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RADIATION FROM HOT NITROGEN*

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Abstract—The equilibrium radiation emitted by shock heated nitrogen has been studied in the wavelength range 3300 to 7100Å at an equilibrium temperature from 6000°–7000°K and densities 0·01 to 0·20 times atmospheric. Identification of the various radiating band systems was accomplished by spectroscopic techniques. The absolute intensity versus wave length profile at thermodynamic equilibrium was obtained using photometric methods. By comparing this profile with theoretical predictions, the electronic *f*-number for the $N_2^+(1-)$ system was found to be 0·09 ± 0·05. CN and O_2 contamination effects were also investigated. By studying the density dependence of the radiation, the collisional deactivation cross-section for this band was found to be greater than 10^{-15} cm^2.

I. INTRODUCTION

RECENT interest in the field of hypersonic aerodynamics and atmospheric physics has made necessary the quantitative understanding of optical radiation from air. The versatility of the shock tube for making spectroscopic study of hot gases has already been shown by many workers, and a method of obtaining electronic transition probabilities for molecules has been demonstrated by KECK *et al.*[1] in studies made of air.

This paper describes a study of the radiation from shock heated nitrogen which was undertaken as a preliminary step in an experiment to determine the dissociation rate of nitrogen. Photographic and spectroscopic methods were employed to examine the gross characteristics of the shock and to identify the various radiating species. Absolute intensity measurements were made so that theory and experiment could be compared. These intensity measurements are presented graphically along with the theoretical calculations based on the known existing electronic transition moments published by other workers. Oxygen and CN contamination effects on the equilibrium radiation were investigated quantitatively as well as qualitatively and comparison between the observations and theory was made.

II. EXPERIMENTAL EQUIPMENT

A schematic diagram of the shock tube, recording equipment and optical arrangement, is shown in Fig. 1. The shock tube has a 15 ft pyrex test section of 1·5 in. inside diameter. The high pressure driver section was separated from the low pressure test section by a steel diaphram. The driver was of stainless steel 3 ft long and 1·5 in. inside diameter. The test section was evacuated by an oil diffusion pump prior to introducing the test gas. Pressures of less than 2·0 μ of Hg and virtual leak rates of less than 1·0 μ of Hg per min were obtained.

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A flow system was used to minimize impurities due to out gassing of the apparatus. Also used was a liquid nitrogen cold trap to remove water vapor from the N_2. Initial pressure in the test section was measured by a manometer with an estimated maximum error of 0·4 per cent.

The shock speeds were measured by observing with a single photomultiplier the radiation from the shock as it passed a series of six equally spaced slits arranged 10 in. apart along

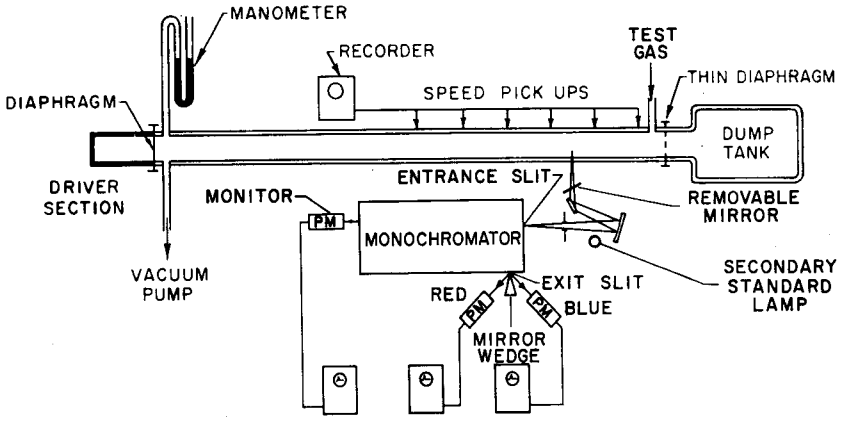

FIG. 1. Schematic diagram of experimental apparatus.

the last half of the shock tube. The output of the photomultiplier was doubly differentiated and displayed on a folded oscilloscope sweep which was normally read to the nearest 0·4 μ sec. A speed profile was constructed and the velocity at the test point was determined with a maximum error of about 1 per cent. At the position in the shock where the equilibrium measurements were made, the error in intensity measurements due to attenuation was less than 2 per cent.

