RADIATION AT HYPERSONIC SPEEDS
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ABSTRACT

The optical radiation from the heated air which envelops a high speed vehicle is of interest in many different problems related to re-entry physics. In the present paper, the data available for the radiation from equilibrated high temperature air are reviewed. The results available are presented in graphical form, showing the absorption coefficient for each radiating species as a function of temperature and wavelength. The temperature range considered is from \( \sim 3000\text{K} \) to \( \sim 8000\text{K} \), the wavelength range from \( \sim 0.2 \) to \( 1.5\mu \). Seven molecular band systems are considered. For two of these (NOy and O\(_2\)S-R) there is good agreement among the various experimental results. For four bands (N\(_2\)(1+), N\(_2\)(1-), NO\(\beta\) and NO\(_2\) continuum) there is substantial disagreement. For the other molecular band system (N\(_2\)(2+), and for the oxygen free-bound and free-free radiation, there is only a single source of data.

INTRODUCTION

The radiation from the high temperature air surrounding a hypersonic vehicle has been the subject of extensive studies since the conception of the intercontinental ballistic missile. It was realized at that time that the radiative contribution to heat transfer was sufficiently important to require careful investigation. With the present interest in return from orbital flight and in circumlunar trajectories, the higher temperatures involved make the radiative aspects of the heat transfer still more important (Ref. 1). Further interest in a detailed knowledge of this radiation has resulted from its importance in observations from glancing re-entry vehicles, and also in its use for ground observation of reentering vehicles (Ref. 2). In addition, the exploration of this field is of importance.

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because the solution of many of the problems which are involved should add considerably to the basic physical knowledge of molecular spectra and atomic and molecular interactions.

A complete description of the optical radiation from the heated air surrounding a hypersonic vehicle involves at least three separate problems. These problems might be enumerated as the determination of the following quantities: 1) the number density of the various chemical species which are present in the flow; 2) the degree of optical excitation of these species; and 3) the radiation that would be obtained from each species for a specified degree of excitation. Unfortunately, not even the basic physical data necessary for the solution of these complicated problems were available at the time that their importance to hypersonic flight became apparent. Since that time, a good deal of research has been directed toward both the determination of the fundamental data and the solution of the problems which use these data. In the case of the first problem listed in the foregoing, many of the rate constants for the reactions of interest have been determined (Ref. 3), and considerable progress has been made on the solution of the complicated aerodynamic and chemical-kinetic flow problem for certain simple bodies (Refs. 4 and 5). The second problem involves the rate at which excited electronic levels of the molecules are populated, as well as the rate of formation of new species in excited levels. The excitation rate can influence the population of excited levels immediately behind the shock; it also determines the density at which the radiation becomes "collision limited" (see Refs. 6, 7 and 8).

The third problem, the determination of the radiation emitted by each gas species present in high temperature air for a given degree of optical excitation, requires the determination of the transition probability for each important optical transition of each species. A large body of research work has been performed in this field, and further work is in progress at the present time. It is the purpose of this paper to present a review of the results that are presently available, along with a very brief discussion of the experimental methods used to obtain these results.

In compiling these data, two earlier reviews were especially helpful. The summary paper by Keck, Camm, Kivel and Wentink (Ref. 6) presents the work done at the AVCO Corporation with high temperature shocks in air, along with sufficient theoretical calculations to permit scaling the results to other temperatures. A later review by Meyerott, Sokoloff and Nicholls (Ref. 9) presents an independent calculation for determining the spectral distribution of the radiation as a function of
temperature, and, for several bands, different transition probabilities are used from those of Ref. 6. The results are tabulated in Ref. 9 for air from 2000 to 12,000K and for densities from 10^-6 to 10 atm.

In the present report, the data are presented graphically, with separate graphs of the spectral absorption coefficient for each major transition of each species. These graphs provide a direct method for comparing the results of different experiments, because the spectral absorption coefficient for the separate species depends only on the temperature of the gas, and this temperature dependence is reasonably well understood. Thus, if better data should become available for any particular transition, the corresponding graphical description should be changed only by a scale factor. The graphs can easily be combined to determine the radiation from equilibrated air by use of tables of species concentration (Ref. 10). For radiation from air that is not in thermodynamic equilibrium, these results still supply the connection between the number density of excited molecules and the observed radiation, since the basic transition probabilities for the component species are independent of the state of the gas.

