrum, as gold, for example, has a multitude of transitions and sputtering may have become a problem. Because of this, a "home-made" discharge lamp was constructed and filled with air. The oxygen transitions of interest were clearly visible in this discharge lamp using a different OMA unit (OMA II Princeton Applied Research) coupled with the spectrometer (quite obviously, this discharge lamp regularly burnt out). The diode laser was tuned until its profile was coincident with the transition of interest. The spectrum was digitally recorded and it was determined where under the oxygen profile the laser was sitting during the experimental run. Greater accuracy in tuning could be achieved using the results from the emission experiments, as the line profile and spectral position were well known for the transition. The diode laser possessed several modes under its gain curve. It was possible to tune the laser to one of its modes within a narrow tuning range. However, in general the laser was not continuously tunable. In fact, during the tuning process, the laser was prone to jump to an adjacent mode leaving spectral regions that were not accessible. The diode laser will be discussed in more detail in the following section. The transition of interest was not perfectly coincident with a stable mode of the diode laser and as such it was extremely difficult to lock the diode laser at the desired wavelength for a long period of time. The uncertainty in the spectral position of the diode laser output within the oxygen profile, was by far the greatest contributor to error in these experiments. It is not altogether clear as to how a more accurate wavelength calibration can be achieved when
oxygen transitions are being investigated by laser spectroscopy. It was only through a knowledge of the spectral position of the 777.196 nm transition obtained from the emission spectroscopic work, coupled with the calibration obtained with the home-made air discharge lamp (that only survived for a brief time) that results were obtained at all. This problem will be of considerable importance to anyone wishing to do similar work in atomic oxygen at these wavelengths.

4.8.2 The infrared CW diode laser
The use of diode lasers in atomic spectroscopy has been discussed at length by Camparo (1985). The diode laser is a semiconductor diode. When electrically excited, the electrons and holes recombine within the junction and emit the recombination energy. Above threshold, which is dependent on the semiconductor type, the emitted radiation is intense enough to make the induced emission rate exceed the spontaneous rate. This emission may be amplified, via multiple reflections, within the crystal assuming other de-excitation processes are slow in comparison.

The diode laser employed in the present experiments was a Liconix Diolite-800 diode laser system driving a split cathode laser diode. The system operated over the spectral range of 775-780 nm using Mitsubishi 780 nm diodes. The spectral output of the diode laser is a Lorentzian shaped line of width less than 50 MHz. The wavelength output is varied by adjusting the temperature of the device, thus changing the cavity dimensions.
Chapter 5

DATA REDUCTION

5.1 Introduction

This chapter details the theory required to reduce the measured parameters to a form suitable for comparison with the theoretical models and previous experimental work. The infrared interferometric data and the Stark broadening measurements must be reduced to electron populations. The theoretical work necessary to do this is discussed in sections 5.2 and 5.3. In order to make comparison between theory and experiment for the emission and absorption measurements, it is necessary to explicitly determine the emission and absorption signals predicted by the two-temperature and single temperature models. The theoretical work necessary to do this is discussed in sections 5.4, 5.5 and 5.6.

5.2 Infrared interferometric fringe analysis

The refractive index of a gaseous plasma consists of contributions from the heavy particles (molecules, atoms and ions) and the free electrons, which must be summed in order to determine the total refractivity. Considering the heavy particles initially, the refractive index, \( n \), of these species is given by
where $\rho$ is the species density and $G$ is the Gladstone-Dale coefficient. The subscript $s$ refers to the species contributing to the refractive index. Thorne (1974) give the refractive index of free electrons (in cgs units) as

$$
(n - 1)_e = \frac{e^2}{2\pi m_e c^2} \lambda^2 N_e,
$$

where $e$ is the electron charge; $m_e$ is the electron mass; $c$ is the speed of light; $\lambda$ is the wavelength of the radiation passing through the plasma and $N_e$ is the electron number density.

Unlike the refractive index of heavy particles, that of the electrons is negative and thereby decreases the total index by an amount proportional to the electron population. The total index of refraction is obtained by summing the components given in equations 5.1 and 5.2. This is expressed as

$$
(n - 1) = \sum_s G_s \rho_s - \frac{e^2}{2\pi m_e c^2} \lambda^2 N_e,
$$

where $\sum_s G_s \rho_s$ may be replaced by $G_m \rho_m + G_A \rho_A + G_I \rho_I$ to give

$$
(n - 1)_{Total} = G_m \rho_m + G_A \rho_A + G_I \rho_I - \frac{e^2 \lambda^2}{2\pi m_e c^2} N_e.
$$

Here the subscripts refer to molecules, atoms and ions. The Gladstone-Dale coefficient has a functional dependence on the wavelength.
The atomic and molecular refractivity for the case where $\lambda_{ij} \ll \lambda$ is given by Thorne (1988) as

$$
(n - 1)_s = \frac{e^2}{2\pi n m_A c^2} \sum_j N_i f_{ij} \lambda_{ij}^2 \left( 1 + \frac{\lambda_{ij}^2}{\lambda^2} + \ldots \right) \quad \ldots (5.5)
$$

where $f_{ij}$ is the oscillator strength; $N_i$ is the lower level population of the transition at $\lambda_{ij}$; $e$ is the electron charge; $m_A$ is the atom mass and $c$ is the speed of light. One notes that the ratio of the refractivity of the electrons, to that of an atom or molecule may be approximated by

$$
\frac{(n - 1)_e}{(n - 1)_s} = \frac{N_e}{N_s} \frac{\lambda^2}{\lambda_{f_0}^2} \quad \ldots (5.6)
$$

where $N_s$ is now the species number density; $\lambda_{0}$ is its resonance transition and $f_0$ is the oscillator strength for this transition. The atomic and molecular constituents of an air plasma have their resonant transitions in the ultraviolet. Therefore for infrared interferometric measurements, the electron contribution to the refractive index will strongly dominate when the ionisation is only a few percent. Since the infrared interferometric experiments were conducted at conditions of very low pressure, heavy particle contributions to the refractive index were considered negligible, resulting in a fringe shift of less than 1/20 of a fringe. This was well below the resolution of the infrared interferometric measurement system.

---

4 For molecular species, $f_0$ will be the effective oscillator strength for the electronic transition which takes into account all the rotational and vibrational structure.
The interference of light passing through the Michelson interferometer is governed by the "fringe equation" (Huber, 1971):

\[ \alpha y + (n' - 1)L' - (n - 1)L = p\lambda \quad , \quad \ldots (5.7) \]

where \((n-1)L\) is the optical path length of the reference arm; \((n'-1)L'\) is the optical path length of the test arm; \(y\) is the vertical fringe position at the image plane; \(p\) is the fringe order number and \(\alpha\) is the angle of the two beams at the image plane. A change in the refractive index \(\Delta n\), for a given wavelength \(\lambda\), results in a change in the fringe order at the image plane. From equation 5.7, this change \(\Delta p\) in the fringe order number is given by

\[ \Delta p = \frac{L}{\lambda} \Delta n \quad . \quad \ldots (5.8) \]

Substituting into equation 5.8 the value for the incremental change in the expression for the refractive index for low pressures and infrared test beams (from equation 5.2),

\[ \Delta n = \frac{e^2 \lambda^2}{2\pi n_e c^2} \Delta N_e \quad , \quad \ldots (5.9) \]

one obtains the fringe shift \(\Delta p\) in terms of the change in the electron number density \(\Delta N_e\) given by equation 5.10

\[ \Delta p = \frac{e^2 \lambda L}{2\pi n_e c^2} \Delta N_e \quad . \quad \ldots (5.10) \]
Equation 5.10 is used to reduce fringe shifts to electron populations. It is noticed that the error in evaluating the electron population depends on the error to which the path length L could be determined (there was assumed to be negligible error in λ). The laser was positioned as close as possible to the tube exit. The error due to uncertainties in the shock tube position were estimated to be 5%. This estimation, which depends on the properties of the Mach cone at the tube exit, was based upon the method discussed in section 4.2.4.

As the fringe field is described by a sinusoid, any fringe shift will be seen as a sinusoidally varying signal. Measuring the maximum and minimum values of a given fringe will yield $A_{\text{max}}$ and $A_{\text{min}}$ with the fringe shift at a given distance $x$ behind the shock being given by

$$\Delta p(x) = K \frac{1}{2\pi} \sin^{-1} \left[ \frac{2A(x) - A_{\text{max}} - A_{\text{min}}}{A_{\text{max}} - A_{\text{min}}} \right] - p(0) \quad \ldots(5.11)$$

where $p(0)$ is the fringe order directly in front of the shock just before it passes through the laser beam of the interferometer. The value of $K$ is $\pm 1$ depending on the direction of the fringe shift.

In the present investigation, the fringes were not of constant amplitude during the entire test time. Due to absorption processes and beam displacement, (discussed in the next chapter), the infrared interferometric results were often a convolution between fringe shifts and absorption (the severity of this convolution was dependent on the shock velocity). Such a result was dealt with by determining the maximum and minimum value, ($A_{\text{max}}$ and $A_{\text{min}}$), for each half fringe and calculating the phase between these points. For conditions where
there was a constant fringe amplitude, the same technique was applied but now the $A_{\text{max}}$ and $A_{\text{min}}$ were constant for all fringes. In all the experiments, the spatial resolution was sufficiently good to allow an accurate determination of the fringe turning points. Fractional fringe shifts were reduced by comparing them to Stark broadened measurements made at the same experimental conditions that resulted in the fractional shifts. The major source of error for the interferometric system was the determination of the optical path length $L$, which could change due to the presence of the Mach cone discussed in chapter four.

5.3 Stark broadened H$_\beta$ profile analysis

Theoretical Stark broadened H$_\beta$ lines were calculated using the broadening parameters of Griem (1964). These parameters were for electron populations of $10^{15}$ and $10^{16}$ cm$^{-3}$. Apart from small corrections, the variation in the line widths of the H$_\beta$ line are essentially linear (over the range of electron populations considered) with respect to the electron number density (see figure 5.1 reproduced from Wiese, 1965). Hence, for electron populations lying between those for which specific parameters were available, linear interpolation was used to determine the theoretical linewidths. The theoretical line profiles were convoluted with an appropriate instrument function before comparisons were made with experimental results. As the profiles were very broad (20 to 70 nm in the present experiments) and the spectrographs slit width was very narrow (50 $\mu$m), the instrument function was essentially a $\delta$-function. Indeed, when convoluted with this function, the FWHM of the theoretical profiles remained unchanged and the only noticeable change was a small drop (of order
Figure 5.1
Calculated FWHM of the Balmer H-beta transition as a function of electron density for the temperature range from 5,000 to 40,000 K. The figure is reproduced from Wiese (1965).
5%) in the amplitude of the profiles. The experimental results were normalized to the theoretical profiles. The source of error for these measurements was mainly due to the lack of knowledge about the temporal history of the line widths in the shock tube environment. Had, for instance, the line centre been populated more rapidly than the wings, the OMA would have seen a convolution between a broad flat Lorentzian and a sharp narrow Lorentzian resulting in an erroneous FWHM measurement. This problem (and its solution) has been discussed in detail in chapter four. The line evolution was measured and shown to be constant, for several detunings across the line, to within about 5% for the duration of the test time.

5.4 Emission from molecular nitrogen

5.4.1 Introduction

Due to the close spectral proximity of the rotational transitions within a given vibrational band, together with the large number of such transitions, errors could have been introduced by inadvertently monitoring rotational lines other than those of interest. Great care was taken to ensure that the ro-vibrational transitions of interest were being observed. Using tables of atomic transition probabilities (Wiese, 1969 & 1980), transitions in Ar, Ne and Hg discharge lamps together with transitions in Ca, Cs, Cd, Ba Ur and Fe hollow cathode lamps were cross-referenced to calibrate the field of view of the OMA at and around the (0,0) and (0,1) band heads of N$_2^+$. This calibration allowed the spectrometer to be placed at a given point in the spectrum to within 0.03 nm of a rotational transition. The average separation of the rotational transitions was predicted (and shown to be) of the order of
The rotational temperature was to be obtained by observing the relative intensity of two rotational transitions. The reduction of such a measurement to a temperature is discussed at a later stage. In order to obtain the correct wavelength setting of the spectrograph, a broadband emission spectrum was obtained around the spectral position of interest before proceeding with the temporally resolved measurements. The molecular spectroscopic considerations required to analyse such a spectrum will now be detailed.

5.4.2 Molecular spectroscopy

Two additional modes of motion that a diatomic molecule can undergo, result in a spectrum that is vastly more complex than the atomic counterpart. Firstly, the molecule can rotate about an axis perpendicular to the internuclear axis and secondly, the molecule can vibrate along its internuclear axis. Quantum theory may be applied to molecular systems undergoing the complex motion of vibration and rotation, and a theoretical spectrum based on this analysis, may be derived. If the temporal evolution of individual rotational-vibrational transitions is to be studied, a precise knowledge of the molecular spectrum is essential.

The total energy of a molecule is, to a very good approximation, the sum of three parts, \( E = E_e + E_v + E_r \) where the subscripts e, v and r refer to electronic, vibration and rotation respectively. In terms of wavenumber units (that is, term values), this is usually expressed by, \( T = T_e + G + F \), where \( T = E/hc \); \( T_e \) is the electronic excitation term; \( G \) is
the vibrational term and F is the rotational term.

A general equation detailing the ro-vibronic transition frequencies within a given electronic transition is derived by Herzberg (1950). Written in wavenumber units, the emission or absorption lines associated with transitions between two electronic states is given by Herzberg as

\[ \nu = (T_\epsilon' - T_\epsilon'') + (G' - G'') + (F' - F'') \]  

...(5.12)

where \( \nu_e = (T_\epsilon' - T_\epsilon'') \) is a constant for a given electronic transition. The vibrational terms in equation 5.12 are given by

\[ G(v) = \omega_e(v + \frac{1}{2}) - \omega_x e (v + \frac{1}{2})^2 + \omega_y e (v + \frac{1}{2})^3 + ... \]  

...(5.13)

\[ v = 0, 1, 2, ... \]

where \( h \omega_e \) is the vibrational frequency that an anharmonic oscillator would have classically for an infinitesimal amplitude; \( v \) is the vibrational quantum number and \( \omega_x e \) gives a measure of the anharmonicity of the oscillator. The values of \( \omega_e, \omega_x e \) and \( \omega_y e \) determine also the shape of the electronic potential well and must therefore be different for different electronic states. The rotational term in equation 5.12 given by

\[ F(J) = B_v J(J + 1) - D_v J^2(J + 1)^2 + ... \]  

...(5.15)

where \( J \) is the rotational quantum number and \( B_v \) is the rotational

---

5 The single-primed letters refer to the upper state and the double-primed letters refer to the lower state. This is the standard nomenclature of molecular spectroscopy.
constant. $D_v$ is the centrifugal distortion constant that is a function of the vibrational frequency $\omega$. It is extremely small compared to the rotational constant. The values of $B_v$ and $D_v$ depend on the vibrational energy of the molecule and are related to the vibrational quantum number as follows:

\[
B_v = B_e - \alpha_e (v + 1/2) + \ldots
\]
and
\[
D_v = D_e - \beta_e (v + 1/2) + \ldots,
\]

where $B_e$, $\alpha_e$, $D_e$ and $\beta_e$ are constants which depend on the electronic state of the molecule.

