Annual Scientific Report

on

INVESTIGATION OF INFRA-RED AND NONEQUILIBRIUM AIR RADIATION

Grant No. NAG 2-910

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For the Period

May 1, 1994 to February 28, 1995

Submitted by

C.H. Kruger, Principal Investigator
High Temperature Gasdynamics Laboratory
Stanford, California 94305-3032

Table of Contents

1. Introduction

This report describes progress on the first year of a research program on the infrared radiation of air plasmas conducted in the High Temperature Gasdynamics Laboratory at Stanford University. This research is supported by a grant from the National Aeronautics and Space Administration (NAG 2-910) and is currently under the direction of Professor Charles H. Kruger, with Dr. Stephen R. Langhoff from NASA-Ames as technical monitor. One Ph.D candidate is currently involved in this program.

This program is intended to investigate the masking of infrared signatures by the air plasma formed behind the bow shock of high velocity missiles. To this date, the radiative emission of air plasmas in the infrared has been the object of few experimental investigations, and although several infrared systems are already modeled in radiation codes such as NEQAIR,[1] measurements are required to validate numerical predictions and indicate whether all transitions of importance are accounted for. As an illustration, previous research[2] on the emission of air plasmas between 2,000 and 8,000 Å indicated that electronic transitions such as NO delta and NO epsilon, very intense radiators in that spectral range, were previously unaccounted for in the most widely used radiation codes. The present program is further motivated by the fact that 9 excited states (A, B, C, D, B', F, H, and H') of NO radiate in the infrared, especially between 1 and 1.5 μm where at least 9 transitions involving can be observed. Because these IR transitions are relatively well separated from each other, excited NO states concentrations can be easily measured, thus providing essential information on excited-state chemistry for use in optical diagnostics or in electronic excitation model validation. Developing accurate collisional-radiative models for these excited NO states is of importance as the UV-VUV transitions of NO (beta, gamma, delta, epsilon, beta prime, gamma prime) produce a major, if not dominant, fraction of the radiation emitted by air plasmas.[2]

During the first year of the program, research has focused on the spectral range 1.0 to 1.5 μm, as detailed in Section 2 of this report. The measurements, conducted in a 50 kW radio-frequency inductively coupled plasma torch operating on air at atmospheric pressure, extend previous shock tube investigations by Wray[3] to a wider spectral range (1.0 to 1.5 μm vs. 0.9 to 1.2 μm) and higher temperatures (7600 K in the plasma torch versus 6700 K in the shock-tube). These higher temperatures in the present experiment have made it possible to observe high-lying excited NO states that were previously undetectable. These measurements are currently being extended up to 5 μm, with particular attention paid to the rovibronic bands of ground state NO, molecular continua, CO transitions, and other systems of importance. Publications and presentations resulting from or related to this work are cited in Section 3, and Section 4 lists the personnel who contributed to this report.

2. Infrared Radiation of Air Plasmas

In the following subsections, we first describe the experimental set-up for spectral measurements (2.1)) and summarize previous results on the thermodynamic state of the plasma under investigation (2.2). In Section 2.3, comparisons are presented between experimental results obtained in the range 1.0 to 1.5 μm and the predictions of the baseline and enhanced NEQAIR models. Details are given about the electronic systems newly added to the code. Finally, section 2.4 summarizes the work currently in progress.

2.1 Experimental Set-up

All measurements presented here were conducted in a 50 kW TAFA model 66 RF induction plasma torch, powered by a LEPEL model T-50-3 power supply operating at a frequency of 4 MHz. The torch head itself consists of a 5-turn copper induction coil surrounding a 3 mm thick quartz tube, and encased in a Teflon body with brass end plates. Overall size of the torch head is approximately 15 cm diameter and 35 cm height. A copper nozzle of 5.0 cm exit diameter was utilized at the top of the upward firing torch (with the nozzle exit being approximately 7 cm above the uppermost coil), and all measurements were conducted 1 cm downstream of the nozzle exit in a region where the flow is laminar.