The transitions for which results are presented herein are all those which should be of importance in determining the radiation from air up to about 8000K. At higher temperatures the number density of ions increases considerably, and the radiation from the capture of electrons by the ions can become appreciable. This is illustrated in Ref. 9, where calculated results for 12,000K show the importance of electron capture by O^+ and N^+.

EXPERIMENTAL DETERMINATION

For the determination of the radiation from the constituent gases of high temperature air, two types of measurement are available. For transitions which connect with the ground electronic state, the absorption coefficient of the gas can be measured, either at room temperature or at elevated temperatures in a shock tube. If the temperature at which the measurement is made is much different from that at which the radiation (or absorption) is to be calculated, different vibrational transitions are involved so that at the higher temperature the absorption is spread over a larger range of wavelengths (see Fig. 1). To complete the calculation, it is necessary that the relative strengths of the bands be known. These are now available from theoretical calculations for all the bands of interest (Ref. 9). In addition, the relevant matrix element of the electronic dipole moment has some dependence on the
internuclear separation within the molecule. Thus for any case where the measured transitions occur at a much different internuclear separation than those to be calculated, this dependence must be obtained experimentally.

In cases where the transition of interest is between two excited electronic levels, it is not possible to perform an absorption experiment because of the small population in the absorbing state. However, the emission from the gas can be measured directly at the high temperatures available in a shock tube. This emission is recorded electrically and compared with that from a calibrated source. In this way, the intensity of band systems of molecular ions can also be measured.

The emission and absorption of a gas at a given wavelength are connected very directly by Kirchhoff’s law (Ref. 11). With either of these data available over the full spectrum for a given band system, the results can be reduced to a "transition probability" for the particular band, that is, if a molecule is in the upper state, there is a certain probability that it will make a radiative transition to the lower state in a specified interval of time. This transition probability can be described in terms of the Einstein A and B coefficients, the f-value of the system, the dipole moment for the transition, etc. (Ref. 11). All of these reductions, however, necessarily involve assumptions, and investigators have reduced their data in different ways. In the present report, for purposes of comparison, all the data have been plotted in terms of the absorption coefficient k of a 1 cm slab of gas at standard density: \( L_0 = (2.54 \times 10^{-9}) \) (molecules/cm\(^3\)). These results as shown are then very closely connected with the high temperature measurements. It is the scaling of room temperature measurements up to the temperatures of interest in the re-entry problem that requires that important approximations be made.

From the values of the absorption coefficients given here, the radiation from a volume of gas dV with a number density n, in the wavelength range d\( \lambda \), and within the solid angle d\( \Omega \), can be calculated from

\[
dW = k \frac{n}{L_0} \frac{1}{\pi} \omega_{bb} dVd\lambda d\Omega \tag{1}
\]

where \( \omega_{bb} \) is the blackbody radiation at \((\lambda, T)\).

For \( dW \) dVd\( \Omega \)d\( \lambda \) in \( W/cm^3 \) ster \( \mu \) the equation becomes

\[
\frac{dW}{dVd\Omega d\lambda} = 1.19 \times 10^{-25} k \left( \frac{n}{L_0} \right)^{3.5} (\epsilon 1.438 \times 10^{-4}/\lambda T_1)^{-1} \tag{2}
\]
with $\lambda$ in microns and $T$ in deg Kelvin. These equations are written with the assumption that the gas is "optically thin" at all wavelengths, i.e., that $\exp(-k \frac{\lambda}{T_o} \ell) \approx 1 \cdot k \frac{\lambda}{T_o} \ell$ at all wavelengths (where $\ell$ = thickness of gas sample). Since the value of $k$ vs. $\lambda$ that is given in the graphs represents a smoothed average, the true value of $k$ may be several times larger at particular wavelengths, and this must be considered when estimating that a given sample of gas is optically thin.