Neglecting for the moment the rotational contributions, all vibrational transitions between two given electronic states are therefore given by equations 5.12 and 5.13 as

\[
v_o = v_e + v_v = v_e + G' - G''
\]

\[
= v_e + \omega_e (v + \frac{1}{2}) - \omega_e \omega_e (v + \frac{1}{2})^2 + \omega_e \omega_e (v + \frac{1}{2})^3 + \ldots
\]

\[
- [ \omega_e (v + \frac{1}{2}) - \omega_e \omega_e (v + \frac{1}{2})^2 + \omega_e \omega_e (v + \frac{1}{2})^3 + \ldots]
\]

\[\text{(5.18)}\]

There is no strict selection rule for the vibrational quantum number $v$. Hence there exist a multitude of vibrational transitions given by equation 5.18. Associated with each vibrational transition is of course a rotational series. Defining $v_o$ as the band origin, the rotational–vibrational wave numbers for emission or absorption are
given by

\[
v = v_e + v_v + v_r = v_0 + (F' + F'')
\]

\[
= v_0 + [B_v J'(J' + 1) - D_v J'^2(J' + 1)^2 + ...] - [B''_v J''(J'' + 1) - D''_v J''^2(J'' + 1)^2 + ...]. \quad (5.19)
\]

Electrons introduce another effect that must be corrected for. As there are electrons about each nuclei in the molecule, the moment of inertia about the internuclear axis is not exactly zero. This fact has a bearing on the selection rule for the rotational quantum number \( J \).

For most stable diatomic molecules in ground electronic states, the component of the angular momentum of the electrons along the internuclear axis, \( \Lambda \), is zero. For transitions involving electronic states with \( \Lambda \) equal to zero, the selection rule is \( \Delta J = \pm 1 \). For a transition involving an electronic state for which \( \Lambda \) is non-zero, the selection rule is \( \Delta J = 0, \pm 1 \) with the restriction \( J=0 \rightarrow J=0 \). The \( \Delta J = \pm 1 \) transitions are associated with the so called P and R branches, while the \( \Delta J = 0 \) are associated with the Q branch transitions. These are derived by Herzberg as

\[
P Branch : \quad v = v_0 + F'(J - 1) - F''(J) = P(J), \quad \Delta J = -1
\]

\[
Q Branch : \quad v = v_0 + F'(J) - F''(J) = Q(J), \quad \Delta J = 0
\]

\[
R Branch : \quad v = v_0 + F'(J + 1) - F''(J) = R(J), \quad \Delta J = +1 \quad \ldots (5.20)
\]

where \( \Delta J' = J' - J'' \).
In the case where the electron spin is not important, the molecule can be treated as a symmetric top (Herzberg, 1950). In such a case, the rotational term must be corrected by an amount $(A - B_v)\Lambda^2$, to account for the effects of the electrons, where $\Lambda$ is a quantum number associated with the angular momentum component $\Lambda$. That is,

$$F(J) = B_v J(J+1) + (A - B_v)\Lambda^2 - D_v J^2(J^2 + 1) + \ldots \ldots (5.21)$$

with, $\Lambda = 0, 1, 2\ldots$; $J = \Lambda, \Lambda + 1, \Lambda + 2, \ldots$. (Different values of $\Lambda$ correspond to different electronic states.) Hence, the rotational levels are now shifted by $(A - B_v)\Lambda^2$ which is a constant for a given vibrational level in a given electronic state. $B_v (=B_e - \alpha_e(v+1/2) + \ldots)$ and $A$ are related to the moments of inertia of the molecule as follows:

$$B_v = \frac{\hbar}{8\pi^2cI_B} \quad \ldots (5.22)$$

and

$$A = \frac{\hbar}{8\pi^2cI_A} \quad \ldots (5.23)$$

where $I_B$ is the moment of inertia of the molecule about an axis perpendicular to the internuclear axis and $I_A$ is the moment of inertia of the electrons about the internuclear axis. The molecular constants used to determine the spectral positions of the P, Q and R branches via equations 5.20 and 5.21 are given in table 5.1.

The aforementioned selection rules are correct for the case when the spin of all the electrons sum to zero. In those cases where the total spin $S$ of the electrons is non-zero, coupling between this spin and the...
### Table 5.1 Molecular constants used to determine the wavelengths of the rotational transitions within the vibrational bands of the transitions listed. The constants were obtained from Huber and Herzberg (1979).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>( T_c ) cm(^{-1})</th>
<th>( \omega_c ) cm(^{-1})</th>
<th>( \omega_c x_c ) cm(^{-1})</th>
<th>( \omega_c y_c ) cm(^{-1})</th>
<th>( B_e ) cm(^{-1})</th>
<th>Transition</th>
<th>( v_{00} ) cm(^{-1})</th>
<th>Band</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2^+ )</td>
<td>( B^3\Sigma_u^+ )</td>
<td>25461.4</td>
<td>2419.84</td>
<td>23.18</td>
<td>-0.538</td>
<td>2.07456</td>
<td>B-X</td>
<td>25566.04</td>
<td>First negative</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>( C^3\Pi_u )</td>
<td>89136.88</td>
<td>2047.17</td>
<td>28.445</td>
<td>-2.15</td>
<td>1.8247</td>
<td>C-B</td>
<td>29671.0</td>
<td>Second positive</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>( B^3\Pi_g )</td>
<td>59619.30</td>
<td>1733.39</td>
<td>14.122</td>
<td>0.0075</td>
<td>1.99824</td>
<td>B-A</td>
<td>9552.0</td>
<td>First positive</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>( A^3\Sigma_u^+ )</td>
<td>50203.6</td>
<td>1460.64</td>
<td>13.87</td>
<td>0.025</td>
<td>1.4546</td>
<td>A-X</td>
<td>49754.78</td>
<td></td>
</tr>
<tr>
<td>( O_2 )</td>
<td>( X^3\Sigma_g^- )</td>
<td>0</td>
<td>2358.57</td>
<td>14.324</td>
<td>1.99824</td>
<td>B-X</td>
<td>49358.15</td>
<td>Schumann-Runge</td>
<td></td>
</tr>
<tr>
<td>( NO )</td>
<td>( B^2\Pi )</td>
<td>45913.6</td>
<td>1037.20</td>
<td>7.70</td>
<td>0.097</td>
<td>1.092</td>
<td>B-X</td>
<td>45481.7</td>
<td>( \beta ) bands</td>
</tr>
<tr>
<td>( NO )</td>
<td>( A^3\Sigma^+ )</td>
<td>43965.7</td>
<td>2374.31</td>
<td>16.186</td>
<td>-0.28</td>
<td>1.9965</td>
<td>A-X</td>
<td>44138.0</td>
<td>( \gamma ) bands</td>
</tr>
<tr>
<td>( NO )</td>
<td>( X^3\Pi )</td>
<td>0</td>
<td>1904.20</td>
<td>14.075</td>
<td>-0.0012</td>
<td>1.67195</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
various angular momenta vectors need to be considered. Hund (see Herzberg, 1950) made the distinction between four different types of coupling. These cases are labelled (a), (b), (c) and (d) and are detailed below.

Considering the orbital angular momentum vector $\mathbf{L}$ and its projection $\Lambda$ along the internuclear axis as well as the spin vector of the electrons $\mathbf{S}$ and its projection $\Sigma$, Hund's case (a) coupling is shown in figure 5.2(a). The molecule will nutate about the direction of the total angular momentum $\mathbf{J}$. Invoking the quantum mechanical rules for quantization of angular momentum, we have that the magnitude of $\mathbf{J}$ must be given by $\hbar\sqrt{J(J+1)}$ while its component along the internuclear axis must be equal to $\hbar\Omega$ where $\Omega = 0, 1, 2, \ldots$; and

$$J = \Omega, \Omega+1, \Omega+2, \ldots.$$

For Hund's case (a) it is assumed that the electronic motion is coupled very strongly to the line joining the nuclei. That is, the total orbital angular momentum vector $\mathbf{L}$ and the total spin vector $\mathbf{S}$ of the electron precess very rapidly about the internuclear axis. The components of $\mathbf{L}$ and $\mathbf{S}$ along the internuclear axis, $\Lambda$ and $\Sigma$, sum together to give $\Omega$. The coupling in Hund's case (a) is thus entirely similar to that for the symmetric top previously discussed except that we now have $\Omega$ in place of $\Lambda$.

For Hund's coupling case (b), the orbiting electrons now generate a relatively weak magnetic field, and as a result, the spin vector of the electrons, $\mathbf{S}$, is no longer coupled to the internuclear axis. As a consequence, $\Sigma$ (and therefore $\Omega$) is not defined. This case is illustrated
Figure 5.2(a) and (b)  
Vector diagram for Hund's coupling cases (a) and (b).  
Vectors  
\( L \): total orbital angular momentum  
\( \Lambda \): projection of \( L \) along the internuclear axis  
\( S \): spin vector of the electrons  
\( \Sigma \): projection of \( S \) along the internuclear axis  
\( \Omega \): resultant electronic orbital angular momentum about the internuclear axis  
\( N \): angular momentum of nuclear rotation
in figure 5.2(b). The orbital angular momentum vector \( \mathbf{L} \) precesses rapidly around the internuclear axis with component \( \Lambda \) which is also the component along the molecular axis of \( \mathbf{K} \), the total angular momentum apart from spin. \( \mathbf{K} \) is also the vector sum of \( \Lambda \) and \( \mathbf{N} \) where \( \mathbf{N} \) is the angular momentum of nuclear rotation. The angular momentum \( \mathbf{K} \) is quantized such that its magnitude is given by 
\[
\hbar \sqrt{K(K + 1)}
\]
and the magnitude of its component \( \Lambda \) is given by \( \hbar \Lambda \) where \( \Lambda = 0, 1, 2, \ldots \); and

\[
K = \Lambda, \Lambda + 1, \Lambda + 2, \ldots \ldots
\]

The angular momentum vectors \( \mathbf{K} \) and \( \mathbf{S} \) form the resultant \( \mathbf{J} \), the total angular momentum including spin. The possible values of \( \mathbf{J} \) for a given \( \mathbf{K} \) are, according to the quantum mechanic rules for vector addition, given by

\[
J = (K+S), (K+S-1), (K+S-2), \ldots, |K-S|
\]

Hund’s coupling cases (c) and (d) are not as common as the cases (a) and (b). Case (c) tends to occur in the excited states of the heavy molecules. It is similar to the LS-type coupling that occurs in atomic systems in a weak electric field where the total angular momentum vector \( \mathbf{L} \) combines with the total spin angular momentum vector \( \mathbf{S} \) to produce a resultant vector \( \mathbf{J} \), which is then coupled to the internuclear axis with a component \( \Omega \). Case (c) type coupling only occurs when the magnetic field is sufficiently weak. In the case of a strong magnetic field, \( \mathbf{L} \) and \( \mathbf{S} \) are uncoupled through the Paschen-Bach effect.
Unlike Hund's cases (a) and (b) in which the internuclear electric field was always strong enough to couple \( L \) to the molecular axis, in Hund's case (d) this is not the case and \( L \) is coupled to \( N \), the angular momentum of nuclear rotation which is separately quantized.

As previously mentioned, Hund's coupling cases (a) and (b) are the most common forms and the selection rules born from these two cases are necessary in order to understand and label the molecular spectrum obtained in the experiment. In light of the discussion on the various coupling cases, it is necessary to state those selection rules which apply generally, as well as those which apply only for the specific coupling cases. In general, the selection rule for the quantum number \( J \) of the total angular momentum is

\[
\Delta J = 0, \pm 1, \text{ with the restriction } J=0 \rightarrow J=0 \text{ not allowed.}
\]

Furthermore positive terms combine only with negative and vice versa:

\[
+ \leftrightarrow -; \; + \leftrightarrow +; \; - \leftrightarrow -.
\]

For homonuclear diatomic molecules, symmetric terms combine only with symmetric and antisymmetric only with antisymmetric:

\[
s \leftrightarrow s; \; a \leftrightarrow a; \; s \leftrightarrow a.
\]

Finally, in the case of a diatomic molecule with nuclei of equal charge, we have the selection rule that even electronic states combine only with odd:
g ↔ u; g ↔ g; u ↔ u.

For Hund's coupling cases (a) and (b) the electronic states are designated with the nomenclature Σ, Π, Δ, .... in accordance with the value of Λ (Σ corresponds to Λ=0, Π to Λ=1, Δ to Λ=2 etc). The selection rule is then

\[ \Delta \Lambda = 0, \pm 1 \]

which thereby allows transitions such as Σ–Σ, Σ–Π, Π–Π and Π–Δ but forbids transitions such as Σ–Δ, Σ–Φ, Π–Φ etc. The selection rule for Hund's case (b) for the quantum number K, is

\[ \Delta K = 0, \pm 1 \quad \text{with} \quad \Delta K = 0 \text{ forbidden for } \Sigma–\Sigma \text{ transitions.} \]

In Hund's case (a), the quantum number Σ of the component of the spin on the internuclear axis must not alter during an electronic transition:

\[ \Delta \Sigma = 0. \]

Furthermore the quantum number Ω of the total electronic angular momentum about the internuclear axis can only change by 0 or ± 1:

\[ \Delta \Omega = 0, \pm 1. \]

If Ω=0 for both electronic states, only transitions with \( \Delta J=\pm 1 \) occur:

\[ \Delta J = 0 \text{ is forbidden for } \Omega = 0 \to \Omega = 0. \]
The $N_2^+$ molecule was specifically studied in the present work because its emissivity was strongest at the experimental conditions. The emission from the (0,0) and (0,1) band heads of $N_2^+$ was observed. This is the electronic transition $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ with $v_o$ at 25,566.04 cm$^{-1}$. The $N_2^+$ molecule has therefore a $^2\Sigma \rightarrow ^2\Sigma$ transition which adheres strictly to Hund's case (b) coupling where the previous selection rule $\Delta K = \pm 1$ applies. This molecule, with multiplicity two ($S=1/2$), has two sublevels $J = K+1/2$ and $J = K-1/2$ for a given $K$. Hence, the band structure for this case is essentially the same as for a $^1\Sigma \rightarrow ^1\Sigma$ transition (Hund's case (a)) with quantum number $K$ instead of $J$. Since $\Lambda=0$ for the upper and lower electronic states, there exists a P and R branch but there is an absence of a Q branch$^6$. Each line of the P and R branch will however be split into three components according to the rule $\Delta J = 0, \pm 1$. In general, the spectral separation of these sublevels is small compared with the separation of the rotational transitions themselves. This proved to be the case in the present experiment. Since $N_2^+$ is a homonuclear molecule, there will be an alternation in intensity for alternative values of $K$ due to the effect of nuclear spin. Since the nuclear spin of $^{14}N$ is 1, the strong lines have twice the statistical weight of the weak lines.