III. EXPERIMENTAL RESULTS

Fig. 2a shows time resolved photograph of a typical shock wave as it passes the test point. Study of the photograph shows an abrupt onset of radiation. Also the photo shows very little change in radiation after the first 5 μ sec. This gives strong evidence that the test gas has reached thermodynamic equilibrium. Note that because of the circular cross-section of the shock tube and the thinness of the test gas, the radiation is stronger at the center then near the walls. Fig. 2c shows the radiation profile taken with a photomultiplier, the resolution of which was 0·13 μ sec, and filter, the wavelength response of which was in the 0·55–1·1 μ region. Here the radiation is observed to rise to peak value in less than a half μ sec and then decay to an equilibrium value which remains relatively constant for approximately 15 μ sec and then is terminated by the driver gas interface. Generally a slight increase in equilibrium intensity was observed as one moved back in the shock because of attenuation effects. This phenomenon would be expected since as one moved back from the shock front, one would be looking at gas which had been heated to a higher temperature than that gas which is observed nearer the shock front.

In order to be certain of the origin of the radiation being studied, spectra were taken of the shock waves using the race track techniques reported by ROSA[2]. Typical race track

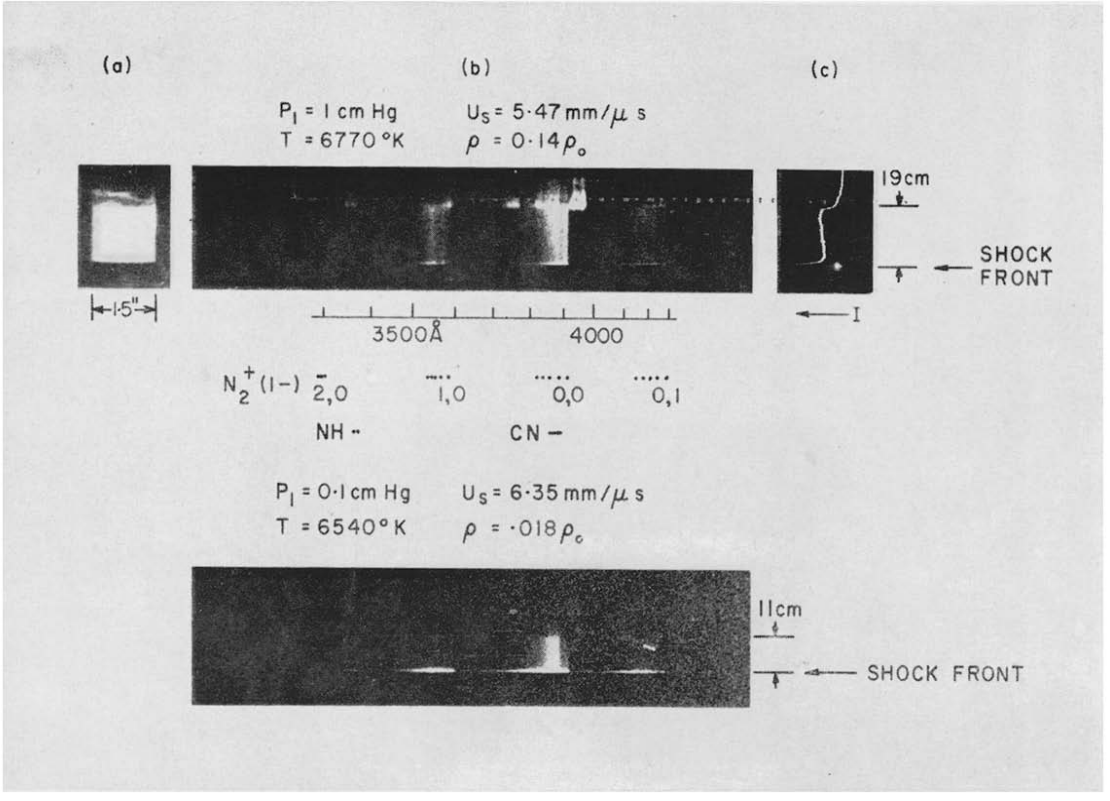

FIG. 2. (a) Time resolved photograph of normal shocks in nitrogen. (b) Race track spectrograms of shock waves in nitrogen. The overshoot and equilibrium radiation of the $N_2^+(1-)$ radiation is clearly identified. (c) Oscillogram record of radiation observed in the 0·55–1·1 μ region showing the radiative overshoot and relatively flat equilibrium region. All pictures on the top line are scaled to the same shock thickness.

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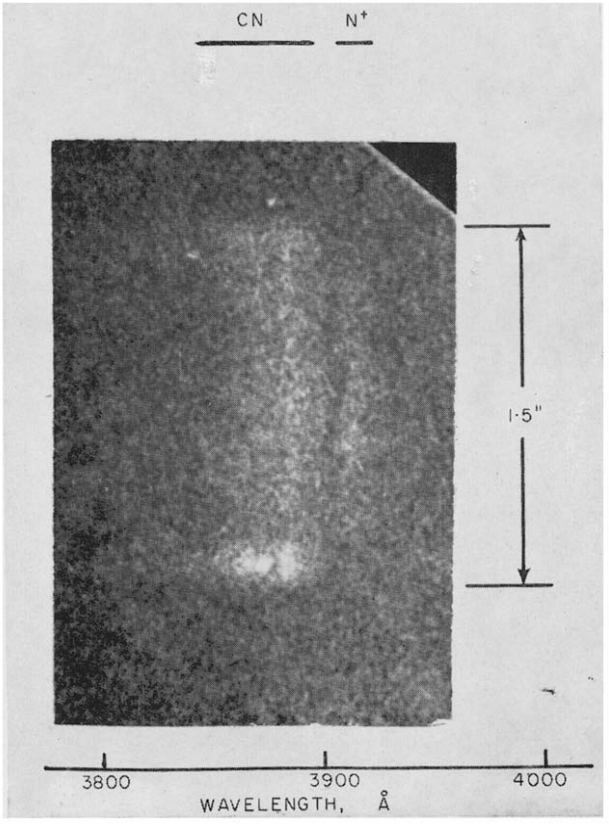

FIG. 3. Spectrogram obtained with slit of spectrograph perpendicular to axis of shock tube driver passage of a 5·1 mm/μ sec shock through nitrogen at a pressure of 1 cm Hg. The CN radiation is confined mainly to the shock tube walls.