**EXPERIMENTAL VALUES**

**Oxygen**

There are three essentially different measurements with the Schumann-Runge system of the oxygen molecule that can be used to determine the radiation at elevated temperatures. The measurement of the absorption of room temperature $O_2$ in the vacuum ultraviolet region (Ref. 12) gives a transition probability ($f$ value) of 0.259. This value has been used in Ref. 9 to calculate the absorption to be expected at high temperatures with the assumption that the matrix element of the dipole moment does not change appreciably with change in internuclear separation. The results are shown in Fig. 3 for the averaged coefficient, averaged over 2000 cm$^{-1}$ intervals in the visible and ultraviolet regions for 4000 and 8000 K. A second determination is the direct measurement of the absorption coefficient of oxygen that has been heated in the shock tube to high temperatures (Ref. 13). Typical absorption spectrograms obtained in this way are shown in Figs. 1 and 2. Using these measurements, a smoothed absorption coefficient for 4000 K was calculated and is shown as a dashed curve in Fig. 3. It can be seen that this gives a result about one-third as large as the calculation based on room temperature measurements, corresponding to a decrease in $f$ value with increasing internuclear separation. A third type of measurement is the direct determination of the radiation from shock heated oxygen (Refs. 14 and 6) at temperatures in the neighborhood of 4000 K. These results are shown in the solid curve of Fig. 3. The agreement between the high temperature absorption and emission measurements is excellent.

The absorption coefficient at higher temperatures can be calculated from these data using the theory described in Ref. 6. The results for 6000 and 8000 K are also shown in Fig. 3.

The variation of line width with density for the separate absorption lines of the Schumann-Runge system has also been
determined experimentally (Ref. 13), so it is impossible to calculate the emission from oxygen even in the case where the gas is not optically thin.

Nitrogen

There are two prominent band systems observed in the radiation from N\(_2\), the first positive system in the visible and infrared region and the second positive system in the ultraviolet. Since both of these systems involve transitions between two excited electronic states of the molecule, it is not possible to perform absorption measurements to determine k. Measurements of the emission from shock heated air have been used (Ref. 6) to determine the intensity of both of these band systems of N\(_2\), and the results are shown in Figs. 4 and 7. In these measurements all of the radiation from air in the spectral range 0.7 to 0.9 \(\mu\) is attributed to the N\(_2\)(l+) system. More recently the emission from pure N\(_2\) that has been heated in a shock tube has been measured (Ref. 5) throughout the 0.8 to 1.5 \(\mu\) region. For these measurements a multichannel infrared spectrometer was used, in which twelve detectors are placed in the focal plane of an Ebert mounted grating. This resulted in unusually good resolution of the vibrational band heads. The results of these measurements show a total radiation of about one-fifth that reported in the air measurements of Ref. 6. The results of Ref. 5 are shown as dotted lines in Fig. 4, scaled to 6000 K for comparison. In Fig. 5 the experimental results at 6630 K from Ref. 5 are shown in a plot of the radiation in w/cm\(^3\) - ster-\(\mu\) along with the calculated results for this temperature from Ref. 6, based on the experimental results for air. The large discrepancy in these results has not been explained but could be due to either an important radiating species in air that has previously been overlooked, or to impurity radiation, such as CN red, in the air experiments. A single experiment with air at 5300 K, reported in Ref. 5, does not show additional radiation in this spectral region.

It has been suggested in Ref. 9 that the air radiation attributed to the N\(_2\)(l+) system in Ref. 6 may also contain radiation from the N\(_2^+\) Meinel system. The data from pure N\(_2\) is not as yet complete enough to determine the answer to this question, but the data at short wavelength (< 0.9\(\mu\)) give no evidence of N\(_2^+\) Meinel radiation. This is illustrated in Fig. 6, where the experimental results for the N\(_2\) radiation (multiplied by the partition function) (see Ref. 15) are plotted vs. the reciprocal of the temperature (Ref. 5). These results should give very nearly a straight line, with a slope equal to the negative of the activation energy for this
radiation. The straight lines are drawn with a slope corresponding to the $\text{N}_2(1^+)$ system and it can be seen that the agreement is excellent.