5.4.3 The thermal distribution of the rotational levels
The Maxwellian-Boltzmann distribution law gives the number of molecules $dN_e$ that have a classical vibrational energy between $E$ and $E+dE$ as being proportional to $e^{-E/kT} \, dE$, where $k$ is the Boltzmann's constant and $T$ is the temperature. Of course quantum mechanically, only discrete values of the vibrational energy are allowed and $E$ must be

---

$^6$ P, Q and R refer here to $\Delta K = -1, 0$ and $+1$. 

replaced by equation 5.13, whence the number of molecules in each vibrational state becomes proportional to

$$e^{-E/kT} = e^{-G(v)hc/kT}$$

...(5.24)

The thermal distribution of rotational levels however is not simply proportional to some Boltzmann factor because each rotational level with total angular momentum $J$ has associated with it a $(2J+1)$-fold degeneracy. The number of molecules $N_J$ in a rotational level $J$ of a particular vibrational state is therefore proportional to,

$$(2J+1) e^{-F(J)hc/kT}$$

...(5.25)

where $F(J)$, (given by equation 5.15), represent the rotational terms for the non-rigid rotator. Equation 5.25 is shown graphically for $N_2^+$ at $T=22,000$ K (the rotational temperature predicted by the $TT_\nu$ model at the peak emission point) in figure 5.3. The maximum in the graph occurs at $J_{\text{max}}$ given by Herzberg (1950) as

$$J_{\text{max}} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2} = 0.5896 \sqrt{\frac{T}{B}} - \frac{1}{2}.$$  

...(5.26)

To obtain the absolute number of molecules $N_J$ in a given rotational level, it is necessary to consider that the total number of molecules $N$ in vibrational state $v$, is proportional to the sum of the Boltzmann factors over all rotational levels in the same vibrational level, that is, the partition function

$$Q_r = 1 + 3e^{-2Bhc/kT} + 5e^{-6Bhc/kT} + \ldots.$$  

...(5.27)
Figure 5.3 The thermal distribution of the rotational levels for the $N_2^+$ molecule at a temperature of $T=22,000$ K. This is the predicted rotational temperature from the two temperature model at the peak emission point behind a shock travelling into $p=13$ Pa at $v=10$ $\text{km/s}$. The two arrows indicate the relative positions on this intensity distribution of the two rotational transitions at which the time resolved emission experiment was conducted, that is, the $P(21)$ and $R(42)$ rotational transitions of the (0,0) vibrational band of $N_2^+$. The curve represents the function $(2J + 1)\exp(-BJ(J+1)hc/kT)$ as a function of $J$. 
Given large $T$ or small $B$, the sum in equation 5.27 may be written as an integral

$$Q_r = \int_{0}^{\infty} (J + 1) e^{-\frac{hcBJ(J+1)}{kT}} dJ = \frac{kT}{hcB}, \quad (5.28)$$

and Herzberg derives

$$N_J = \frac{N}{Q_r} = (2J + 1) e^{-\frac{BJ(J+1)hc}{kT}}$$

$$= \frac{NBhc}{kT} (2J + 1) e^{-\frac{BJ(J+1)hc}{kT}} \quad , \quad (5.29)$$

for the population of molecules with rotational quantum number $J$. From these results it is understood that the intensity distribution of the rotational transitions in a given vibrational band should be given simply by the thermal distribution of those rotational levels. That is, the intensity of a rotational transition should be proportional to equation 5.25. This assumes however that the transition probabilities are the same for all rotational transitions in a given vibrational band. There is however a slight dependence on $J$ and $\Delta J$.

The intensities of the ro-vibronic transitions may be expressed in terms of a product of the line strength $S_J$ and the Boltzmann factor given for absorption as

$$I_{abs} = \frac{2C_{abs} v}{Q_r} S_J \exp\left[-\frac{B''J''(J''+1)hc}{kT}\right] \quad \ldots(5.30)$$

and emission as
where the $S_J$ are given by the well known Honl-London formulae and $C_{\text{abs}}$ and $C_{\text{em}}$ are constants depending on the change of dipole moment and the number of molecules in the initial vibrational level. $C_{\text{abs}}v/Q_r$ and $C_{\text{em}}v^4/Q_r$ are almost constant for the ro-vibrational transitions in the same vibrational band and a given temperature. In the case of the $N_2^+$ molecule, considered in the experiment, $\Lambda=0$ since the transition is from one $\Sigma$ to another $\Sigma$ state. For this case if

$\Delta J=+1$ then $S_J = J + 1$

and

$\Delta J=-1$ then $S_J = J$.

(Note $J = J' + \Delta J$ in accordance with the standard convention, regardless of whether the transition is observed in emission or absorption.)

Given equation 5.31, the rotational temperature may be reduced by comparing the relative intensity of two rotational transitions in the same vibrational band via the equation

$$ T = \frac{Bhc}{k} \left[ \frac{J_1(J_1+1)-J_2(J_2+1)}{\ln \left[ \frac{S_{J_1}}{S_{J_2}} \right] + \ln \left[ \frac{I_2}{I_1} \right]} \right] \quad \ldots(5.32) $$
The uncertainty in the value of $T$, $\delta T$, as a function of the errors associated with the measurement of $I_1 (\delta I_1)$ and $I_2 (\delta I_2)$ is obtained in the usual way (Taylor, 1982) to give

$$\delta T = \sqrt{\left(\frac{\partial T}{\partial I_1} \delta I_1\right)^2 + \left(\frac{\partial T}{\partial I_2} \delta I_2\right)^2}.$$ ...

5.5 Atomic and ionic oxygen emission analysis

The three atomic transitions discussed in chapter four were imaged by the OMA, the results of which were downloaded to a microcomputer. The line profiles were integrated over wavelength to obtain a total emissive power. The resolution of the experimental system was not sufficient to completely separate two of these transitions in wavelength, and as such the lines overlapped slightly. Assuming that the overlap was a constant for all the experimental conditions, there would have been no error in ignoring it and having a situation in which all the results had an effective emissive power offset by an amount equal to this overlap, that could have been factored out. However this assumption was not made. As the shock velocities and pressures varied substantially, from 6 to 11 kms$^{-1}$ and 13 to 1333 Pa respectively, the effects of changing temperatures and pressures on the line profiles of these transitions had to be considered. Because of this, the overlap was accounted for by extrapolating the line profiles into the region where the lines encroached upon each other and the overlap subtracted during the integration. The extrapolation was made by individually fitting a Lorentzian to each line profile in the emission spectrum.
5.5.1 Atomic transitions as temperature indicators

One of the easiest and most direct techniques for determining the temperature of a plasma utilizes the spectral line intensities emitted from atoms when the state densities of these species are in equilibrium. The emission from an atomic state in an optically thin layer of shock heated gas is readily obtained. The intensity of spontaneous emission emitted per unit solid angle from a unit volume is given by

\[ I_{em}^{nm} = A_{nm} N_n h v_{nm} \]  \hspace{1cm} ...(5.34)

where \( N_n \) is the upper state population, \( A_{nm} \) is the Einstein A coefficient and \( v_{nm} \) is the line centre frequency of the transition from state n to m.

For optically thin conditions, the Boltzmann distribution may be used to express the emission intensity as a function of the temperature

\[ I_{em}^{nm} = \frac{A_{nm} h v_{nm} N g_n \exp(-E_n/kT)}{Q(T)} \] \hspace{1cm} ...(5.35)

where \( g_n \) is the degeneracy of the state n; \( N \) is the total population and \( Q(T) \) is the partition function.

Equation 5.35 indicates a technique whereby the temperature may be determined. If two separate transitions are chosen with a common lower state, then it is possible to reduce the temperature via

\[ kT = \frac{E_2 - E_1}{\ln(I_1/I_2) - \ln(A_1 v_1/A_2 v_2)} \] \hspace{1cm} ...(5.36)

where the subscripts 1 and 2 are used to denote the two separate
transitions. This technique is very sensitive to the transition energies. For this method to yield an accurate measure of the temperature, $E_2 - E_1$ should be large compared with $kT$. Unfortunately for high temperature plasmas, this is not usually the case. To overcome this deficiency, it is often desirable to observe transitions from different stages of ionisation, thereby forcing a large energy difference equal to $E_2 - E_1$ plus the ionisation potential. Consider figure 5.4. Under the condition of thermodynamic equilibrium, the number density of neutral atoms in a state $j$ is related to the number density of ions in a different state $k$ by combining the Saha and Boltzmann equations and is given by Thorne (1988) as

$$\frac{N_j N_{ik}}{N_{aj}} = \frac{2(2\pi nkT)^{3/2}}{h^3} \frac{g_{ik}}{g_{aj}} \exp \left[ \frac{-I - E_b + E_a}{kT} \right]. \quad ...(5.37)$$

Thorne subsequently gives the relative intensity of excited levels of different stages of ionisation in an optically thin plasma as

$$\frac{I_{ik}}{I_{aj}} = \frac{A_{ik} g_{ik} \nu_{ik}}{A_{aj} g_{aj} \nu_{aj}} \frac{2(2\pi nkT)^{3/2}}{h^3} \frac{1}{N_e} \exp \left[ \frac{-I - E_b + E_a}{kT} \right], \quad ...(5.38)$$

where $I_{ik}$ is the transition intensity of the $k^{th}$ level of an ion and $I_{aj}$ is the transition intensity of the $j^{th}$ level of an atom.

It should be emphasized that the application of equation 5.38 to derive a temperature in the present work would be, strictly speaking, incorrect, since the derivation of this equation has assumed that there exists one
Figure 5.4 The level scheme for an atom and ion of a given atomic species $N$ is the number density, $E$ is the energy and $I$ is the ionization potential. Subscripts $a$ and $i$ refer to atom and ion respectively.
temperature $T$ characterizing the plasma. This is of course not the case, for in the present experiments, there are two temperatures characterizing the flow. Because of this, equation 5.38 needs to be corrected for the special case in which the plasma is in a state of chemical, but not thermal equilibrium. Igra and Barcessat (1979) present such an expression for the Saha equation when there exist two temperatures characterizing the plasma. The expression derived for this "modified" Saha equation is given as

$$\alpha_E \left( \frac{\alpha_E}{1 - \alpha_E} \right)^{\frac{T_i}{T_e}} = \frac{\rho_I}{\rho} \left( \frac{T_e}{\theta_I} \right)^{3/2} \exp \left[ \frac{-I}{kT_e} \right], \quad ...(5.39)$$

with the characteristic plasma density $\rho_I$ being expressed as

$$\rho_I = 2 \frac{g_i}{g_a} \left( \frac{2\pi k \theta_I}{h^3} \right)^{3/2} \frac{m_e^{3/2} m_a}{\cdots} \quad ...(5.40)$$

where $\alpha_E$ is the ionisation fraction at equilibrium; $\rho$ is the density; and $\theta_I$ is the ionisation temperature ($\theta_I = I/k$).

Equation 5.38 is now re-derived with the appropriate correction for the case where chemical but not thermal equilibrium prevails. This equation is given by

$$\frac{I_{ik}}{I_{aj}} = \frac{A_{ik} v_{ik}}{A_{aj} v_{aj}} \left\{ \frac{2g_i (2\pi m k T_e)^{3/2}}{h^3} \frac{1}{N_e} \exp \left[ \frac{-I + E_i - E_a}{kT_e} \right] \right\} \left( \frac{T_i}{T_e} \right). \quad ...(5.41)$$

It is observed that, when $T = T_e$, this equation reduces to equation 5.38.
The theoretical values of the translational-rotational temperature $T$ and the electron-vibrational temperature $T_v$ predicted by the TTV model were used to obtain a theoretical plot of the ionic to atomic oxygen intensity ratio to which the experimental data could be compared. There were two methods in which the OMA data was reduced and the intensity ratio obtained. Either the total integrated area under the entire OMA spectrum was obtained for both the $O$ and $O^+$ results and these areas compared, or a profile was fitted to each line and the integrated areas under these individual curves was compared. Both techniques resulted in an intensity ratio within 7% of each other.

One feature of this technique, highlighted in the analysis, is that an accurate measure of the electron population is required if the intensity ratio is to be calculated. This ties in neatly with the electron population measurements made with the infrared interferometry and Stark broadening experiments which has shown that the TTV model accurately predicts these populations.

5.6 Infrared CW diode laser absorption by atomic oxygen

Quite clearly, the results presented by Park for predictions made by the TTV model do not include a predicted absorption profile for the particular laser, transition and detuning employed in the present experiment. Because of this, the predictions of the TTV model, namely the temperatures, electron population and molar fractions of atomic oxygen, had to be converted and presented in the form of an absorption profile given the experimental parameters. The following discussion details the necessary theory required for this process. (The conversion
from species molar fractions to absolute number densities is detailed in appendix E.)

Incident radiation of intensity $I_0$ will, upon passing through a plasma, be absorbed by an amount

$$I = I_0 e^{-k_v L}, \quad \ldots(5.42)$$

where $k_v$ is the frequency dependent absorption coefficient and $L$ is the thickness of the absorbing plasma. If the incident radiation field is chosen with a sufficiently narrow bandwidth, only discrete atomic transitions will absorb the photons in the incident field. By spatially and temporally resolving the absorption of the light passing through the plasma, it is possible to determine the population of the discrete level. Traving (1968) gives

$$k_v = \frac{\pi e^2}{m_e c} f_{ij} N_i P(\Delta v) \left[ 1 - \frac{g_i N_j}{g_j N_i} \right] \quad \ldots(5.43)$$

for the atomic absorption coefficient of a spectral line in a gas, where $f_{ij}$ is the oscillator strength of the transition $i \rightarrow j$; $g_m$ is the degeneracy of level $m$; $N_m$ is the population of level $m$ and $P(\Delta v)$ details the line profile and magnitude of the absorbing transition as a function of detuning from line centre. The term in square brackets in equation 5.43, is a correction term that accounts for the induced emission produced by the laser passing through the plasma. The rate of stimulation of the upper level depends on the relative populations of the upper and lower states.
P(Δv) describes a lineshape of finite width that is influenced by three major broadening processes:

1) Natural broadening,
2) Doppler broadening, and
3) Pressure broadening.

Natural broadening:
Natural line broadening results as a direct consequence of the uncertainty principle. In the form ΔEΔt ~ ℏ, Heisenberg’s principle requires a spread in energy inversely proportional to the uncertainty in time associated with finding an atom in a given state. A full quantum mechanical treatment gives the FWHM (δv) due to natural broadening as (Thorne, 1988)

\[ \delta v_N = \frac{1}{2\pi \tau_1} + \frac{1}{2\pi \tau_2} \] ...(5.44)

where \( \tau_1 \) and \( \tau_2 \) represent finite lifetimes of levels 1 and 2. All atomic transitions are affected by natural broadening by a magnitude of approximately \( 10^{-5} \) nm. This width is insignificant compared to other broadening processes in the environment of the present investigation.

Doppler broadening:
Unlike natural broadening, Doppler broadening does contribute significantly to the line shape of spectral transitions. Doppler broadening results from the shift in the wavelength of moving sources. In the shock tube environment, these shifts arise from the thermal motion of emitting atoms or molecules. If the motion of the particles in
the plasma are purely thermal (and the plasma is optically thin), a Maxwellian velocity distribution is obtained for the emitters and the absorption profile has a Gaussian shape described by

\[ P_D(\Delta v) = \frac{1}{\sqrt{\pi} \Delta v_D} \exp\left[-\left(\frac{\Delta v}{\Delta v_D}\right)^2\right] \] \hspace{1cm} \text{(5.45)}

where \( \Delta v_D \) is the Doppler width given by

\[ \Delta v_D = \frac{v_0}{c} \sqrt{\frac{2kT}{M_A}} \] \hspace{1cm} \text{(5.46)}

where \( T \) is the translational temperature; \( M_A \) is the atomic mass and \( v_0 \) is the line centre frequency. The Doppler broadening process is therefore functionally dependent on the translational temperature.