The experimental set-up for spectral measurements in the range 1.0 to 1.5 μm is shown in Fig. 1. This set-up includes a Jarrell-Ash model 82-020 1/2 meter Ebert-type scanning monochromator fitted with a Judson model J15-D cryogenically cooled mercury-cadmium-telluride infra-red detector, and a 590 lines/mm grating blazed at 1.2 μm. A longpass filter with cut-off at 0.84 μm was inserted in the optical path before the detector to reject high-order structure from shorter wavelengths. Absolute intensity calibrations were performed using a water-cooled Globar, which is a silicon-carbide rod operating at 4 amps and acting as a 900 °C gray body of emissivity 0.9 approximately.

For the planned measurements in the extended spectral range 1.5 to 5 μm, the equipment includes a SPEX model 750M 3/4 meter scanning monochromator, a Cincinnati Electronics model SDD-20E1-S1 indium-antimonide cryogenically-cooled infrared detector, two gratings with 300 and 150 lines/mm blazed at 2.6 and 4.0 μm, respectively, and three long-pass filters with cut-offs at 1.4, 2.0 and 3.5 μm for high-order interference rejection. Absolute calibrations up to 6 μm are obtained with an NIST traceable radiance standard (Optronics model OL-550).

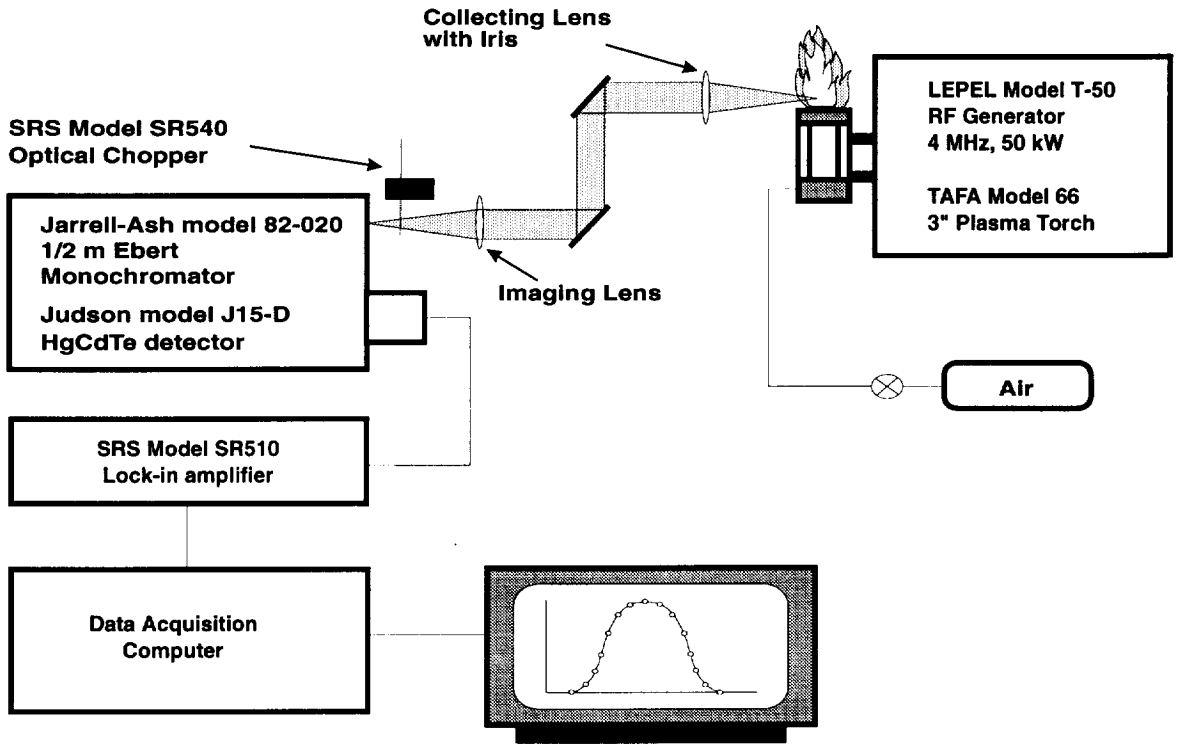

Figure 1. Experimental schematic for emission measurements in the range 1.0-1.5 μm. (See text for modifications to this set-up in the range 1.5-5 μm.)