The second positive system of the nitrogen molecule contributes appreciable radiation in the ultraviolet region at high temperature. The only measurements available are those of Ref. 6, deduced from the experimental results with shock heated air. They are shown in Fig. 7.

The $\text{N}_2^+$ radiation that has been observed in high temperature air is the first negative system in the visible and ultraviolet. This system is especially important in the spectral region $0.3 \leq \lambda \leq 0.5 \mu$ at temperatures above $\sim 7500$ K. From the high temperature air measurements an $f$ value of $0.18 \pm 0.07$ was determined for this $\text{N}_2^+$ radiation (Ref. 6). In a different type of measurement (lifetime measurement of nitrogen radiation excited by an electron beam), Bennett and Dalby (Ref. 16) obtained a value of $0.037 \pm 0.002$. Recently this radiation has been measured in pure nitrogen heated in a shock tube (Ref. 17). The pure nitrogen experiments have the advantage over the air experiments in that the nitric oxide radiation is not present, and the ratio of $\text{N}_2^+$ ($1^{-}/N$)($2^+/N$) radiation is five to ten times greater than in air at the same temperature. As the result of these experiments a value of $f = 0.09 \pm 0.05$ is given, although from the experimental data shown it appears that a somewhat lower value would provide a better fit. In view of this fact, and the large uncertainty quoted in the results, as well as the low value obtained from the lifetime measurements (Ref. 16), a value of $f = 0.06$ was used in the calculated results shown in Fig. 8. These results are then 0.3 of the values given in Ref. 9, where an $f$ value of 0.20 was used in the calculations.

Nitric Oxide

There are two important band systems of nitric oxide, both in the ultraviolet region, the NO$_\gamma$ and NO$_\beta$ systems. They have both been studied in absorption at room temperature (see Refs. 18, 19 and 20), the gamma system has been measured in absorption (Ref. 21) at about 2000 K, and both have been studied in emission from air (Ref. 6). A table of the principal results for the transition probabilities, expressed in terms of the electronic $f$ value are shown on the next page.

For the $\gamma$ system there is good agreement between the absorption measurements (Refs. 19 and 20) at room temperature. The absorption measurements at 2000 K involve the measurement of different vibrational bands (transitions from the 1st, 2nd and
Table 1

<table>
<thead>
<tr>
<th>Method</th>
<th>Reference</th>
<th>$f_{el_y} \times 10^3$</th>
<th>$f_{el_g} \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption, room temperature NO</td>
<td>Weber and Penner (Ref. 19)</td>
<td>2.4 ± 0.4</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>Weber (Ref. 18)</td>
<td>...</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Bethke (Ref. 20)</td>
<td>2.2 ± 0.1</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>Absorption, shock heated NO</td>
<td>Daiber and Williams (Ref. 21)</td>
<td>3.4 ± 0.8</td>
<td>&lt;6</td>
</tr>
<tr>
<td>(~ 2000 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emission, shock heated air</td>
<td>Keck et al. (Ref. 6)</td>
<td>1 ± 0.5</td>
<td>6 ± 2</td>
</tr>
<tr>
<td>(~ 8000 K)</td>
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</tr>
</tbody>
</table>

3rd excited vibrational states), but it does not seem that this could account for a 50% increase in $f$ value. Thus Weber and Penner's value ($2.4 \times 10^{-3}$), used in the calculation of the tables of Ref. 9, is also favored here. In Fig. 9 these results are plotted in histogram form for 2000, 4000, 6000 and 8000 K. There is relatively little temperature dependence because of the low-lying energy levels that are involved in the absorption. The measured absorption coefficient for 2000 K (Ref. 21) is also plotted on this graph. The lower $f$ value (0.001) determined from the high temperature air measurements (Ref. 6) can be compared with these results using the formulas of Ref. 6. These results are plotted for 8000 K, and generally give a lower value, along with a somewhat different shape. In the spectral region where the NO$\gamma$ transition probability was determined in the air experiments, the two methods give radiation intensities which differ by a factor of 1.8 for the NO$\gamma$ system, but only a factor of about 1.2 in the total radiation (including NO$\beta$ and O$_2$ Schumann-Runge). Thus it appears that the results shown in Fig. 9, taken from Ref. 9, are not inconsistent with the air-radiation data of Ref. 6. The limit of error for this $f$ value quoted in Ref. 6 ($\pm50\%$) is almost enough to account for the discrepancy.