**Pressure broadening:**
Natural and Doppler broadening are the dominant processes that define lineshapes at low densities. As the densities increase however, collisional effects between ions and electrons begin to influence the interaction of the electromagnetic radiation and the plasma particles. This so called Pressure broadening process may dominate the observed spectral lineshape. The strongest interactions will occur between the emitting particles and the ions and electrons that constitute the plasma. As there is an interaction between the electric fields of the particles, this broadening process is known as Stark broadening. The long range Coulombic forces dominate when the degree of ionisation is significant, at least 1% of the total particle density, and so the Stark broadening will dominate at high degrees of ionisation. Another
broadening process occurs between the interactions of neutral particles of the same type if one of the levels in the emitted or absorbed line has a transition to the ground state, the so called resonance broadening. When considering absorption or emission between two levels in an excited state, resonance broadening will still occur if one of the transitions is connected to the ground state. Interactions between dissimilar atoms gives rise to Van der Waals broadening. The interactions in this instance take place between the interatomic potentials. In the experiment, the only broadening processes are the Doppler and Stark processes. The atomic oxygen transition studied in the absorption experiment, is directly connected to the ground state, and, as such, resonance broadening should be considered. The resonance broadening process is proportional to the oscillator strength of this particular resonant transition. It transpires that the oscillator strength of this resonant transition is exceedingly small \( f_R = 3.6 \times 10^{-7} \) and as such this broadening mechanism was substantially dominated by the aforementioned processes.

Traving (1968) derives the Lorentzian profile

\[
P_L(\Delta \nu) = \frac{1}{2\pi} \frac{\gamma}{(\Delta \nu)^2 + \gamma^2/4}
\]

...(5.47)

to describe the pressure broadened dispersion profile where \( \Delta \nu \) is the detuning from line centre and \( \gamma \) is the FWHM of the profile.

The half-width \( \Delta \lambda_{1/2} \) and the shift \( \Delta \lambda_s \) of atomic transitions due to the Stark broadening process is given (in Å units) by Wiese (1965) as
\[ \Delta \lambda_{1/2} = 2 \left( 1 + 1.75 \times 10^{-4} N_e^{1/4} \alpha \left( 1 - 0.068 N_e^{1/6} T^{-1/2} \right) \right) 10^{16} \omega N_e \quad \text{(5.48)} \]

and

\[ \Delta \lambda_s = \left[ \frac{d}{w} \right] \pm 2 \times 10^{-4} N_e^{1/4} \alpha \left( 1 - 0.068 N_e^{1/6} T^{-1/2} \right) 10^{16} \omega N_e \quad \text{(5.49)} \]

where \( d \) is the shift, \( w \) the half-half width due to electron impacts and \( \alpha \) is the ion broadening parameter. The \( \pm \) sign in equation 5.49 is negative only for those transitions that have a negative \( d/w \) at low temperatures.

The result of folding the Gaussian profile of the Doppler broadening with the Lorentzian profile of the Stark broadening process, results in the Voigt function \( H(\alpha, \nu) \) given by Traving as

\[ H(\alpha, \nu) = \frac{\alpha}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-y^2)}{\alpha^2 + (\nu - y)^2} \, dy \quad \text{(5.50)} \]

where \( \alpha \) is the ratio of the Stark width to the Doppler width, that is, \( \alpha = \nu / 2 \Delta \nu_D \) and \( \nu \) is the detuning from line centre in units of the Doppler width, that is, \( \nu = \Delta \nu / \Delta \nu_D \). For the two extreme cases, \( \alpha = 0 \) results in a pure Gaussian profile, while \( \alpha = \infty \) results in a pure Lorentzian profile. Equations 5.43 to 5.50 are used to convert the predictions of the TTV model into a theoretical absorption profile given the experimental parameters.

The opacity of the plasma may be estimated by determining the absorption coefficient \( k_\nu \) and the magnitude of the optical depth \( k_\nu L \) (L
is the optical path length) in equation 5.43. A portion of gas is defined as being optically thin if $k_r L < 1$ and optically thick if $k_r L > 1$. In the present experiment $k_r L < 1$ for all transitions examined and hence the plasma (for those transitions) is taken as being optically thin (this is shown to be the case in the atomic oxygen emission experiments in chapter 6).
Chapter 6

EXPERIMENTAL RESULTS

6.1 The experimental limitations

It would appear at first glance that the experimental methodology embodied in this investigation was relatively straightforward. Certain experimental techniques employed are based on well developed and well trusted theories; for example, the Stark broadening of the $H_\beta$ profile to determine electron populations. On the contrary however, several factors impeded the progress of the research program. It was essential that these problems were overcome in order to fulfil the aims of the work. The problems faced, and their solutions, are discussed in detail below. There were experimental difficulties imposed by the operational limitations of the free piston shock tube, as well as the ionisation diagnostic.

The experiments conducted in the present investigation were in one sense very elegant and yet in another very problematic. The elegance lay in the relatively simple way in which the raw experimental data could be reduced to meaningful numbers (although perhaps not so simply for the CW laser absorption experiments). Infrared fringe shifts were readily equated to electron number densities, while emission ratios were reduced to temperatures. It was in acquiring the raw data however, in which difficult experimental problems were encountered. One aim of the experiment was to obtain a database of
results for differing pressures and shock velocities at and around the
condition of interest for the AOTV, that is, p=13 Pa, v=10 kms\(^{-1}\). It was
hoped that conditions ranging from 13 Pa to 650 Pa, at shock velocities
from 7 kms\(^{-1}\) to 12 kms\(^{-1}\) could be achieved. Unfortunately, it transpired
that an experimental window existed, and this limited the
experimental results to a pressure of 13 Pa and shock velocities of
between 9 kms\(^{-1}\) and 10.8 kms\(^{-1}\).

As detailed in chapter 4, the infrared interferometric signals were of
only very small amplitudes. For a complete fringe shift, peak-to-peak
values of only 10 mV were typical. A major component of the research
consisted of using a very sensitive piece of electronics, the infrared
detector, capable of measuring small changes in phase, in the
electrically noisy environment of the laboratory. The small signal
amplitudes associated with the interferometric diagnostic, made the
acquisition of data very difficult. This problem was amplified by the
even smaller signals that were associated with fractional fringe shifts.
This problem, coupled with the presence of an inverse Bremsstrahlung
absorption profile convoluted with the fringe data, set a lower limit on
the minimum resolvable fringe shift of approximately \(\Delta p=1/2\) before
uncertainties became unacceptable. At velocities less than 9 kms\(^{-1}\) in
air and nitrogen at 13 Pa, the resultant fringe shift was somewhat less
than \(\Delta p=1/2\) as the ionisation fraction was small. The only way to
overcome this problem would have been to increase the wavelength or
pathlength considerably. Neither option was possible in the present
work. Hence a lower limit on the experimental resolution was set by
the infrared interferometric diagnostic. Although Stark broadening
would have worked at lower ionisation fractions, this technique gives
no measure of the temporal change in the electron number density using the OMA system.

As will be detailed in section 6.2.1, the experimental system was able to resolve up to 7 fringes in 1 μs. This was many times the expected requirement and as such there would appear to have been no realistic upper limit set by the ionisation diagnostic. However, an upper bound was set by the operational limitations of the free piston shock tube. DDT was being run at a volumetric compression ratio of 95, with a corresponding enthalpy of approximately 50 MJ/kg. This is an extremely harsh operational condition for the facility, indeed it transpired that the piston rings required replacement every 10-15 experimental runs. At velocities greater than 10.8 kms$^{-1}$, there was severe and constant driver gas contamination, that destroyed the integrity of the test gas (due to the contact surface instabilities, see Houwing, 1982a). This problem is discussed in more detail in the following section.

It was extremely fortuitous that the specific condition of interest for which data was available for comparison to the TT$_v$ model, namely, p=13 Pa, v=10kms$^{-1}$, lay within the experimental window detailed above. However, even inside the experimental window, driver gas contamination presented problems. The occurrence of contamination inside the window appeared to be random in character, with some results appearing to be free of contamination and others not. As a result of the inherent randomness of the severity of the contact surface contamination, experimental repetition overcame the problem to some extent. Many experimental runs were conducted with the interferometric system (and indeed all the experiments) in order to
obtain uncontaminated results over the limited range of conditions. It was not considered constructive to perform the same repetition for all the experiments over a range of shock velocities. Because of this, the atomic/ionic and molecular emission, together with the CW laser absorption experiments, were confined to the conditions for which direct comparison to the two-temperature kinetic model could be made, that is, p=13 Pa, v=10kms⁻¹.

6.1.1 Test gas contamination

Driver gas contamination placed a severe constraint on the experimental test time. The arrival of the contact surface was determined by observing the emission emanating from the impurities present in the driver gas (specifically sodium), the intensity of which was greater than that emission coming from the shock heated air. Furthermore, (and perhaps a more sensitive indicator as to the degree of contamination), it was possible to observe the effect on the fringe shifts and the molecular and atomic emission due to the driver gas contamination. The interface between a clean experimental run with no contamination and a result with contamination was extremely sensitive to the driver condition.

Photographic plate number 1 shows the observed spectrum from 351.08 nm to 393.03 nm (this encompasses the strong (0,0) and (1,1) bands of N₂⁺). No electronic shuttering was employed to obtain this photograph and as such it contains emission from the constituents of both the shock heated air as well as the impurities present in the driver gas. This result was scanned and digitized to obtain a high resolution image of the spectrum (this result is not presented as it is over two
meters long). Suffice is to say, there were "possibly" areas of molecular structure in this photograph. The photograph clearly has the signature of an atomic spectrum, reminiscent of the iron or chromium spectra with a plethora of lines. Any molecular structure was strongly swamped by the atomic emission from the impurities present.

Figures 6.1(a) and 6.2 show an observed fringe shift and molecular emission spectrum, at a driver condition in which there was severe contamination of the test slug. These results are nonsensical when compared to the results of figure 6.1 (b) and other "clean" molecular spectrum presented in later sections of this thesis. These results were obtained when there was no observed contamination until well after a satisfactory test time. The contamination process was very sensitive to the amount of argon present in the driver gas. A reduction in the amount of argon by as little as 133 Pa (from the optimal driver condition) resulted in contamination. Figure 6.1(b) shows the signature of a "clean" experimental interferometric result. Such results displayed an approximate symmetry, in respect to phase, about a plateau (seen as a region in which the phase is not changing) in the electron population. This type of result is to be discussed at length at a later stage.
Photographic plate # 1

Observed emission from the shock front and contact surfaces around the band systems of N₂⁺. The photograph is not shuttered. The emission lines, with a definite atomic signature, comprise mostly the iron and chromium impurities in the flow at the contact surface. There was no definite sign of molecular emission as this is swamped by the strong atomic transitions.
Figure 6.1(a) and 6.1(b)
Contaminated and non-contaminated fringe shifts observed at similar experimental conditions. The contamination (evident by the chaotic behaviour of the phase) is due to the arrival of the driver gas and its consequent mixing with the test gas. This fringe shift is in stark contrast to the non-contaminated shift, in which there exists an approximate symmetry with respect to the phase and a well defined plateau in the electron population.
Figure 6.2
Optical Multichannel Analyser emission spectrum around the (0,0) and (1,1) vibrational band heads of $N_2^+$. This spectrum exhibits the signature of atomic impurities (a consequence of the contaminants present in the driver gas) convoluted with the molecular emission from the rotational transitions of the aforementioned vibrational bands. The amplitude of the rotational transitions is very small due to the cooling effects of the driver gas.
6.2 Infrared interferometry

6.2.1 Argon results
Once the infrared interferometric system was operational, it was deemed prudent to test its capabilities by measuring the electron populations behind shock waves for which results were fairly well known. Argon was the obvious choice of gases as a lot of experimental and theoretical work has been carried out on it. Furthermore, high electron number densities are achieved in an argon flow for two reasons. Firstly, diatomic and polyatomic test gases absorb energy into several degrees of freedom such as vibration and rotation. More thermal energy is therefore available for ionisation in monatomic gases such as argon, which cannot absorb energy in this manner. Secondly, for a given specific enthalpy, there is a high energy per atom in the flow due to the large molecular weight of argon. Hence for moderate conditions, argon readily ionises and electron populations some two orders of magnitude greater than that expected for the conditions of interest for the AOTV would easily be obtained.

The infrared interferometric system was used to measure the electron populations behind shock waves travelling into 133 Pa and 1333 Pa of argon, respectively. These results are shown in figures 6.3 and 6.4. The theoretical peak electron populations for 133 Pa and 1333 Pa of argon are approximately $10^{16}$ and $10^{17}$ cm$^{-3}$ respectively. These values imply a fringe shift of the order of 10 to 200 fringes, within a few µs. This resulted in a high signal frequency which was not resolvable over the total test time. Furthermore, the inverse Bremsstrahlung absorption process, at these electron densities, absorbs almost 100% of
the test beam. This absorption is clearly seen in both figures 6.3 and 6.4 as an initial drop in the trace almost immediately behind the shock\textsuperscript{7}. Hence resolvable fringe shifts were obtained only a certain distance behind the electron cascade front, and, as such, no measure of the population could be ascertained until well into the quasi-equilibrium region. Since the fringes could not be monitored throughout the relaxation zone, there was no way of determining the order number of the first resolvable fringe. Because of this, the theoretical value for the electron population, at the position behind the shock front where the first fringe became resolvable, was used to evaluate the theoretical order number of that first fringe. Given that order number, each subsequent fringe could be numbered, and the decay in the electron population could be determined. These results are shown in figures 6.5(a) and 6.5(b). They are in fairly good accord with the theoretical profile. (It could be argued that in some sense this is a circular argument. It should be realised that this process, at the very least, demonstrates the functionality of the ionisation diagnostic.)

6.2.2 Nitrogen and air results

Having tested the operational efficiencies of the infrared interferometric diagnostic in an argon flow, the first diatomic gas to be run with the system was N\textsubscript{2}. These results were the first to highlight the problems with driver gas contamination discussed in section 6.1, as well as the first results tending to support the hypothesis that two temperatures were characterizing the flow.

The results throughout the experiment, were either digitally, or

\textsuperscript{7} Figure 6.3 has been inverted. The trace of figure 6.4 ends abruptly. This point coincided with the 'end-of-memory' state for the LeCroy transient recorder.
photographically recorded, depending on the data acquisition technique being employed. The method of data acquisition tended to change during the experiment, due to both equipment failure and the acquisition needs of other research projects being run simultaneously with the present work. Figures 6.6 to 6.12 show the observed fringe shifts (and their digital counterparts) for the following conditions.

- Figure 6.6 \( v=10.2 \text{ kms}^{-1} \) into 13 Pa of air.
- Figure 6.7 \( v=10.9 \text{ kms}^{-1} \) into 13 Pa of air.
- Figure 6.8 \( v=10.8 \text{ kms}^{-1} \) into 13 Pa of N\(_2\).
- Figure 6.9 \( v=10.2 \text{ kms}^{-1} \) into 13 Pa of air.
- Figure 6.10 \( v=10.5 \text{ kms}^{-1} \) into 13 Pa of N\(_2\).
- Figure 6.11 \( v=10.5 \text{ kms}^{-1} \) into 13 Pa of air.
- Figure 6.12 \( v=10.6 \text{ kms}^{-1} \) into 13 Pa of air.