2.2 Thermodynamic State of the Plasma

The plasma torch was operated here for the same conditions as in earlier studies[2,4] wherein electronic, vibrational, and rotational temperatures, along with electron number densities, had been measured by means of emission spectroscopy. In these earlier works it was found that the plasma was close to local thermodynamic equilibrium (LTE), and the most accurate temperature profile had been determined from Abel-inverted lateral profiles of absolute intensity of the atomic oxygen transition at 7773 Å. Figure 2 summarizes some results from these previous works. Since the O-line temperature profile completely characterizes the thermodynamic state of the plasma, numerical modeling can be performed using chemical equilibrium concentrations and Boltzmann distributions for the populations of all internal energy states.

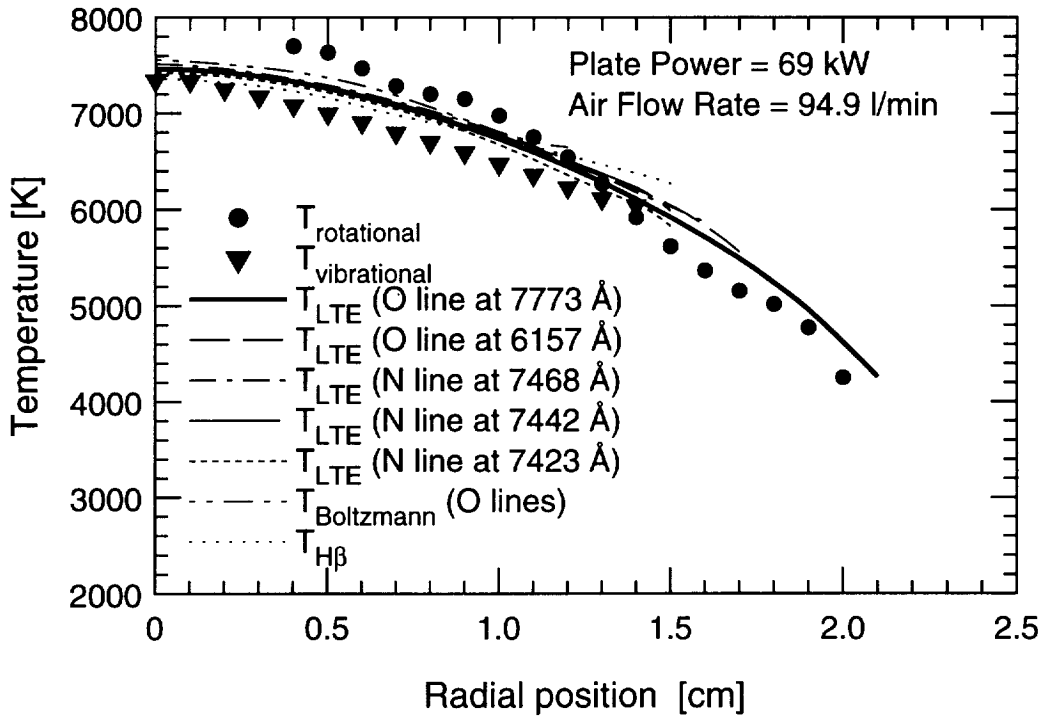

Figure 2. Measured electronic, vibrational, and rotational temperature profiles in the air plasma, 1 cm downstream of the 5 cm diameter nozzle exit.

2.3 Comparison between measurements and numerical simulations

The experimental infrared spectrum presented below was recorded along the plasma diameter, with a triangular spectral slit function of FWHM = 0.00275 μm. This spectrum was corrected for the spectral response of the detection system and calibrated in intensity as described earlier. The accuracy of the spectral intensities is estimated to be better than 10% over the whole spectral range. Numerical simulations were conducted with the NEQAIR2 code[5,6] by dividing the plasma into 50 slabs of 1-mm thickness in which the concentrations and temperature were assumed uniform and given by the measured temperature profile. Prior to the changes described below, NEQAIR2 included a limited number of infrared transitions: N_2 first positive, CN red, atomic oxygen and nitrogen lines, and atomic oxygen and nitrogen continua. The comparison presented in Fig. 3 between the baseline NEQAIR2 model and the experiment shows that while atomic lines were accurately modeled in the baseline code, several spectral features were missing between the atomic lines.

