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EMISSION OF OPTICAL RADIATION
FROM HIGH PRESSURE GASES

by

Ralph Zirkind

December 1964

POLYTECHNIC INSTITUTE OF BROOKLYN

DEPARTMENT
of
AEROSPACE ENGINEERING
and
APPLIED MECHANICS

PIBAL REPORT NO. 814
EMISSION OF OPTICAL RADIATION FROM HIGH PRESSURE GASES

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Ralph Zirkind**
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SUMMARY

The observed spectral emittance of high temperature and density nitrogen was examined where the gas was compressed isentropically to a temperature and pressure of 7200°K and 4500 kg/cm² respectively. The analysis indicated that the radiation was composed of a near black body continuum and of nitrogen band emissions where the predominant bands were $N_2^+(1\mathbf{+})$, $N_2(1\mathbf{+})$ and $N_2(2\mathbf{+})$. Examination of the ratio of the latter two bands then made possible the reconstruction of the temperature history of the gas in the vicinity of peak compression. It was determined also that in comparison to the temperature, the relatively high density ratio of 250 played a minor role in the emitted radiant intensity.

†This research was conducted under the sponsorship of the Office of Naval Research under Contract No. Nonr 839(34), Project No. NR 061-135.
**Visiting Professor, Aerospace Engineering
SECTION I
INTRODUCTION

The ability to compress a gas, isentropically or adiabatically, permits the examination of the role that density plays in the spectral emittance of the compressed gas at optical frequencies.

In reference 1, Vodar and Vu reviewed the recent literature which pertains to the effects of pressure upon spectral line and band broadening; however, no considerations were included relative to density effects. In references 2 and 3, research on gases isentropically compressed to pressures as high as 8000 kg/cm² were reported. The methods used by both investigators are similar; that is, a piston is driven ballistically into a closed cylinder. The relationships of the state variables for fixed pressure ratio functions of \( \gamma \), the ratio of specific heats, are

\[
\frac{T_1}{T_0} = \left(\frac{P_1}{P_0}\right)^{\frac{\gamma - 1}{\gamma}} \quad \text{and} \quad \frac{\rho_1}{\rho_0} = \left(\frac{P_1}{P_0}\right)^{1/\gamma}
\]

where \( P, \rho \) and \( T \) have their usual meaning and subscripts "1" and "0" refer to final and initial conditions respectively. Now the value of \( \gamma \) is greatest for a monatomic gas, 5/3, and therefore can produce the highest temperature. In both instances argon gas was the working fluid.

The effects of adiabatic compression will be studied through the results obtained from the utilization of shock tubes. The real difference between the methods of compression is that for the same pressure ratio, the Rankine-Hugoniot conditions preclude a density ratio greater than \( \sim 4 \); The work in the United States at NOL, White Oaks, is relatively new in comparison to that in the U.S.S.R. and apparently is conducted without knowledge of it.
whereas, isentropically, a value of 250 can be achieved. That is, under the assumption of no ionization in argon (valid for shock velocities $M_1 < 10$), the density ratio is given by Eq. (2),

$$\frac{\rho_1}{\rho_0} = \frac{(\gamma + 1)M_1^2}{(\gamma - 1)M_1^2 + 2}.$$  

Hence, for $\gamma = 1.6$, the asymptotic value for $\rho_1/\rho_0$ is approximately 4, which is significantly different from the value in the isentropic case.

Since the intensity of absorption varies as the square of the density, one might expect a notable difference between the two cases.

The paper will present the experimental data and an analysis thereof, followed by a discussion of the results and comparison with theory.

SECTION II
EXPERIMENTAL DATA

In reference 2 the results of an experiment on high pressure industrial argon were reported. The constituents of the analyzed gas were found to be as follows: Argon - 94%; $N_2$ - 4%; $H_2O$ - 2%, and trace amounts of $O_2$. A maximum compression of 4500 kg/cm$^2$ was achieved in the experiment discussed here and the duration of radiation emission was 200 microseconds. The thermodynamic relation between pressure and temperature indicates that the gas temperature at peak compression is about 7200°K.

The published data in reference 2 are not complete; however, a sufficient quantity are available for meaningful analysis.

In Fig. 1, the intensity is plotted as a function of wavelength in the spectral range of $\lambda 265.0 - 420.0$ nm at three specific times, maximum compression and $\pm$ 10 microseconds thereof. The second set of data are time-resolved spectra which yielded an indication of the available species and contaminants, e.g., OH. The time-resolved spectrograms obtained prior to maximum compression, namely, those at 45 and 52 microseconds and the one at maximum compression, 100 microseconds, provided a
measure of \( N_2^+(2+) \) and \( N_2^-(1+) \).