The electron population was taken to be zero in front of the shock front. There may have been some precursor ionisation, although insignificant, and certainly not measurable with any of the ionisation diagnostics described. The observed fringe shifts exhibit several characteristics that require addressing. Firstly, the shock front was taken to coincide with the beginning of the fringe shift. The TT\(_v\) model predicts that for ionising air the electron population should attain a measurable population, within the resolution of the present experiment, at approximately 1 mm behind the shock front. This corresponds to a time interval of 0.1 \( \mu \text{s} \) and was not resolvable in this work. A second notable feature was that all the fringe data exhibit a fringe reversal and a return to the initial starting phase. This feature was indicative of a peak in the electron population, a plateau (when
contamination was not too severe) and a return to zero population a
certain distance behind the shock front.

The radiative losses are in no way fast enough to account for the rapidly
observed decrease in the peak electron population. Indeed the plateau
should remain constant for some considerable distance behind the
shock front. The fact that it did not was cause for some concern as the
only other possible cooling process was that due to the arrival of the cold
driver gas. Indeed, luminosity experiments looking at the radiation
coming from the contaminants within the driver gas, demonstrated a
correlation between the drop in the plateau in the electron population
and the contact surface arrival. Free electrons produced via the
ionisation of these contaminants were insufficient to yield the densities
of electrons being observed. Furthermore, no plateau should be
associated with the ionisation of any contaminant nor was there any
coincidence between the impurity emission and the measured
ionisation. Hence the electron densities produced as a result of
contaminant ionisation was deemed negligible. The plateau region
was to assume valuable importance in the work. It became a sensitive
indicator of the extent to which driver gas cooling had taken place and
thereby defined the test time (distance behind the shock) over which the
experimental results were valid. In the most severe case of
contamination, as demonstrated by figures 6.6, 6.7 and 6.8, no plateau
was observed and the results are therefore valid only up to the point
where the fringe reversal occurs and the electron population starts to
decrease before its pseudo-equilibrium population had been obtained.
After the turning point, subsequent fringe shift information is invalid.
When conditions were favourable, results of figures 6.9, 6.10, 6.11 and
6.12 were obtained where the plateau in the population is clearly seen.
No correlation was observed between the shock velocity and the fringe reversal. This is due more in part to the fact that only a relatively narrow velocity regime was studied and that the contamination is a random process.

One final feature of interest was the observed decrease in the fringe amplitude near the end of the fringe system. This anomaly is seen very clearly in figures 6.6, 6.9, 6.10 and 6.12. It was initially assumed that this decrease in fringe amplitude was due to some absorption process taking energy out of the test arm, possibly bound–free or free–free absorption. This was discounted however as the decrease in amplitude was not coincident with the peak electron population. No infrared atomic or molecular transitions were considered likely to cause the absorption, especially in light of the fact that the absorption was not taking place in the region where the populations of these species were at a maximum. The decrease in amplitude was again attributed to the arrival of the contact surface. It was concluded that the test beam was being slightly deflected off the infrared detector due to changes in refractive index associated with the contact surface and the driver gas, and causing the decrease in amplitude. This was occurring in a random manner as it was assumed to be a function of the contact surface instability, and therefore did not always occur. This was the only explanation that was consistent with the position behind the shock of the observed amplitude change and its random appearance.

Figures 6.13 and 6.14 show results of the electron population resulting from shock velocities \( v = 10.5 \) and \( 10.7 \text{ kms}^{-1} \) in \( \text{N}_2 \) compared to the
theoretical model of the one-temperature model, Vardavas (1984). The overshoot in the electron population predicted by the one-temperature model is a consequence of the rapid ionisation of $N_2$ to form $N_2^+$. The initial ionisation rate follows exactly the rate of production of $N_2^+$. Furthermore, the peak in the electron population is closely related to the peak in the $N_2^+$ density. During this time, there is a constant dissociation of $N_2$ with a corresponding drop in the temperature. At the point behind the shock front where the $N$ population exceeds the $N_2$ population, the electron number density peaks and proceeds to decrease, following the production of $N^+$. The decrease in electron population is very likely the result of the decrease in flow temperature caused by dissociation. It appears that the ionisation of $N_2$ proceeds more rapidly than its dissociation even though more energy is required for the former process. The reduction of the electron number density is thus likely to be caused by ionic recombination processes accompanying the drop in temperature.

Figures 6.15 to 6.26 show results for the electron population for shock waves with velocities between 9.6 and 10.8 kms$^{-1}$ travelling into 13 Pa of air. Figure 6.15 is particularly important as this result is compared to both the one and two-temperature models. Unfortunately, theoretical predictions based on the two-temperature model are limited to a small set of experimental conditions. Furthermore, the code was not available for use. This made it impossible to make comparisons for the complete range of data presented here. This is in contrast with the one-temperature code, which was available and whose data deck could be changed. As is evident from these results, the one-temperature model significantly overestimates the electron populations. Figures
6.15 to 6.21 display the plateau in the electron population. Figures 6.21 to 6.26 do not attain a plateau and hence these results are only valid till the point at which the peak in the electron population is attained. These results do however provide a check on the results for which a plateau exists, for the same experimental conditions, as the ionisation rates before contamination are identical.
Figure 6.3
Multiple fringe shifts resulting from the large ionisation fraction in 133 Pa of argon. This trace, digitally recorded, is not correctly orientated in that increased absorption corresponds to the upper section of the trace, ie, the signal is inverted. The condition for this result is $p=133$ Pa argon, $v=6.08$ km/s.

Distance behind electron cascade front (cm)
Figure 6.4
Multiple fringe shifts resulting from the large ionisation fraction in 1333 Pa of argon. This trace, digitally recorded, is now correctly orientated. Both traces of figure 6.3 and 6.4 show the severe absorption (and its effect on the fringe amplitude) due to inverse Bremsstrahlung process. The condition for this result is \( p = 1333 \text{ Pa argon}, v = 4.72 \text{ kms}^{-1} \).
Results of the infrared interferometric experiments in 133 and 1333 Pa of argon at shock velocities of $v=6.08$ and $4.72 \text{ km/s}^{-1}$ respectively.
Figure 6.6
Observed fringe shift for $v=10.2 \text{ km/s}^{-1}$ shock into 13 Pa of air. There is no appearance of the plateau in the electron population, only the sudden turning point attributed to the arrival of the contact surface. Both the CRO trace and its digitized counterpart are presented. The horizontal scale is 1 $\mu$s per division and the vertical scale is 10 mV per division.
Figure 6.7
Observed fringe shift for $v=10.9 \text{ km s}^{-1}$ shock into 13 Pa of air. There is no appearance of the plateau in the electron population, only the sudden turning point attributed to the arrival of the contact surface. Both the CRO trace and its digitized counterpart are presented. The horizontal scale is 1$\mu$s per division and the vertical scale is 10 mV per division.
Figure 6.8
Observed fringe shift for $v=10.8 \text{ km/s}^{-1}$ shock into 13 Pa of $N_2$. There is no appearance of the plateau in the electron population, only the sudden turning point attributed to the arrival of the contact surface. Both the CRO trace and its digitized counterpart are presented. The horizontal scale is 1$\mu$s per division and the vertical scale is 10 mV per division.
Figure 6.9
Observed fringe shift for $v=10.2 \text{ km s}^{-1}$ shock into 13 Pa of air. There is an observed plateau in the electron population at approximately 1.5 $\mu$s from the shock front, lasting 0.35$\mu$s, followed by the turning point attributed to the arrival of the contact surface. Both the CRO trace and its digitized counterpart are presented. The horizontal scale is $1/2$ $\mu$s per division for the upper trace and 1$\mu$s per division for the lower trace the vertical scale is 10 mV per division. All traces are from the same experimental run.
Figure 6.10
Observed fringe shift for $v=10.5\text{km}s^{-1}$ shock into 13 Pa of N$_2$. There is an observed plateau in the electron population at approximately 1.4 $\mu$s from the shock front, lasting 0.4$\mu$s, followed by the turning point attributed to the arrival of the contact surface. Both the CRO trace and its digitized counterpart are presented. The horizontal scale is 1$\mu$s per division and the vertical scale is 10 mV per division.
Figure 6.11
Observed fringe shift for $v=10.5 \text{ km} s^{-1}$ shock into 13 Pa of air. There is an observed plateau in the electron population at approximately 1.3 $\mu$s from the shock front, lasting 0.7$\mu$s, followed by the turning point attributed to the arrival of the contact surface seen also as a disturbance in the test beam. Both the CRO trace and its digitized counterpart are presented. The horizontal scale is 1/2 $\mu$s per division and the vertical scale is 5 mV per division.
Figure 6.12

Observed fringe shift for $v=10.6 \text{ km s}^{-1}$ shock into 13 Pa of air. There is an observed plateau in the electron population at approximately 1.2 $\mu$s from the shock front, lasting 1.5 $\mu$s, followed by the turning point attributed to the arrival of the contact surface. Both the CRO trace and its digitized counterpart are presented. The horizontal scale is 1$\mu$s per division and the vertical scale is 5 mV per division.
Figure 6.13: Electron population V’s distance behind shock front for: $p_\infty = 0.1$ Torr, $v = 10.5$ kms$^{-1}$ in N$_2$

- - - - - : Theoretical (Vardavas, 1980)

•••••• : Experimental

+: Typical error bar
Figure 6.14: Electron population $V$'s distance behind shock front for: $p_o = 0.1$ Torr, $v = 10.7$ kms$^{-1}$ in N$_2$

---: Theoretical (Vardavas (1980))

.........: Experimental

↑: Typical error bar
Electron population \( \frac{1}{10} \times 10^3 \) (cm) behind shock front for \( p_m = 0.1 \) Torr, \( v = 10.0 \) kms\(^{-1}\) in air

*---* : Theoretical (Vardavas, 1980)
--- : Theoretical (Park, 1989)
*: Experimental
\( \dagger \) : Typical error bar

Figure 6.15 : Electron population V's distance behind shock front for \( p_m = 0.1 \) Torr, \( v = 10.0 \) kms\(^{-1}\) in air
Figure 6.16: Electron population V's distance behind shock front for: \( p_\infty = 0.1 \text{ Torr}, v = 10.1 \text{ kms}^{-1} \text{ in air} \)
- ---: Theoretical (Vardavas, 1980)
- ······: Experimental
- : Typical error bar
Figure 6.17: Electron population V's distance behind shock front for: $p_\infty = 0.1$ Torr, $v = 10.2$ km s$^{-1}$ in air

- : Theoretical (Vardavas, 1980)

- - - - - - : Experimental

• : Typical error bar
Figure 6.18: Electron population $V$'s distance behind shock front for $p_w = 0.1$ Torr, $v = 10.5$ kms$^{-1}$ in air

--- Theoretical (Vardavas, 1980)

..... Experimental

i: Typical error bar
Figure 6.19: Electron population V's distance behind shock front for \( p_0 = 0.1 \) Torr, \( v = 10.6 \) kms \(^{-1}\) in air

- - - - - : Theoretical (Vardavas, 1980)
••••••• : Experimental
\( \dagger \) : Typical error bar
Figure 6.20: Electron population V's distance behind shock front for \( p_\infty = 0.1 \) Torr, \( v = 10.7 \) km s\(^{-1}\) in air

---: Theoretical (Vardavas, 1980)
::: Experimental
\#: Typical error bar
**Figure 6.21**: Electron population V's distance behind shock front for $p_\infty = 0.1$ Torr, $v = 9.6$ kms$^{-1}$ in air

- **-** : Theoretical (Vardavas, 1980)
- •••••• : Experimental
- i : Typical error bar
Figure 6.22: Electron population V's distance behind shock front for $p_\infty = 0.1$ Torr, $v = 10.2$ km/s in air

---: Theoretical (Vardavas, 1980)

•••••: Experimental

*i*: Typical error bar
Figure 6.24: Electron population V's distance behind shock front for $p_\infty = 0.1$ Torr, $v = 10.4$ km/s in air

- Theoretical (Vardavas, 1980)
- Experimental
- i: Typical error bar
Figure 6.25: Electron population $N_e$'s distance behind shock front for: $p_\infty = 0.1$ Torr, $v = 10.7$ kms$^{-1}$ in air

--- Theoretical (Vardavas, 1980)

...... Experimental

•••••••• Typical error bar
Figure 6.26: Electron population V's distance behind shock front for: $p_0 = 0.1 \text{ Torr}, v = 10.8 \text{ km/s}^{-1}$ in air

--- Theoretical (Vardavas, 1980)

... Experimental

••••••••: Typical error bar
6.3 The Stark broadened $H_\beta$ profile

The Stark broadening technique was confined to experiments in air. Two experimental techniques were outlined in section 4.5. Temporally resolved emission spectra, at several detunings from line centre for the $H_\beta$ transition, were obtained for $v = 10 \text{ km}^{-1}$ in 13 Pa of air. These results are presented in figures 6.27. As is evident in this figure, all the $H_\beta$ emission results, at particular detunings, have fundamentally the same profiles, the peak in their amplitude occurring at approximately 1/2 cm behind the shock front. When all curves are normalized, their overlap is such that only one curve is seen. This is not very illustrative and therefore, the results have been presented non-normalized. These results highlight the fact that the time evolution of the line profile is effectively constant to about 5% from line centre to detunings of ± 40 nm. This was essential if the Stark broadened measurements of the $H_\beta$ line using the optical multichannel analyser were to produce non-convoluted results.

Figure 6.28 presents a result of the $H_\beta$ line emission in the pseudo-equilibrium region obtained from the experiments utilizing the optical multichannel analyzer. The centre dip is seen and is an important signature confirming that one is actually looking at the hydrogen transition and not some other atomic impurity (no atomic constituent of air has a coincidence with the hydrogen transition). The results of figure 6.29 and 6.30 (normalized and scaled to the theoretical profile) were obtained by simply taking that portion of the OMA spectrum containing the $H_\beta$ profile and appropriately converting channel numbers to detunings measured in units of wavelength.
Chapter 6 : Experimental results

There was no observed line shift, when compared to a hydrogen discharge lamp prior to the experimental run, and hence the position of the dip was taken as corresponding to line centre. It may be considered inaccurate to remove the profile from the total OMA spectrum without any consideration to the effects suffered by the wings of the transition, lying just within the noise. It is true that some error may have been introduced to the wings of the profile during the subtraction process. However, the FWHM of the profile is used to reduce the electron population (and the half maximum is well above the noise). Consequently, any distortions to the wings of the profile were considered to have a negligible effect on the results.

Figures 6.29 and 6.30 are for the conditions of shock velocity \( v = 10 \text{ k.ms}^{-1} \) into 13 Pa of air and \( v = 10.6 \text{ k.ms}^{-1} \) into 13 Pa of air, respectively. There is good agreement between these Stark broadening results and the measured electron populations using the infrared interferometry. The electron populations for the results of figures 6.29 and 6.30 are \((9.1 \pm 0.6) \times 10^{14} \text{ cm}^{-3}\) and \((6.1 \pm 0.6) \times 10^{15} \text{ cm}^{-3}\) respectively, 1.5 cm behind the shock front. This is compared to the results obtained with the interferometric ionisation diagnostic which gave results, at the equivalent experimental conditions and position behind the shock, of \((1.0 \pm 0.2) \times 10^{15} \text{ cm}^{-3}\) and \((6.0 \pm 0.2) \times 10^{15} \text{ cm}^{-3}\) respectively.
Figure 6.27
Temporally resolved emission from the hydrogen beta transition at various detunings from line centre.
Figure 6.28
Optical Multichannel Analyser spectrum of the hydrogen beta transition for the condition $p=13$ Pa, $v=10.0$ kms$^{-1}$ in air. Maximum noise amplitude 25 counts.