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spectrograms with the radiating species identified are presented in Fig. 2b. Most of the radiation is seen to be due to N_2^+ molecules, and small amounts due to impurity CN and NH molecules. Attempts to reduce the impurity level provided evidence that most of the CN molecules were at, or near the walls of the pyrex tube. This was verified by the spectrogram shown in Fig. 3. The fact that the radiation intensity from N_2^+ appears to diminish near the edges of the tube shows that N_2^+ molecules are evenly distributed across the tube, while the fact that the radiation from CN is most intense at the edges of the tube proves that the CN molecules are more dense along the walls of the tube.

For 4–7 mm/μ sec shock waves in pure nitrogen at initial pressures from 20–1·0 mm Hg, the N_2^+ (1−) and N_2 (1+) radiation was observed to rise abruptly at the onset of the shock front to a peak value then decay in a few μ sec, corresponding to a temperature relaxation to an equilibrium level. This equilibrium level was observed to remain relatively constant for approximately 15 μ sec until the passage of the driver gas interface. Radiation from impurities was observed to be confined mainly to the shock tube walls.

IV. MEASUREMENTS

A. Apparatus and calibration

Measurements of the spectral intensity at equilibrium were made using a calibrated dual-channel grating monochromator. The experimental apparatus is shown schematically in Fig. 1. The entrance slit of the monochromator was imaged perpendicular to the shock tube at the center of the test gas by an optical train consisting of two aluminized mirrors. The monochromator was equipped with three photomultipliers; two which measured the radiation intensity in adjacent narrow wavelength bands selected by the monochromator and the third which monitored a fraction of the radiation passing through the entrance slit. Dumont 6292 and K1292 photomultipliers were used, and their outputs were fed directly to Tektronix 545 oscilloscopes equipped with 53K/54K preamplifiers.