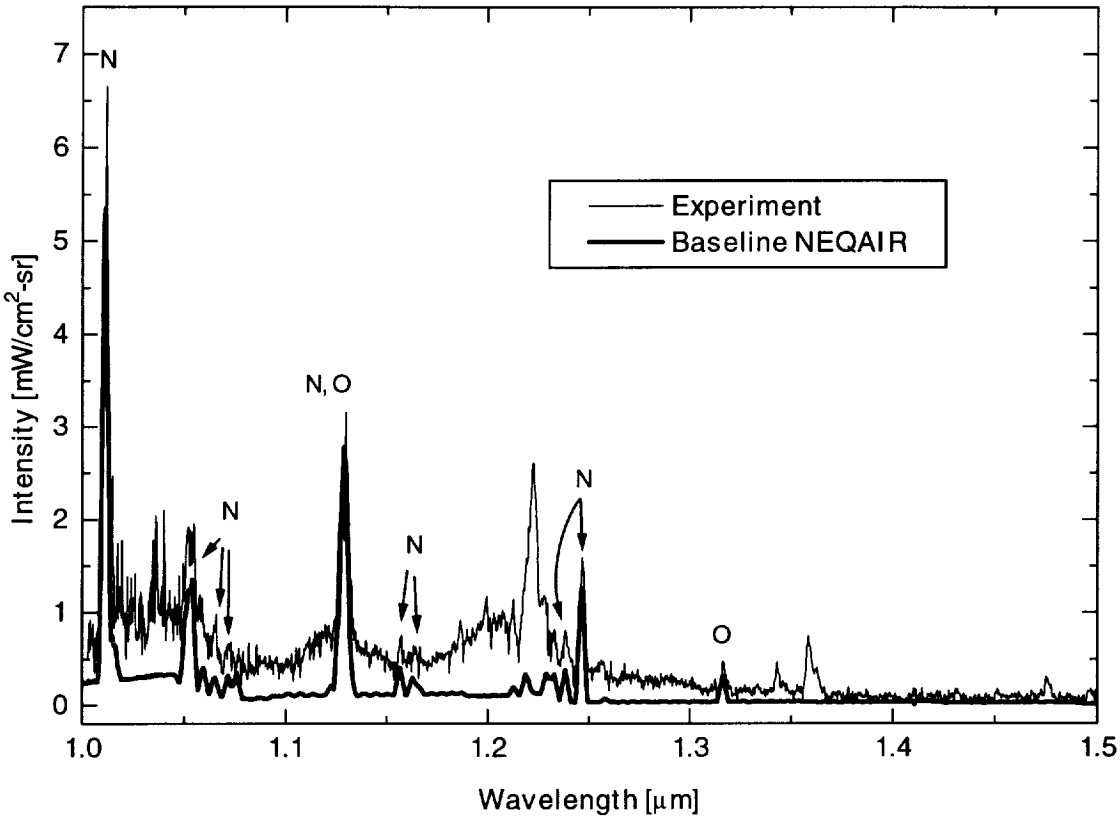

Figure 3. Comparison between the measured spectrum and the predictions of the baseline NEQAIR2 model (which includes only atomic lines of O, N and C, and the first positive system of N_2).

In order to improve the agreement between the measurements and the model, several electronic transitions were added to the baseline NEQAIR2. The newly introduced transitions, listed in Table 1, involve essentially high-lying Rydberg states of NO. For the D-A band system (also called the "11,000 Å" system), transition probabilities were obtained from the recent accurate *ab initio* electronic transition moment function computed by Sheehy et al.[7] For the C-A system (or "12,000 Å" system), the electronic transition moment function was assumed to be the same as for the D-A system (this is justified since the potential energy curves of the C and D states are very nearly identical, at least in the potential well for the first four or so vibrational levels which are the only levels with appreciable vibrational Boltzmann fractions).