Dip in the Hβ profile due to the absence of the unshifted Stark component
Figure 6.29
Reduced hydrogen beta line shape from OMA emission spectrum, together with the theoretical profile for $N_e=10^{12}$ cm$^{-2}$ obtained from the broadening parameters of Griem (1964). The theoretical profile has been convoluted with the appropriate instrument function such that direct comparison to experimental data could be made. The experimental condition is $p=13$ Pa, $v=10.0$ km s$^{-1}$ in air.
Figure 6.30
Reduced hydrogen beta line shape from OMA emission spectrum, together with the theoretical profiles for $N_e = 10^{15}$ and $10^{16}\text{ cm}^{-3}$ obtained from the broadening parameters of Griem (1964). The theoretical profiles has been convoluted with the appropriate instrument function such that direct comparison to experimental data could be made. The experimental condition is $p = 13\text{ Pa}$, $v = 10.6\text{ kms}^{-1}$ in air.
6.4 Emission from molecular nitrogen

The molecular emission experiments were conducted in order to make a measurement of the rotational temperature. Emissivity calculations, together with experimental data, have shown that the strongest emitters in shock heated air at the temperatures applicable to the AOTV are the first negative system of \( N_2^+ \) and the second positive system of \( N_2 \). In agreement with this, the two-temperature kinetic model predicts that the majority of radiation at wavelengths between 400 and 420 nm would comprise mostly of the first negative system of \( N_2^+ \). Experiments were conducted in both the T3 and DDT shock tubes (the experimental arrangement of which is shown in figure 4.7) to obtain a OMA spectrum of the rotational structure centered between the (0,0) and (1,1) band heads of the first negative system of \( N_2^+ \) at 391.1 and 388.1 nm respectively.

Prior to the measurements on individual transitions, a temporally resolved, digitally recorded emission profile was obtained and is presented in figure 6.31. The intent was to obtain such a measurement for comparison with the broadband emissive predictions of the two-temperature kinetic model. In the experiments of Allen et al (1962), as a consequence of the shock front curvature, the determination of its exact position was not possible and, as such, the relaxation lengths were determined solely from the observed luminosity profiles. The foot of the emission profile was determined by drawing a straight line through the rising portion of the luminosity trace and extrapolating this back to the “distance behind shock front” axis. The same procedure was followed in the theoretical work of Park (1989) and
is adopted in the present experiment. The various parameters shown in figure 6.31 are those employed by Park. $x_p$ represents the distance to the point of peak luminosity as measured from the luminosity foot. A relaxation time $\tau_p$ is obtained from this distance and the shock velocity. $x_e$ represents the equilibrium point, defined in the experiments of Allen et al as being equal to 1.1 times the equilibrium radiation value. Again $x_e$ is measured from the foot of the luminosity and the corresponding time $\tau_e$ determined. The theoretical emission profile given by Park (1989) (see figure 3.4) has been convoluted with a Gaussian slit of 0.5 mm width at half height. This was done in order to allow the comparison of the theoretical profile to the experiments of Allen et al (1964). In these experiments, the emission was observed through a slit of 0.5 mm width. In the present experiments, a photodiode was imaged into the shock tube and hence the results were convoluted with an instrument function with a smaller FWHM. Because of this, the observed emission profile is not as broad as that presented by Park. To allow a direct comparison to be made of the observed emission and the theoretical profile, the experimental data is convoluted with the appropriate Gaussian function (the use of the Gaussian instrument function is discussed in chapter 7). The broadband emission profile obtained in the present work, and suitably convoluted for comparison to Park's model, is presented in figure 6.32. It must be stressed that this experimental emission trace is normalized to the theoretical profile. No measure was made of the power spectrum. The predictions of the two-temperature kinetic model for these profiles are given in W/cm$^3$. One deficiency of this experiment was that the power density was not determined.
Figure 6.33 is representative of the initial OMA results obtained for the spectrum of the rotational structure at the (0,0) and (1,1) band heads of the first negative system of $N_2^+$ at 391.1 and 388.1 nm respectively. As is clearly evident, profiles with a definite atomic signature were obtained around 389.4 nm. These lines do not correspond to any constituent of shock heated air. Atomic oxygen has one transition ($2p^33s - 2p^3(^4S^0)3p$) at 394.7 nm which is just outside the wavelength window. Atomic nitrogen has no transitions in this spectral region, the closest being the transition $2p^2(^3P)3s - 2p(^1D)3p'$ at 409.9 nm. The absence of any molecular structure was suggestive of a driver gas contamination problem. One of the strongly emitting contaminants present in the contact surface is chromium. Chromium has a relatively strong set of transitions surrounding 388.6 nm (the $a^5Z - z^5D^0$ multiplet). Iron, another contaminant, has a coincidence with chromium at 388.6 nm as well as a multitude of weaker transitions throughout this spectral region. It was concluded that these atomic transitions, in the contact surface mixing zone, resulted in the emission spectra of figure 6.33.

Figure 6.34 shows the results of replacing 400 Pa of helium in the helium/argon driver mix, with 400 Pa of argon. This had the effect of slowing the shock speed slightly and alleviating slightly the driver gas contamination. This spectrum has been displaced (by adjusting the spectrometer) to a position of lower wavelength. This was an attempt to include in the spectrum the atomic oxygen transition at 394.7 nm. The chromium / iron contamination is still present in this spectrum, albeit at a greatly reduced intensity. There is however structure present that is consistent with ro-vibronic transitions of a molecular band system. The oxygen transition was not observed. This was most probably due to its low oscillator strength coupled with the fact that it is now competing
with the molecular emission.

Figure 6.35 (now moved back to the same spectral position as that of 6.33) presents the results of a further 250 Pa reduction of helium driver replaced by the same quantity of argon. Figure 6.35 demonstrates the sensitivity of the driver gas contamination process to the driver conditions. No sign of atomic emission is present in this figure, the only anomalous peaks in the spectrum now correspond to the band heads at 388.1 nm (the (1,1) band head of N$_2^+$) and at 391.1 nm (the (0,0) band head of N$_2^+$). As described in chapter 4, the resolution of the molecular emission experiment was such that the individual rotational transitions could be resolved. This is clearly seen in figure 6.35.

Using Ar, Ne and Hg discharge lamps together with Ca, Cd, Cs, Ba, Ur and Fe hollow cathode lamps, the spectrum of figure 6.35 was accurately calibrated using the wavelength and transition probabilities of Wiese et al (1969 & 1980). Subsequently, the wavelength of each transition was determined. Each rotational transition was then assigned a quantum number based on the comparison between the experimental spectrum and the theoretical spectrum. Testament to the accuracy of this process was the very distinct patterns (the approximately equally spaced lines and band heads etc, with respect to the quantum number) that appeared in the rotational structure.

From these calibrated spectra it was possible to position the spectrometer on a rotational transition to within ± 0.03 nm. Temporally resolved emission measurements were then conducted on the P(43) and R(20) lines in the (0,0) band of N$_2^+$ in order to obtain a measurement of
the rotational temperature by comparing the ratios (at the peak emission point) of these transitions. The splitting of these rotational transitions according to $J=K\pm1/2$ (described in section 5.4) was not observed, because their separation could not be resolved by the present experimental system.

The rotational temperature reduced from these measurements was $(24,500 \pm 4,700)$ K at the peak emission point, 0.59 cm behind the shock front.
Figure 6.31
Experimentally determined time resolved broadband emission behind shock front $p = 13$ Pa, $v = 10.0 \, \text{km} \cdot \text{s}^{-1}$ in air. Both figures are identical except for the parameters indicated on the second figure defined by Park (1989).
Figure 6.32
Experimentally determined time resolved broadband emission behind shock front p=13 Pa, v=10.0 kms⁻¹ in air, together with the emissive predictions of the TTv model, Park (1989). The experimental data has been convoluted with a Gaussian instrument function to allow the direct comparison of the data with the code.
Figure 6.33
Optical Multichannel Analyser emission spectrum near the (0,0) and (1,1) vibrational band heads of $N_2^+$ exhibiting the signature of atomic impurities.
transitions of the aforementioned vibrational bands.

Figure 6.34
Optical Multichannel Analyser emission spectrum near the (0,0) and (1,1) vibrational band heads of $N_2^+$ exhibiting the signature of atomic impurities convoluted with the molecular emission from the rotational transitions of the aforementioned vibrational bands.
Figure 6.35
Optical Multichannel Analyser emission spectrum at and around the (0,0) and (1,1) vibrational band heads of N$_2^+$. At the optimal conditions, the signature of atomic impurities disappear, with the result that only the molecular emission from the rotational transitions is present. The condition is $p=13$ Pa, $v=10.0$ km s$^{-1}$ in air.
6.5 Atomic and ionic oxygen emission

Figure 6.36 shows a typical (typical when conditions were favourable) emission spectrum obtained with the optical multichannel analyser of the atomic oxygen transitions (transition array $2p^33s - 2p^3(^4S^0)^3p$ multiplet, $^5P^0 - ^5P$) at 777.196, 777.418 and 777.540 nm. These levels have a degeneracy of 7, 5 and 3 and oscillator strengths of 0.431, 0.307 and 0.184, respectively. The signal-to-noise ratio for these experiments was very high (especially at elevated pressures) as there was very little extraneous emission at these wavelengths. An optical filter was employed to remove from the spectrum the intense emission coming from the (0,0) and (1,1) ro-vibrational transitions of $N_2^+$ at 388.1 and 391.0 nm. These band systems overlap in second order with the oxygen transitions.

Figure 6.37 (a-e) present the observed effect of progressively decreasing the test gas pressure on the emissivity of atomic oxygen (proportional to the population of the atomic oxygen). Figure 6.37 (a) is for a free stream pressure of 1333 Pa; figure 6.37 (b), 400 Pa; figure 6.37 (c), 133 Pa; figure 6.37 (d), 40 Pa and figure 6.37 (e), 13 Pa. Figure 6.37 (f) shows an argon calibration transition at 772.30 nm, together with the three oxygen transitions from the “home-made” discharge lamp. These transitions allowed a calibration of the spectra to be made. The atomic line emission spectrum obtained at several pressures, figure 6.37, were integrated over the frequency range to obtain a total emissive power and were normalized by pressure to give the emissive power per particle. These results are shown in figure 6.38.
The OMA emission spectrum of the atomic (figure 6.37(e)) and ionic oxygen transitions at \(v=10 \text{ kms}^{-1}\) and \(p_{\text{e}}=13 \text{ Pa}\), (obtained over several accumulation cycles), is presented in figure 6.39. The 777.196 nm transition in atomic oxygen and the 464.914 nm transition in ionic oxygen were used to evaluate the ion-to-atom intensity ratio for comparison to theory. The experimental measurement was made at a distance of 1.48 cm behind the shock front. This is presented in figure 6.40. The plot associated with \(T=T_{\text{e}}\) is calculated using equation 5.38, which represents the ion-to-atom ratio for thermal equilibrium. The plot associated with \(T\neq T_{\text{e}}\) is calculated using equation 5.41, corrected for the case of chemical but not thermal equilibrium. This accounts for the truncation of the theoretical plot below 0.6 cm, where chemical nonequilibrium prevails. It has been shown that at this point behind the shock front the electron population is reaching a maximum and pseudo-equilibrium is being attained.
Figures 6.37 (a) to 6.37 (e)
OMA spectra showing the decrease in the emission from the excited states of atomic oxygen with decreasing free stream pressure (wavelength is increasing left to right). Figure 6.37 (f) shows the Argon calibration line together with the three oxygen lines of interest obtained from a "home made" discharge lamp.
Figure 6.38
Emissive power per particle versus the pressure. This result is obtained from the results of figure 6.37 (a)-(e).
Figure 6.39 (a) and 6.39 (b)

The three transitions in neutral oxygen and the three transitions in ionised oxygen after several accumulation cycles on the OMA. Both results $p_\infty = 13$ Pa, $v=10.00$ kms$^{-1}$ in air
Theoretical ionic to atomic intensity ratio for oxygen. The predictions of Park's model are used to evaluate this plot from equation 5.41 at the condition $p_\infty = 13\ Pa$, $v=10.00\ kms^{-1}$.
6.6 Infrared CW diode laser absorption by atomic oxygen

Of all the experiments, this was the most problematic. The difficulties associated with the driver gas contamination, of course, persisted throughout. Compounding this difficulty, was the erratic behavior of the diode laser. It was true that this device would operate, with high stability, within a given mode. However these modes were very well defined and there were spectral regions in which lasing was impossible. Because of this, it was not possible in this experiment to conduct several temporally resolved experiments at different detunings across the transition of interest. Had it even been possible to continuously tune across the oxygen profile, an accurate determination of the detuning, would have been difficult. Optogalvanic tuning is excluded as continuous oxygen plasmas are not readily generated in discharge. It is not immediately understood how future work in laser absorption spectroscopy in shock heated oxygen can be performed without a method of accurately measuring the wavelength. Hence, in this experiment, the spectral position of the laser was placed such that it was as close as possible to line centre, while still being sufficiently under the profile (allowing for line shift and broadening) to give a measurable absorption signal. The absorption obtained in this manner is shown in figure 6.41. The accuracy with which the spectral output of the laser could be positioned, with respect to the oxygen profile, was not as good as was initially hoped. The uncertainty is clearly seen in this figure which shows the change in the predicted absorption given the error in which the detuning was determined.
The fluctuation in the absorption signal at the tail end of the experimental trace is due most probably to real time variations in the atomic oxygen populations. This is not unexpected, as mixing with the driver gas is, once again, most probably taking place here.
Figure 6.41
Experimentally observed absorption signal due to atomic oxygen v's time from the shock front. The absorption predicted by the TTv model is also presented. The two curves represent the limit of uncertainty due to errors in determining the detuning. The condition is $p = 13$ Pa, $v = 10.01$ km$^{-1}$ in air.
Chapter 7

DISCUSSION

7.1 Electron number density measurements in air

As is evident, there is excellent agreement between the theoretical electron population as predicted by the TT$_v$ model and the interferometric and Stark broadening results. The one-temperature nonequilibrium model however, overestimates the populations at the conditions studied. This discrepancy is explained as follows (Taloni et al, 1989). In the chemical relaxation zone, both heavy particles and electrons participate in excitation, dissociation and ionisation collisions. However, since inelastic collisions involving electrons have a much larger cross section than those involving only heavy particles, the rate at which electrons partake in inelastic processes is much larger. As a result, the electrons lose energy more rapidly. Furthermore the energy transfer between electrons and heavy particles through elastic collisions is many orders of magnitude lower than that between different electrons and different heavy particles. This is a consequence of the large mass disparity between the electrons and heavy particles. The electrons are thus expected to establish a Maxwellian velocity distribution at one temperature T$_e$, while the heavy particles establish a distribution at a different temperature T with T$_e < T$. The assumption that the vibrational and electron temperatures are, to a good approximation, equal, is based on the fact that the
transfer of energy between the translational energy of the free electrons and the vibrational modes on the N₂ molecule is extremely rapid. Since the electrons interact strongly with the vibrational and electronic levels, these levels are expected to establish a Boltzmann distribution at the electron temperature. Rotational levels on the other hand are readily excited by heavy particle collisions and are thus expected to establish a Boltzmann distribution based on the translational temperature of the heavy particles.