The NO$\beta$ system emits appreciable radiation throughout the ultraviolet and visible region. It is an important contributor to the total radiation from air at both low ($\sim 4000$ K) and high ($\sim 8000$ K) temperatures. The absorption measurements at room temperature by Weber (Ref. 19) are in substantial agreement with the emission measurements by Keck et al. (Ref. 6).
The absorption coefficient for high temperatures, calculated in Ref. 6 from Weber's f value (Ref. 19) is shown in Fig. 10 for 8000 K, along with the values given in Ref. 3 for 4000, 6000 and 8000 K, as determined from the air emission measurements. In the absorption experiments at 2000 K, the NO$\beta$ system was not observed (Ref. 21), so that only a rough upper limit to the f value could be determined. This limit is not in serious disagreement with any of the measured values. However, the detailed measurements by Bethke (Ref. 20) on the absorption of 9$\beta$ bands of NO in the ultraviolet present a definite disagreement with the other data. If Bethke's f value were taken in the calculation of Ref. 9, it would result in about one-fifth the observed radiation in the spectral region 0.35 to 0.50 $\mu$ where the intensity of the $\beta$ bands was determined. The reason for this discrepancy is not known, but in that the N$_2^+$ determinations of Ref. 6 are high by a factor of 2 or 3, it might well be expected that the curves shown in Fig. 10 should be decreased.

Free Electron Radiation

Radiation due to electron scattering (Brehmsstrahlung) is appreciable in the infrared region at very high temperatures. At 8000 K the electron-ion scattering is negligible, but radiation from air has been studied at this temperature in the 2 to 5 $\mu$ region by Wentink et al. (Ref. 22) and more recently by Taylor (Ref. 23). This radiation has been attributed to electron scattering by neutral atoms and molecules, and the data of Ref. 22 can be fitted (see Ref. 6) with the Kramers formula, considering the oxygen atom as the important scatterer

$$\frac{dI}{d\Omega d\lambda} = Z^2 \frac{16\pi}{3\sqrt{3}} \frac{e^6}{mc^2} \left(2\pi mkT\lambda\right)^{1/2} \lambda^{-2} [\sigma]_e \lambda^{-1} e^{-hc/kT\lambda} \tag{3}$$

and with $Z^2 = 0.04$. The more recent and much more complete measurements of Ref. 23 result in about half this radiation, so that a value of $Z^2 = 0.02$ gives a better description. However, the measured radiation falls off much more rapidly with increasing wavelength than would be predicted by the Kramers formula with a fixed effective nuclear charge. For air at 8000 K and with a density of 0.9 atm, the radiation falls smoothly from about 1.5 $w/cm^3$-ster-$\mu$ at 2$\mu$ to 0.15 at 5$\mu$. Since data are not available for any other test conditions, graphs of the radiation are not included in the present paper.

The radiation from collisions of electrons with ions ($z = 1$) becomes important at temperatures above 8000 K, along with electron capture by ions. These effects are calculated for air at 12,000 K in Ref. 9.
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The capture of electrons by neutral oxygen atoms to form $O^-$ results in a continuum radiation throughout the visible and ultraviolet region. Since this continuum is completely overlapped by the more intense molecular bands in high temperature air, shock tube experiments have not produced a measure of this radiation. However, it can be calculated from measurements of the $O^-$ photodetachment cross section by Branscomb et al. (Ref. 24). The results of these calculations are given in Ref. 9 for air at 6000, 8000 and 12,000 K for a range of air densities from $10^{-5}$ to 10 atm. They are plotted in Fig. 11 in terms of an absorption coefficient for $O^-$. Since there are no known bound states of $O^-$ other than the ground state, this absorption coefficient is independent of temperature. The values obtained in Ref. 6 for 8000 K air are consistent with these.