The intensity ratio of the 428.0 \( \mu m \) and 568.0 \( \mu m \) bands of \( N_2^+(2+) \) and \( N_2^-(1+) \), as estimated from reference 2, is given in Table 1. The estimate provides for the contribution due to the continuum. In Fig. 2, the data of Table 1 are plotted together with calculated results.

The first and second positive \( N_2 \) bands were selected for study since they were readily identified and sufficiently displaced in wavelength.

**TABLE 1**

<table>
<thead>
<tr>
<th>Time (microseconds)</th>
<th>( I(5680)/I(4280) )</th>
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<tbody>
<tr>
<td>48</td>
<td>5.00</td>
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<tr>
<td>52</td>
<td>3.33</td>
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<tr>
<td>100</td>
<td>2.0</td>
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**SECTION III**

**DISCUSSION**

In Fig. 1, the relative spectral intensity at several wavelengths, 262, 362, and 410 \( \mu m \), for several times, maximum compression \( \neq 10 \ \mu \text{secs} \) are compared to the spectral intensities expected from a black body at 5500-7200\(^\circ\)K. The latter value corresponds to the temperature at maximum compression. In the spectral region of 2600 \( \mu m \) to 3600 \( \mu m \) the slope of both the pre-maximum and post-maximum data points, when normalized to the intensity at 262 \( \mu m \), yields a temperature of about 6500\(^\circ\)K. At maximum compression, the slope would correspond to approximately 7200\(^\circ\)K. The real departure from a black body occurs for the wavelength value of 4100 \( \mu m \). The possible contributions at this wavelength are (1) \( N_2^+(1-) \) and (2) NO 8. The latter possibility may be discarded for the following two reasons:
(1) the spectrograms show a marked intensity drop between 470-540 mμ, which would be filled in if NO was significant, and
(2) above 4000°K, the temperature regime of interest here, NO commences to dissociate, the dissociation becoming nearly complete at ~6500°K.

If the contribution of N2⁺(l⁻) is subtracted from the total, the value at 410 mμ drops to ~19 and the data points behave more nearly like a black body.

In Fig. 2, the calculated relative intensity ratio of N2⁺(l+) to N2(2+) at wavelengths 568, 428 mμ respectively, are plotted as a function of temperature and density ratio. The experimental values, Table 1, obtained at times equal to maximum compression (ρ/ρ0 ~ 250) and somewhat earlier times, are also presented. The value at maximum compression gives a temperature value of 7250°K, which corresponds very closely to the expected temperature of the compressed Argon gas. The temperature of the gas, as estimated from Fig. 2, would be about 6000°K and 5100°K, which is reasonable. These data further support the argument made above, that NO contributes little or no radiation to the total observed radiation.

SECTION IV
CONCLUDING REMARKS

The observed optical radiation from industrial argon (argon plus nitrogen) has been examined and analyzed. From a comparison of the time-resolved spectra, the relative contributions from the continuum and band emitters have been estimated.

The first result obtained is that the compressed argon gas behaves like a black body emitter where the temperatures correspond to those values calculated from the standard laws for ideal gases. Secondly, NO⁺ does not contribute to the radiation as expected, and the primary band emitters are N2(2+) and N2(l+) with a contribution from N2⁺(l⁻). Finally,
the optical behavior of gas at densities ratio as high as 250 is still primarily determined by the gas temperature.

The experimental method discussed in this paper would provide an interesting procedure for the study of electronic excitation of molecules. The latter area is an important region and at present inadequately covered.

SECTION V

REFERENCES


FIG. 1. RELATIVE INTENSITY vs $\lambda$ FOR SEVERAL TIMES
FIG. 2. BAND INTENSITY RATIO AS A FUNCTION OF TEMPERATURE

- EXPERIMENTAL ($\frac{\rho}{\rho_0} = 250$)
- CALCULATED
The observed spectral emittance of high temperature and density nitrogen was examined where the gas was compressed isentropically to a temperature and pressure of 7200 K and 4500 kg/cm² respectively. The analysis indicated that the radiation was composed of a near black body continuum and of nitrogen band emissions where the predominant bands were $N_2(1-), N_2(1+)$ and $N_2(2+)$. Examination of the ratio of the latter two bands then made possible the reconstruction of the temperature history of the gas in the vicinity of peak compression. It was determined also that in comparison to the temperature, the relatively high density ratio of 250 played a minor role in the emitted radiant intensity.
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