Difficulties arise in the modeling of line positions for the NO $C^2\Pi$ state. This state is strongly perturbed by homogeneous and heterogeneous interactions with near resonant levels of the NO $D^2\Pi$ ($v \geq 0$) and $B^2\Pi$ ($v \geq 7$) states.[8-10] If these perturbations are neglected, the synthesized spectra fail to reproduce the measurements. This point is illustrated in Fig. 4 where the position of the synthesized Q branch of the C-A (0-0) band

is shifted by approximately 70 Å and its peak intensity is higher than the experiment by a factor 1.6. For this reason, rotational line positions for the (C, v=0) state were computed here as the eigenvalues of an 11×11 Hamiltonian whose elements represent the interactions between the (C, v=0) , (B, v=7-10) and (D, v=0) states. The matrix elements and related spectroscopic constants (term energies, rotational constants, spin-splitting and Λ-doubling constants, and electronic interaction parameters) were taken from Amiot and Vergès.[10] The model is presently limited to rotational levels of the (C, v=0) level which is the only vibrational level analyzed by Amiot and Vergès.[10] Nevertheless, it can be seen in Fig. 4 that significantly better agreement is already obtained with the measured C-A transition. This is because the (0-0) band is responsible for the dominant fraction (~55%) of the total C-A emission at the present plasma temperatures (T_{max} = 7600 K). We are currently extending the model to perturbations in higher vibrational levels in the C state. It is expected that the discrepancy between the numerical and measured spectra in the range 1.18 to 1.21 μm will be significantly reduced when perturbations in the (1-1) band (responsible for approximately 25% of the C-A total emission) are adequately modeled.

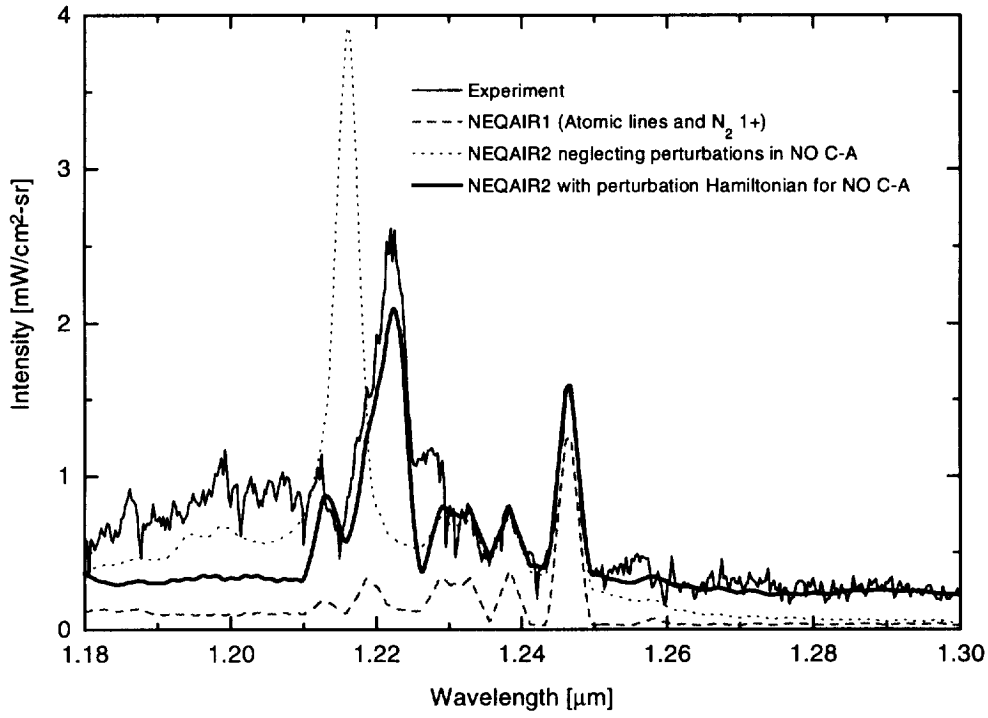

Figure 4. Measurements and simulations of the NO C-A band system. Note the large error in the model when perturbations are neglected.