$NO_2$

At the lower temperatures ($\sim 3000$ K) that are of interest for radiation from wakes, recent measurements (Ref. 5) show a relatively strong continuum radiation from $\sim 0.4$ to $\sim 1.5 \mu$. This radiation is present in air, but not in $N_2$ or $O_2$ separately. It has been attributed to $NO_2$, both from the bound states and from the radiative recombination

$$NO + O \rightarrow NO_2 + h_\nu$$

Results for five experiments performed at temperatures in the neighborhood of 3700 K are shown in Fig. 12. The absorption coefficient shown is based on the population of $NO_2$ molecules, and the correlation is good. Further identification of the radiation is given by the slow rise in intensity behind shocks at lower temperatures ($\sim 2800$ K) consistent with the slow rate of formation of NO molecules. The curve drawn through the points is taken from the measurements of Fontijn and Schiff (Ref. 25) on the radiative recombination of NO + O observed at room temperature for the wavelength interval 0.40 to 0.62$\mu$, and a smooth curve is drawn through the longer wavelength data for each temperature. The absolute value of the total radiation is about one-twentieth the amount that would be predicted from the room temperature data (Ref. 25) based on the NO and O populations, but this decreased reaction rate constant is not unexpected at the higher temperatures. The values of the absorption coefficient between 3000 and 4000 K was determined experimentally to vary as

$$k_{NO_2} = k_{NO_2}^{3700^oK} \left( \frac{T}{3700} \right)^{1.5}$$ (4)
The total integrated emission from this radiation in air can be compared with values calculated by Kivel and Bailey (Ref. 26), based on NO$_2$ room temperature absorption measurements (Ref. 27). The room temperature absorption is strongest in the ultraviolet and violet regions of the spectrum. For air at 3700 K and 1 atm density, the NO$_2$ radiation predicted in Ref. 26 is 0.071 W/cm$^3$. The value determined from Fig. 12 is 0.66 W/cm$^3$. This difference is caused by the shifting of the absorption curve toward longer wavelengths at high temperatures, so that there is considerable emission in the red and infrared regions.

**CONCLUSION**

The data available for the radiation from air at temperatures up to 8000 K is compared graphically in terms of the absorption coefficients for the component species.

1) For the NO$_y$ and O$_2$ Schumann-Runge systems, there is substantial agreement among the various results.

2) There is a disagreement of a factor of 5 in the red-infrared region, where the N$_2$(1+) system is thought to be the sole contributor. For the N$_2^+$(1-) system, the results available also differ by a factor of about 5. In both cases, it is suggested in the present report that the lower values are to be preferred. For NO$_2$ (important at lower temperatures) the absorption and emission data disagree by a factor of about 10. There is also a sizable disagreement between room temperature absorption measurements and shock tube emission measurements for the NO$\beta$ system.

3) For N$_2$(2+), and free electron scattering, the data come from a single source, so that no comparison is possible.

**ACKNOWLEDGMENT**

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**REFERENCES**


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Fig. 1 Ultraviolet absorption spectra of oxygen at varying temperatures; optical pathlength ~ 50 cm·Atm (L = 6.4 cm, \( \rho \sim 8 \rho_o \)).
Fig. 2 Absorption spectrum of the (0,13) band; $T=3410$ K, $\rho = 3.6 \rho_0$. 
Fig. 3 $O_2$ Schumann-Runge absorption coefficient.
Fig. 4 $N_2(1+)$ absorption coefficient.
Fig. 5  Radiation from nitrogen first positive system; temperature = 6630 K, density = 0.88 $\rho_0$. 
Fig. 6 Temperature dependence of $N_2(1^+)$ radiation (Ref. 5).
Fig. 7 $N_2(2+)$ absorption coefficient.
Fig. 8  \( \text{N}_2^+ \) absorption coefficient (taken from Ref. 9 and scaled to \( f \)-value = 0.06).
Fig. 9 NO\textsubscript{y} absorption coefficient.
Fig. 10 NOβ absorption coefficient.
Fig. 11 0^- absorption coefficient, free-bound radiation (Ref. 9).
Fig. 12 NO₂ absorption coefficient near 3700 K (Ref. 5).