Some distance behind the shock (about 10 mm) the chemical species approach a state of "pseudo-equilibrium" where the recombination reactions balance the dissociative/ionisation reactions. The gas, however, remains in a state of thermal nonequilibrium for a considerable distance behind the shock because the energy transfer between electrons and heavy particles by elastic collisions is low. As the electron temperature is lower than the heavy particle temperature, this will result in a lower electron population than would be expected at thermal equilibrium. This conclusion is supported even more strongly in light of the results obtained in the experiments looking at the intensity ratio of the transitions in O and O⁺. It is shown that the magnitude of the ion-to-atom intensity ratio predicted by theory (equation 5.41) increases when the flow is characterized by one temperature. This implies that the electron number density has increased. When two temperatures were allowed to characterize the flow, there was a drop in the intensity ratio, indicative of a drop in the electron population. The experimental result obtained at 1.48 cm behind the shock front, supports the theoretical predictions that characterize the flow by two temperatures.
Park does take into account radiation losses through an iterative technique but has found that their effects on the general flow properties are insignificant (see Park, 1989). This is to be expected at these low density conditions. The radiation losses are not significantly fast to cause a rapid change from the peak electron population. The observed decrease in electron number density following the plateau region is attributable to the arrival of the contact surface and mixing of the cooler driver gas with the shock heated test gas.

One implicit assumption made in the reduction of the infrared interferometric fringe shifts was that the initial fringe shift corresponded to the arrival of the shock front. In the experiment, there was no independent way of determining the exact position of the shock front. Typically, flow visualization in the visible would have been conducted simultaneously with the interferometry, in order to correlate the shock front position and the electron population. Due to the low density however, this was not possible. Certainly the electron populations measured were behind the shock front, as the ionisation diagnostic was below the resolution required to resolve any precursor ionisation. Hence, if as Park suggests, there is no ionisation until at least 1 mm behind the shock front, then there would be a small offset in the position of the infrared fringe shifts. This would result in the experiments and the TTv model being in greater accord with respect to the ionisation rate, than is suggested by the experiments. Unfortunately, no indication can be given as to the occurrence or possible magnitude of this offset.

The interferometric results not only give temporally and spatially resolved measurements of the electron population behind the shock
front, but also provide a measure of the ionisation rate. An average ionisation rate was determined by measuring the slope \((\Delta n_e/\Delta t)\) of a line drawn from the shock front (starting at \(x=0\)) to the point where the plateau in the electron population was just being reached. For the condition \(v=10\, \text{km/s}^{-1}, p_0=13\, \text{Pa}\), this rate was measured as \((1.6 \pm 0.2) \times 10^{21}\, \text{cm}^{-3}\text{s}^{-1}\). The theoretical prediction of the TT, model for this average ionisation rate was \(1.34 \times 10^{21}\, \text{cm}^{-3}\text{s}^{-1}\). These two values are in fair agreement with each other but are markedly different from the value of \(5.34 \times 10^{21}\, \text{cm}^{-3}\text{s}^{-1}\) predicted by the one-temperature model.

As was detailed in chapter 2, the dominance of particular ionising reaction sequences is very sensitive to the shock velocity. Figure 2.1, chapter 2, reproduced from Wilson (1966), presents a plot of the theoretical and observed ionisation distances behind shock waves in air. The theoretical curves are obtained from the work conducted by Lin and Teare (1963) which is described in chapter 2. The overall ionisation time was defined as the time between the shock front and the time at which a line drawn through the maximum slope of the rising electron population reached peak signal. This ionisation time was then multiplied by the shock velocity to give the ionisation length. This ionisation length was then normalized by the upstream mean-free-path which is 0.48 mm at 13 Pa. The ionisation distance divided by the mean free path measured in the present experiment was 15.7±0.4 at \(v=10\, \text{km/s}^{-1}, p=13\, \text{Pa}\) and 24.3±0.6 at \(v=10.6\, \text{km/s}^{-1}, p=13\, \text{Pa}\). These results are in good agreement with the other experimental results (obtained by observing the rate of emission of infrared luminosity), and suggest that the dominant ionising reaction sequences are, as expected at the experimental velocities studied, the electron impact ionisation.
reactions, with the initial electron production resulting from atom–atom collisions detailed in chapter 2.

Figure 6.29 and 6.30 shows the comparison between the theoretical and measured profile for the Stark broadened Hβ line. The two curves have been normalized by the experimental height of the two maxima in the profile. The theoretical Hβ lines, Stark broadened by electron populations of \( N_e = 10^{15} \text{ cm}^{-3} \) and \( N_e = 10^{16} \text{ cm}^{-3} \) respectively, were produced by broadening parameters obtained from Griem. The experimental Stark broadened lines are seen to be in good agreement with the theory and the populations reduced from their FWHM are in good agreement with the interferometric measurements. There are however some discrepancies between the observed and calculated profiles. Initially it is seen that the central dip is not as pronounced in the experiment as is predicted by theory. This disparity may be explained by the effects of ion motion or perhaps inelastic collisions between perturbing electrons and radiating atoms.

Lee (1973) undertook a theoretical study of the spectral line broadening of the Hβ transition in a plasma and attempted to include ion dynamic effects into this analysis. First attempts to model line broadening took the path of a static field approach, (Griem, 1959) This analysis included electron broadening in a modification to the static assumption. When the electron dynamics were included, the central dip decreased in magnitude, (in the static approximation there was zero intensity at line centre) but there was still a discrepancy with observation. Lee demonstrated a marked change in the central dip with the inclusion of ion dynamic broadening, but found virtually no
change in the theoretical profiles exclusive of ion dynamic broadening at detunings beyond ± 0.02 nm of the two peaks.

Hill et al (1971) compare measured Stark broadened profiles of the Hβ, Hγ and Hδ transitions with the theoretical calculations of Kepple and Griem (1968). Hill et al include in their comparison contributions to the line broadening from inelastic collisions between perturbing electrons and radiating atoms. It was found that the values of the electron densities deduced from the theoretical profiles, with the inclusion of inelastic collisional effects, improved the qualitative agreement near line centre. However, the Gaunt factors used in the calculations caused the magnitude of the effect on the broadening to be overestimated.

The separation of the two maxima in the profile of the Hβ transition is not as pronounced in the experiment as in the theory. When Ne becomes greater than 10^{17} cm^{-3}, the separation of the maxima of the Hβ profile reaches more than 1.5 nm. It has been suggested by Okasaka, Nagashima and Fukuda (1975) that the difference between the separation of the maxima results mainly from the way in which the micro-field distribution is correlated.

There exists a good symmetry in the observed profile about line centre. Typically, any asymmetry of the Hβ line becomes more noticeable with increasing electron number density, particularly for densities greater than 10^{16} cm^{-3}. 
Unfortunately, a direct quantitative comparison between the experimental results obtained in this study and the theoretical and experimental work undertaken by those discussed in the literature review (apart from Park, 1989 and Vardavas, 1984), is not altogether possible. The problem lies with the fact that the conditions considered by these other studies falls well outside the experimental regime of the present work. Typically, shock velocities of 6 km s⁻¹ into air pressures of 133 Pa were considered. This makes a quantitative comparison difficult, considering the conditions of the present experiments were 10 km s⁻¹ into air pressures of 13 Pa. On the other hand, certain qualitative comparisons could be made. Zalogin et al (1980) measured the electron number densities via an infrared interferometric technique similar to that described in chapter 4. Although the experimental conditions of this study were considerably different, there was good qualitative agreement between those results and those of the present work. The ionisation distances were similar and both results exhibit the rise to a plateau in the electron population, followed by a rapid decrease. (No explanation is given for this decrease and it is assumed that similar processes are occurring with respect to driver gas cooling.)

7.2 Emission from molecular nitrogen

Park (1989) makes a comparison between the emission profile of the experiments of Allen, Rose and Camm (1962) and the predictions of the TTᵥ model. He points out that, in these experiments, the exact position of the shock front was unknown due to its curvature. Because of this, he determined the relaxation length from the time resolved emission
profile in the manner described in chapter 6. Park adopts this process in order to determine the relaxation length and the present work follows suit. The emission profiles are in very good agreement with the TT\textsubscript{v} model, in so much as their peak emission points and general profiles are very similar. Figure 6.31 presents the raw experimental emission profile labelled with the various relaxation parameters. Figure 6.32 presents the same profile, convoluted with a 0.5 mm FWHM Gaussian, together with the predictions of the TT\textsubscript{v} model, similarly convoluted. Park presents his data in this form to allow the comparison to be made between his model and the experiments of Allen \textit{et al} (1962) who had such an instrument function in their experiments. It is not at all clear how an experimental instrument function with a FWHM of 0.5 mm can be represented by a Gaussian. Nonetheless, in the present experiment, the same convolution has been made for comparison. Clearly theoretical data can be convoluted with any function and as long as the experimental data is convoluted with the same, a comparison between the two is valid. A Gaussian instrument function has not been used in any other data reduction in this work, apart from that displayed in figure 6.32. The predicted and observed emission profiles are shown to be in good agreement. There is some difference between the experimental and theoretical profiles after the peak emission point. This disparity is most probably an effect of the response time of the photodiode. The response time of the photodiode used in this experiment was approximately 100 ns. Such a response time, convoluted with the observed data, would bring the experimental and theoretical profiles into greater accord.
Figure 3.5, chapter 3, reproduced from Park (1989), presents a plot of the theoretical relaxation time parameter $\tau_{p_\infty}$ versus the shock velocity. The experimental results of the present work for the characteristic relaxation times are in good agreement with the predictions of the $TT_v$ model for the condition $v=10\text{km s}^{-1}$, $p_\infty=13\ \text{Pa}$ (these results appear in figure 3.5 as filled circles). No measure was made however of the emissive power of these results, and as such, the validity of this prediction of the $TT_v$ model cannot be commented on.

The time resolved profiles of the P(43) and R(20) lines in the (0,0) band of $N_2^+$ were measured as a function of distance behind the shock front. The intensity ratio at the peak emission point, 0.59 cm behind the shock front, was measured to obtain an accurate measure of the rotational temperature. This provides only a point-wise measurement of the rotational temperature, but this was more than sufficient to make a comparison with the nonequilibrium codes and check the disparity between the translational-rotational and vibrational-electronic-electron temperatures. The rotational temperature reduced from these measurements was $(24,500 \pm 4,700)\ \text{K}$. At this distance behind the shock front, the $TT_v$ model predicts a rotational-translational temperature of 20,500 K. This temperature lies within the experimental error bound quoted above. This is significantly different from the prediction of the one-temperature model which predicts a temperature of 11,500 K at 0.59 cm behind the shock front. This temperature is less than half that measured and is equal to the vibrational-electron-electronic temperature $T_v$ predicted by the $TT_v$ model at this point behind the shock. Clearly there is an underestimation of the translational-rotational temperature in the one-temperature model.
The peak in the rotational temperature was found not to be coincident with the peak in the electron population. At $v=10 \text{ km/s}$, $p_{\infty}=13 \text{ Pa}$ of air, the electron population was shown to peak at approximately 1 cm behind the shock front. If an offset, discussed in section 7.1 were to exist, this would have had the effect of pushing the experimental peak in the electron population further back behind the shock front and thus create a larger difference between the points at which this peak and the peak in the rotational emission occurred. This observation is consistent with the predictions of the TTV model in that the theoretical peak emission point was not coupled to the peak in the electron population, but rather, as assumed by Park, dependent on the emission emanating from the $\text{N}_2^+$ molecules which have been shown to be the dominant radiation emitters.

7.3 Atomic and ionic oxygen emission

Each atomic line emission spectrum displayed in figure 6.37, was integrated with respect to frequency to obtain a total emissive power and then normalized by pressure to give an emissive power per particle. The results are shown in figure 6.38. As can be seen, there is a significant decrease in the emission for pressures less than 133 Pa. There would appear to be two competing processes at work. At the higher pressures, collisional de-excitation may quench radiative de-excitation and hence the emission per atom will decrease. However, at lower pressures, the rate of collisional excitation, the dominant excitation process, is progressively lowered. In all the oxygen emission experiments, the relative line intensities remained constant with decreasing pressure, indicating that the plasma is optically thin. This
conclusion is confirmed by both opacity calculations and the results of the emission and absorption experiments.

The integrated emission from the 777.2 nm transition in O and the 464.9 nm transition in O\(^+\) was measured at a point behind the shock front where the electron population had reached a plateau and pseudo-equilibrium prevailed. The position corresponded to 1.48 cm behind the shock front at which point both experiment and theory (the TTV\(_\nu\) model) showed that pseudo-equilibrium had been reached. The OMA was gated for a period of 0.5 \(\mu\)s, a time in which it was expected that conditions would not change substantially in the pseudo-equilibrium region. The O\(^+\) transition was monitored and accumulated over several successive experimental runs at the same condition. Due to the problems described concerning the driver gas contamination, it took many experiments before a "clean" result was obtained.

The point-wise measurement of the intensity ratio of the transitions in O and O\(^+\) (figure 6.39) is seen to be in good agreement with the behaviour of the intensity ratio predicted by the TTV\(_\nu\) model, that is T\(\neq\)T\(_e\) (figure 6.40). The electronic excitation temperature corresponding to the observed intensity ratio is 9,500 K.

### 7.4 Infrared CW diode laser absorption by atomic oxygen

In order to reduce the predicted parameters of the TTV\(_\nu\) model to an absorption profile, it was necessary to obtain an understanding of the
way in which the oxygen profile was changing, that is, its width and shift had to be well described. The factors affecting the line profile in the present experiment were the Doppler and Stark broadening processes. The Stark broadening was determined using the experimentally measured electron populations. It is true that the Stark width and shift are functionally dependent on both the electron population and the temperature, however the dependence on the temperature is very weak, see equations 5.48 and 5.49.

To present a theoretical absorption profile based on the predictions of the TT$_v$ model, the equations outlined in section 5.6 must be employed. The absorption coefficient, equation 5.43, contains the linewidth parameter $P(\Delta v)$. It was beyond the scope of the present work to obtain linewidth information within the nonequilibrium zone immediately behind the shock front. Because of this, the theoretical absorption profile (figure 6.41) is truncated below 0.5 cm behind the shock front. This position is approximately where the electron population is starting to peak and pseudo-equilibrium begins to prevail. From this point onwards, Stark broadening is the dominant broadening process, and is readily described, at the TT$_v$ model has been shown to accurately predict the electron densities. Furthermore, at this position behind the shock, the predicted translational temperature has dropped significantly and the Doppler broadening accounts for only 15% of the FWHM of the transition profile. Hence, the line shape was due mainly to the Lorentzian profile of the Stark broadening at the experimental detuning.

The largest contributor to the error in these experiments was the uncertainty in the detuning of the laser under the oxygen profile. The
laser wavelength was determined to be $(777.15 \pm 0.03)$ nm. The size of the shaded area in figure 6.41 reflects this uncertainty. It is considered that the difficulty in accurately determining the wavelength when working in oxygen (in the absence of optogalvanic tuning or other techniques that use tuning to the transition in question) will make future work with these transitions very difficult.

The predicted absorption is seen to be in at least fair agreement with the experimentally observed absorption. However, the result is far less conclusive than the results of the electron population, rotational temperature and molecular and atomic emission experiments.
Chapter 8

CONCLUSION

Conclusion:

In the present work it has been shown that to accurately model the reaction kinetics at the low density, high shock enthalpy flight regime of the AOTV, one requires a kinetic model that accounts for more than one characteristic temperature.