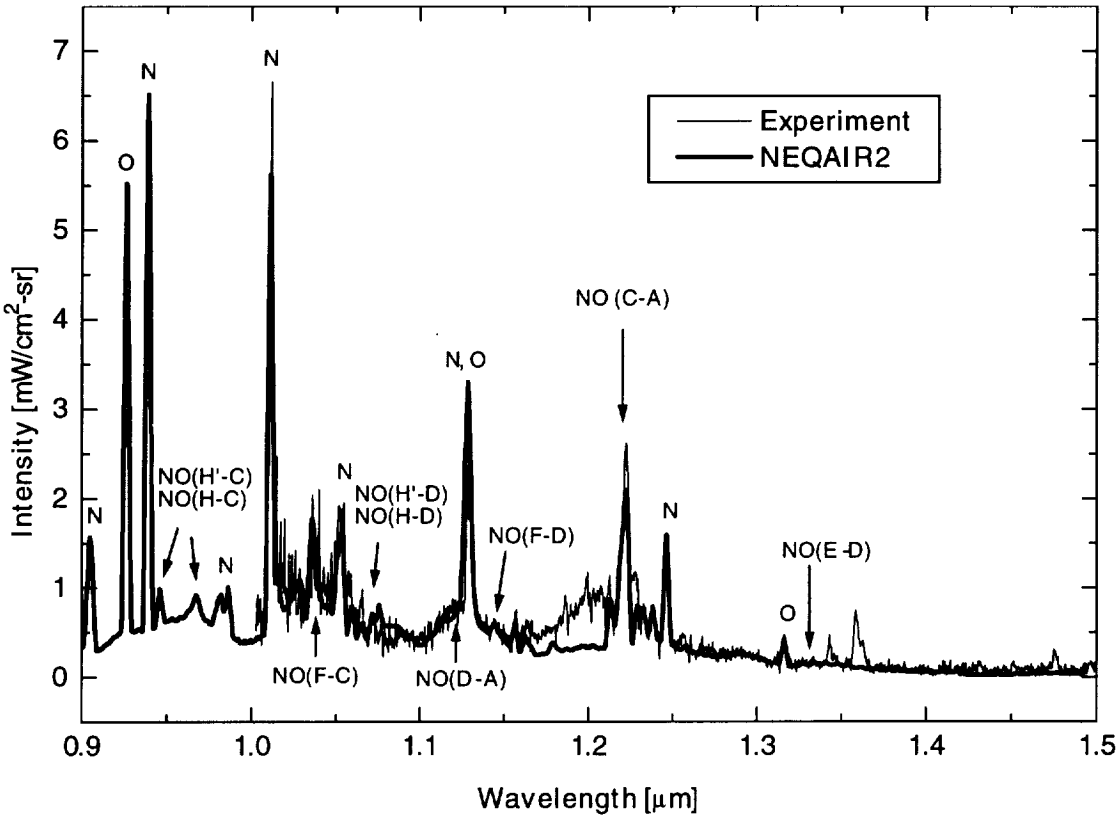

Figure 5. Comparison between the measured spectrum and the predictions of the enhanced NEQAIR2 model.

Transition probabilities for the E-C, E-D, F-C, F-D, H-C, H'-C, H-D, and H'-D systems are not as well established as those for the C-A and D-A systems. However, these transitions are so strongly diagonal (Franck-Condon factors for the $\Delta v = 0$ bands are typically greater than 0.95) that a measured value of the transition probability for any one band of a given system is sufficient to establish the transition probabilities of the other bands of the same system with some confidence.

Oscillator strengths were measured by Wray[3] for the (0-0) or (1-1) bands of the F-C, H-C, H'-C, H-D, and H'-D systems. These values, listed in Table 1, were used here to infer transition probabilities for the other, non-measured bands. These constants provide good agreement with the measurements, except for the F-C system for which better agreement was obtained using an oscillator strength three times larger than the one measured by Wray.[3] More work is required to resolve this discrepancy.

For the E-D and F-D bands, we are not aware of any prior transition probability measurements or calculations. Therefore, we estimated transition probabilities for these two (weak) systems by direct comparison with the measured spectrum. These values are listed in Table 2 along with our estimate for the transition probability of the F-C system.

A comparison is presented in Fig. 5 between the numerical predictions of the current NEQAIR2 model and the experimental spectrum. As can be seen, good agreement is obtained, with the following exceptions. As discussed earlier, the discrepancy in the range 1.16-1.21 μm is apparently due to the neglecting of perturbations in the C-A (1-1) band. Near 1.35 μm, two minor features appear in the measurememts that have not been identified (it is suspected that these features are atomic lines).

The overall good agreement in the spectral region 1.0 to 1.5 μm confirms the accuracy of the transition probabilities computed by Sheehy et al.[7] for the D-A or C-A systems, as well as of those measured by Wray[3] for the H-C, H'-C, H-D, and H'-D systems. Moreover, it indicates that all radiating systems of importance in air plasmas over the spectral range 1.0 to 1.5 μm are now modeled in the code.

Electronic Transition	(v'-v")	Band-origin (μm)	Absorption Band Oscillator Strength	Source
$C\ ^2\Pi \leftarrow A\ ^2\Sigma^+$	(0-0)	1.2168	0.4648	(a)
	(1-1)	1.2156	0.4638	
$D\ ^2\Sigma^+ \leftarrow A\ ^2\Sigma^+$	(0-0)	1.1007	0.2575	Sheehy et al.[7]
	(1-1)	1.1083	0.2557	
$E\ ^2\Sigma^+ \leftarrow C\ ^2\Pi$	(0-0) or (1-1)	1.178	< 0.06	Wray[3] (b)
$F\ ^2\Delta \leftarrow C\ ^2\Pi$		1.033	0.22	
$H\ ^2\Sigma^+ \leftarrow C\ ^2\Pi$		0.968	0.24	
$H'\ ^2\Pi \leftarrow C\ ^2\Pi$		0.967	0.15	
$H\ ^2\Sigma^+ \leftarrow D\ ^2\Sigma^+$		1.062	0.25	
$H'\ ^2\Pi \leftarrow D\ ^2\Sigma^+$		1.061	0.25	

Table 1. Absorption oscillator strengths for electronic transitions between NO Rydberg states.
(a) Computed using the same transition moment as determined for the C - A transition by Sheehy et al.[7]
(b) Ref. 3 lists emission band oscillator strengths; in this table, they are converted to absorption strengths.

Electronic Transition	(v'-v")	Band-origin (μm)	Absorption Band Oscillator Strength
$F\ ^2\Delta \leftarrow D\ ^2\Sigma^+$	(0-0)	1.143	0.45
$F\ ^2\Delta \leftarrow C\ ^2\Pi$	(0-0)	1.184	0.66
$E\ ^2\Sigma^+ \leftarrow D\ ^2\Sigma^+$	(0-0)	1.321	0.75

Table 2. Estimated absorption oscillator strengths for NO F-D, F-C, and E-D transitions.
(For the F-C transition, the proposed value here is 3 times greater than the value measured by Wray[3]).

2.4 Conclusions and Work in Progress

Experimental benchmark spectra of the infrared emission of high-temperature (7600 K) air are being measured in the range 1.0 to 5 μm. The preliminary measurements presented here in the range 1.0 to 1.5 μm were used to guide model enhancements to the NEQAIR code. Good agreement is now obtained with the experiment in this spectral range, with the exception of some NO bands including the C state as one of the states of the transition. Modeling difficulties arise for the NO C state which is strongly perturbed by the NO B and D states; at present, the C-A (0-0) band has been accurately modeled using the Hamiltonian proposed by Amiot and Vergès.[10] More work is currently under way to extend the treatment to higher vibrational C-A transitions as well as to other transitions involving the C state.

Above 1.5 μm, the baseline NEQAIR2 model is limited to the free-free continua of atomic nitrogen and oxygen and to the first positive system of N_2. To extend this model, the Meinel system of N_2^+ and the rovibrational transitions of NO have been added to NEQAIR2 with transition probabilities from Langhoff et al.[11,12] The contribution the Meinel system of N_2^+ is found to be significant in the range 1.5 to 3.5 μm, with maximum emission at approximately 2 μm. Among the other systems to be added are the infrared rovibronic bands of CO, the infrared atmospheric bands of O_2, and possibly carbon dioxide and water vapor bands. Extended spectral measurements up to 5 μm are also under way.