It has been demonstrated that the level of ionisation predicted by a one-temperature model is significantly overestimated. This result is very important when one considers the role that electrons, and to perhaps a lesser extent, ions, play in the reaction sequences. The deviation in the electron number density is a direct consequence of the fact that the temperature characterizing the electrons is significantly lower than the temperature that characterizes the bulk properties of the flow. On the other hand, the two-temperature model and the experiment, are shown to be in very good agreement; a consequence of the decrease in the temperature characterizing the electrons.

The temporal, point-wise measurement of the translational-rotational temperature is shown to be in good agreement with the predictions of the two-temperature model but again, in contrast, the one-temperature model predicts a temperature that is lower than that measured. The ionic-to-atomic oxygen ratio is shown, again via a point-wise
measurement, to support the hypothesis that two temperatures are characterizing the flow. Furthermore the theoretical plots of this ratio yield results that support the aforementioned conclusion that the decrease in the electron population is due to a lower electron temperature.

The emissive predictions of the two-temperature model are in excellent agreement with the results of the experiment, in so far as the overall profile, peak emission point and relaxation times are in accord. Unfortunately, no comment can be made as to the emissive power that is predicted by the two-temperature model and indeed this parameter was normalized out in the data reduction.

The least conclusive result is that of the infrared CW diode laser absorption experiment. Although the predicted-to-measured absorption profiles are in fair agreement, the error is considerable and is due to an experimental deficiency, namely accurate measurements of the detuning.

Further work in this field will require the development of new technologies designed specifically to investigate the population dynamics. The first hurdle that must be overcome are those problems associated with the contamination of the test slug. At present, there is no way of overcoming this problem with the shock tube facilities as it was described. One possible solution may be to take DDT to double-diaphragm configuration. It may transpire that this would allow an increase in the experimental test time (before contamination) with an increase in the shock velocity. Unfortunately, the
double–diaphragm configuration has a smaller tube diameter (path length).

Oxygen is an important reactant in many processes and a better understanding of its dynamics will be essential to future work. As the strong oxygen transitions are in the infrared, a very accurate technique of measuring the wavelength in this spectral region will be necessary. Lasers must also be developed, or existing lasers applied, to the absorption spectroscopic study of the resonant transitions in atomic nitrogen.

To continue the present work, more advanced optical diagnostic techniques such as Coherent anti-Stokes Raman Scattering (CARS) or Laser Induced Fluorescence (LIF) will be required to study the population dynamics of N\textsubscript{2}, O\textsubscript{2} and perhaps, most importantly, NO (as this species is a vigorous catalyst). Conditions are ideal for such studies. LIF will be especially useful as collisional quenching will be small due to the low pressures. Timing may however be a problem, especially if high resolution is required within the relaxation zone.


### Appendices

#### Appendix A  Reaction sequences for ionising atomic and molecular collisions

<table>
<thead>
<tr>
<th>Reaction Sequence</th>
<th>Energy (eV)</th>
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<tbody>
<tr>
<td>$N + O + 2.8 \text{ eV} \leftrightarrow NO^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$N + N + 5.8 \text{ eV} \leftrightarrow N_2^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$N + O_2 + 6.5 \text{ eV} \leftrightarrow NO_2^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$O + O + 6.9 \text{ eV} \leftrightarrow O_2^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$O + NO + 7.9 \text{ eV} \leftrightarrow NO_2^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$N + NO + 7.9 \text{ eV} \leftrightarrow N_2O^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$X + NO + 9.3 \text{ eV} \leftrightarrow X + NO^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$O + N_2 + 11.2 \text{ eV} \leftrightarrow N_2O^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$N_2 + O_2 + 11.2 \text{ eV} \leftrightarrow NO + NO^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$O + O_2 + 11.7 \text{ eV} \leftrightarrow O_3^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$X + O_2 + 12.1 \text{ eV} \leftrightarrow X + O_2^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$X + O + 13.6 \text{ eV} \leftrightarrow X + O^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$X + N + 14.6 \text{ eV} \leftrightarrow X + N^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>$X + N_2 + 15.6 \text{ eV} \leftrightarrow X + N_2^+ + e^-$</td>
<td></td>
</tr>
</tbody>
</table>
Appendix B  Reaction sequences for the charge transfer reactions

\[
\begin{align*}
N_2^+ + N &\rightleftharpoons N_2 + N^+ + 1.0 \text{ eV} \\
N_2^+ + O &\rightleftharpoons N_2 + O^+ + 2.0 \text{ eV} \\
N_2^+ + O_2 &\rightleftharpoons N_2 + O_2^+ + 3.5 \text{ eV} \\
N_2^+ + NO &\rightleftharpoons N_2 + NO^+ + 6.3 \text{ eV} \\
N^+ + O &\rightleftharpoons N + O^+ + 0.9 \text{ eV} \\
N^+ + O_2 &\rightleftharpoons N + O_2^+ + 2.5 \text{ eV} \\
N^+ + NO &\rightleftharpoons N + NO^+ + 5.3 \text{ eV} \\
O^+ + O_2 &\rightleftharpoons O + O_2^+ + 1.6 \text{ eV} \\
O^+ + NO &\rightleftharpoons O + NO^+ + 4.4 \text{ eV} \\
O_2^+ + NO &\rightleftharpoons O_2 + NO^+ + 2.8 \text{ eV} \\
N_2^+ + O &\rightleftharpoons NO + N^+ - 2.2 \text{ eV} \\
N_2^+ + O &\rightleftharpoons NO^+ + N + 3.1 \text{ eV} \\
N_2 + O^+ &\rightleftharpoons NO + N^+ - 4.2 \text{ eV} \\
N_2 + O^+ &\rightleftharpoons NO^+ + N + 1.1 \text{ eV} \\
N_2^+ + O_2 &\rightleftharpoons NO + NO^+ + 4.5 \text{ eV} \\
N_2 + O_2^+ &\rightleftharpoons NO + NO^+ + 0.9 \text{ eV} \\
O_2^+ + N &\rightleftharpoons NO + O^+ - 0.2 \text{ eV} \\
O_2^+ + N &\rightleftharpoons NO^+ + O + 4.2 \text{ eV} \\
O_2 + N^+ &\rightleftharpoons NO + O^+ + 2.3 \text{ eV} \\
O_2 + N^+ &\rightleftharpoons NO^+ + O + 6.7 \text{ eV}
\end{align*}
\]

Appendix C  Reaction sequences for the electron attachment reactions

\[
\begin{align*}
e^- + O_2 &\leftrightarrow O_2^- \\
e^- + O_2 + X &\leftrightarrow O_2^- + X \\
e^- + O &\leftrightarrow O^- + \text{hv} \\
e^- + O_2 &\leftrightarrow O + O^- \\
e^- + NO &\leftrightarrow N + O^-
\end{align*}
\]
<table>
<thead>
<tr>
<th>Reaction Sequence</th>
<th>T</th>
<th>C</th>
<th>n</th>
<th>E/k</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ + M ⇔ O + O + M (M=N, O)</td>
<td>VTv</td>
<td>2.900E+23</td>
<td>-2</td>
<td>5.975E+04</td>
<td>2.855</td>
<td>0.988</td>
<td>-6.181</td>
<td>-0.023</td>
<td>-0.001</td>
</tr>
<tr>
<td>O₂ + M ⇔ O + O + M (M=N₂, O₂, NO)</td>
<td>VTv</td>
<td>9.680E+22</td>
<td>-2</td>
<td>5.975E+04</td>
<td>2.855</td>
<td>0.988</td>
<td>-6.181</td>
<td>-0.023</td>
<td>-0.001</td>
</tr>
<tr>
<td>N₂ + N ⇔ N + N + N</td>
<td>VTv</td>
<td>1.600E+22</td>
<td>-1.6</td>
<td>1.132E+05</td>
<td>1.858</td>
<td>-1.325</td>
<td>-9.856</td>
<td>-0.174</td>
<td>0.008</td>
</tr>
<tr>
<td>N₂ + O ⇔ N + N + O</td>
<td>VTv</td>
<td>4.980E+22</td>
<td>-1.6</td>
<td>1.132E+05</td>
<td>1.858</td>
<td>-1.325</td>
<td>-9.856</td>
<td>-0.174</td>
<td>0.008</td>
</tr>
<tr>
<td>N₂ + M ⇔ N + N + M (M=N₂, O₂)</td>
<td>VTv</td>
<td>3.700E+21</td>
<td>-1.6</td>
<td>1.132E+05</td>
<td>1.858</td>
<td>-1.352</td>
<td>-9.856</td>
<td>-0.174</td>
<td>0.008</td>
</tr>
<tr>
<td>N₂ + NO ⇔ N + N + NO</td>
<td>VTv</td>
<td>4.980E+21</td>
<td>-1.6</td>
<td>1.132E+05</td>
<td>1.858</td>
<td>-1.352</td>
<td>-9.856</td>
<td>-0.174</td>
<td>0.008</td>
</tr>
<tr>
<td>N₂ + ions ⇔ N + N + ions</td>
<td>VTv</td>
<td>8.300E+24</td>
<td>-1.6</td>
<td>1.132E+05</td>
<td>1.858</td>
<td>-1.352</td>
<td>-9.856</td>
<td>-0.174</td>
<td>0.008</td>
</tr>
<tr>
<td>NO + M ⇔ N + O + M (M=N, O, N₂, O₂, NO, ions)</td>
<td>VTv</td>
<td>7.950E+23</td>
<td>-2</td>
<td>7.550E+04</td>
<td>0.792</td>
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<td>-6.761</td>
<td>-0.091</td>
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</tr>
<tr>
<td>NO + O ⇔ O₂ + N</td>
<td>T</td>
<td>8.370E+12</td>
<td>0</td>
<td>1.945E+04</td>
<td>-2.063</td>
<td>-1.480</td>
<td>-0.580</td>
<td>-0.114</td>
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<tr>
<td>N₂ + O ⇔ NO + N</td>
<td>T</td>
<td>6.440E+17</td>
<td>-1</td>
<td>3.837E+04</td>
<td>1.066</td>
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<td>0.004</td>
</tr>
<tr>
<td>O₂ + O ⇔ O₂ + O⁺</td>
<td>T</td>
<td>6.850E+13</td>
<td>-0.52</td>
<td>1.560E+04</td>
<td>-0.276</td>
<td>0.888</td>
<td>-2.180</td>
<td>0.055</td>
<td>-0.003</td>
</tr>
<tr>
<td>N₂ + N⁺ ⇔ N₂ + N</td>
<td>T</td>
<td>9.850E+12</td>
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<td>1.210E+04</td>
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<td>-1.076</td>
<td>-0.878</td>
<td>-0.004</td>
<td>-0.001</td>
</tr>
<tr>
<td>NO + O ⇔ NO + O⁺</td>
<td>T</td>
<td>2.750E+13</td>
<td>0.01</td>
<td>5.100E+04</td>
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<td>-1.011</td>
<td>-4.121</td>
<td>-0.132</td>
<td>0.006</td>
</tr>
<tr>
<td>N₂ + O⁺ ⇔ N₂ + O⁺</td>
<td>T</td>
<td>6.330E+13</td>
<td>-0.21</td>
<td>2.220E+04</td>
<td>2.979</td>
<td>0.382</td>
<td>-3.237</td>
<td>0.168</td>
<td>-0.009</td>
</tr>
<tr>
<td>NO + O₂ ⇔ NO + O⁺</td>
<td>T</td>
<td>1.030E+16</td>
<td>-0.17</td>
<td>3.240E+04</td>
<td>0.424</td>
<td>-1.098</td>
<td>-1.941</td>
<td>-0.187</td>
<td>0.009</td>
</tr>
<tr>
<td>NO + N ⇔ N₂ + O</td>
<td>T</td>
<td>1.700E+13</td>
<td>0.40</td>
<td>3.550E+04</td>
<td>2.061</td>
<td>0.204</td>
<td>-4.236</td>
<td>0.119</td>
<td>-0.006</td>
</tr>
<tr>
<td>N + O ⇔ NO + e⁻</td>
<td>T</td>
<td>1.530E+09</td>
<td>0.37</td>
<td>3.200E+04</td>
<td>-7.053</td>
<td>-0.532</td>
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</tr>
<tr>
<td>O + O ⇔ O₂ + e⁻</td>
<td>T</td>
<td>3.850E+09</td>
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<td>8.060E+04</td>
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<td>-3.110</td>
<td>-6.950</td>
<td>-0.151</td>
<td>0.007</td>
</tr>
<tr>
<td>N + N ⇔ N₂ + e⁻</td>
<td>T</td>
<td>1.790E+09</td>
<td>0.77</td>
<td>6.750E+04</td>
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<td>-8.693</td>
<td>0.269</td>
<td>-0.013</td>
</tr>
<tr>
<td>O + e⁻ ⇔ O + e⁻</td>
<td>Tv</td>
<td>3.900E+33</td>
<td>-3.78</td>
<td>1.585E+05</td>
<td>-6.113</td>
<td>-2.035</td>
<td>-15.31</td>
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<td>0.004</td>
</tr>
<tr>
<td>N + e⁻ ⇔ N + e⁻</td>
<td>Tv</td>
<td>2.500E+33</td>
<td>-3.82</td>
<td>1.686E+05</td>
<td>-3.441</td>
<td>-0.577</td>
<td>-17.67</td>
<td>0.099</td>
<td>-0.005</td>
</tr>
</tbody>
</table>
Appendix E

Reduction of output in Species Mole Fractions to absolute number densities

With a knowledge of the time histories of the species mole fractions and the temperature $T$, it is possible to reduce the molar fractions to absolute number densities as follows.

Defining the temperature $T$; $n_i$ the number density of species $i$; $N$ the total number density; $P$ the pressure; $q_i$ the mole fraction; $m_i$ the mass of species $i$; $\rho$ the density and $m_{av}$ the average molecular mass, one can write the equation of state and the momentum equation as

$$p = kT \sum n_i$$

and

$$P = P_1 + \rho_1 u_1^2 (1 - \rho_1/\rho)$$

(where the subscript 1 indicates conditions in front of the shock).

Knowing that the molar fraction is defined by

$$x_i = \frac{n_i}{N}$$

and that the average molecular mass is given by

$$m_{av} = \sum x_i m_i$$
the density \( \rho \) may be expressed as;

\[
\rho = m_{av}N = N \sum \chi_i m_i
\]

and therefore

\[
N = \frac{\rho}{\sum \chi_i m_i}.
\]

The equation of state can now be written

\[
P = \frac{kT \rho}{\sum \chi_i m_i}
\]

Substituting the state equation into the momentum equation one obtains the following quadratic in \( \rho \);

\[
\left( \frac{kT \rho}{\sum \chi_i m_i} \right) \rho^2 - \left( p_1 + p_1 u_i^2 \right) \rho + p_1^2 u_i^2 = 0
\]

This equation may be solved for \( \rho \) with

\[
a = \left( \frac{kT \rho}{\sum \chi_i m_i} \right), \quad b = -(p_1 + p_1 u_i^2), \quad c = p_1^2 u_i^2
\]

to deduce the species number density

\[
n_i = \chi_i N = \frac{(\rho \chi_i)}{\sum \chi_i m_i}
\]

as a function of distance behind the shock front.