2.5 References

1. Park, C., "Nonequilibrium Air Radiation (NEQAIR) Program: User's Manual," *NASA TM 86707*, Ames Research Center, Moffett Field, CA 94035, 1985.
2. Laux, C.O., Gessman, R.J., and Kruger, C.H., "Modeling the UV and VUV Radiative Emission of High-Temperature Air," *AIAA Paper 93-2802*, AIAA 28th Thermophysics Conference, Orlando, FL, July 6-9 1993.
3. Wray, K.L., "Oscillator Strengths of Transitions between Rydberg States of Nitric Oxide in the Near IR," *JQSRT*, Vol. 9, pp. 255-276, 1969.
4. Laux, C.O., "Optical Diagnostics and Radiative Emission of Air Plasmas," Ph.D. Thesis, *HTGL Report T-288*, Stanford University, August 1993.
5. Laux, C.O., Moreau, S., and Kruger, C.H., "Experimental Study and Improved Modeling of High-Temperature Air Radiation," *AIAA 92-2969*, AIAA 23rd Plasmadynamics and Lasers Conference, Nashville, TN, July 6-8, 1992.
6. Moreau, S., Laux, C.O., Chapman, D.R, and MacCormack, R.W., "A More Accurate Non-Equilibrium Air Radiation Code: NEQAIR Second Generation," *AIAA-2968*, AIAA 23rd Plasmadynamics and Lasers Conference, Nashville, TN, July 6-8, 1992.
7. Sheehy, J.A., Bauschlicher, C.W., Jr., Langhoff, S.R., and Partridge, H., "Theoretical Study of the Nitric Oxide ε and 11 000 Å Bands," *Chem. Phys. Letters*, Vol. 225, pp. 221-228, 1994.
8. Lagerqvist, A. and Miescher, E., "Absorptionsspektrum des NO-Moleküls Feinstruktur-Analyse der δ- und β-Banden und Homogene Störung $C^2\Pi$–$B^2\Pi$," *Helv. Phys. Acta*, Vol. 31, pp. 221-262, 1958.
9. Gallusser, R. and Dressler, K., "Multistate Vibronic Coupling between the Excited $^2\Pi$ states of the NO molecule," *J. Chem. Phys.*, Vol. 76, pp. 4311-4327, 1982.
10. Amiot, C. and Verges, J., "Fine Structure of the $C^2\Pi$–$A^2\Sigma^+$ and $D^2\Sigma^+$–$A^2\Sigma^+$ Band Systems of the NO Molecule: Homogeneous and Heterogeneous Perturbations," *Phys. Scripta*, Vol. 25., pp. 302-311, 1982.
11. Langhoff, S.R. and Bauschlicher, C.W., Jr., "Theoretical Study of the First and Second Negative Systems of N_2^+," *J. Chem. Phys.*, Vol. 94, p. 6638, 1991.
12. Langhoff, S.R., Bauschlicher, C.W., Jr., and Partridge, H., "Theoretical Dipole Moment for the $X^2\Pi$ state of NO," *Chem. Phys. Letters*, 223, 416-422, 1994.

3. Publications and Presentations

Laux, C.O., Gessman, R.J., Hilbert, B., and Kruger, C.H., "Experimental Study and Modeling of Infrared Air Plasma Radiation for Signature Masking and Collisional-Radiative Modeling," To be presented at the 30th AIAA Thermophysics Conference, San Diego, CA, June 19-22, 1995.

4. Personnel

The following personnel contributed to this report:

Charles H. Kruger	Vice-Provost, Dean of Research and Graduate Policy, Professor, Department of Mechanical Engineering.
Christophe O. Laux	Research Associate, High Temperature Gasdynamics Laboratory, Department of Mechanical Engineering. (Ph.D. Mechanical Engineering, Stanford University 1993).