Calibration of the complete optical train including shock tube windows and appropriate filters to prevent overlapping of orders was made using a secondary standard tungsten ribbon filament lamp which had been compared against a primary standard. The brightness temperature of the primary standard lamp was given as a function of lamp current at a wavelength of 6530Å by the National Bureau of Standards. The spectral intensity of the lamp was calculated at other wavelengths using data on the emissivity of tungsten given by DeVos[3]. The secondary standard lamp was placed permanently in position on the monochromator stand with a front surfaced aluminized mirror which could be swung into position in front of the shock tube in order to image the tungsten ribbon filament at the entrance slit of the monochromator. A section of shock tube was placed in the spectral path directly in front of the lamp to correct for transmission of light through the shock tube wall. The calibrated secondary lamp was used to calibrate from 3300Å to 7100Å and frequent checks were made on the calibration of the system. Thus, error due to voltage and photomultiplier drift was essentially eliminated.

The brightness temperature of the primary and secondary standards were checked using a Leeds and Northrup optical pyrometer. The temperatures checked to within 9° of that given by the National Bureau of Standards. The total maximum reading error of absolute intensity measurements was $\pm$15 per cent.

The monochromator was calibrated for wavelength with a mercury lamp. The error in setting the monochromator was $\pm$5Å.

B. Spectral distribution

Figure 4 shows absolute intensity measurements in the 3300Å–7100Å region of the equilibrium radiation from shocks in pure nitrogen at an initial pressure of 1·0 cm Hg. Since all the runs were not at exactly the same shock speed, they were extrapolated to 4·8 mm/μ sec equivalent to an equilibrium temperature of 6300°K as obtained from FELDMAN'S tables.[4] The variation of intensity with shock speed given by the theory outlined in reference (1) was used as a guide in this extrapolation. For each run there were two measure-

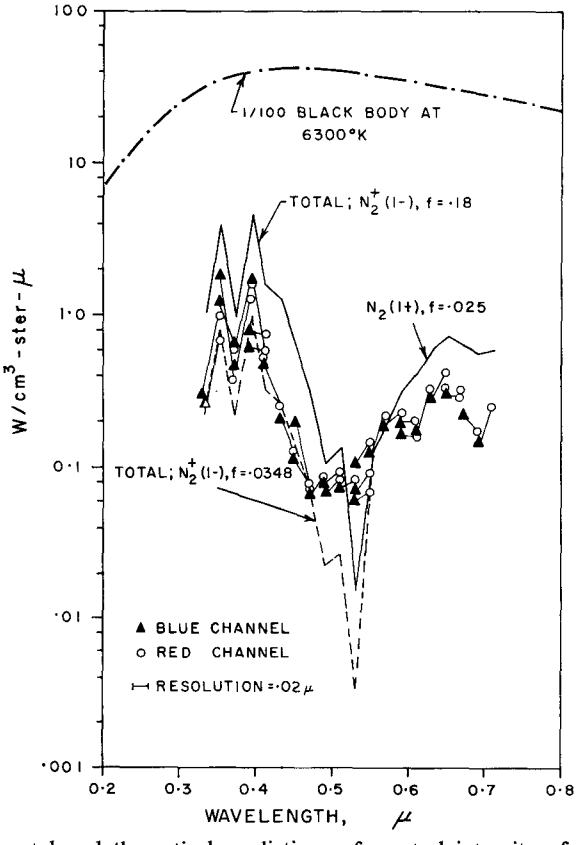

FIG. 4. Experimental and theoretical predictions of spectral intensity of nitrogen at $T =$ 6300°K and $\rho = 12\rho_0$ ($P_1 = 1$ cm Hg and $U_s = 4{\cdot}8$ mm/μ sec). The theoretical lines are based on f-numbers reported by the various workers mentioned in the text.

ments in adjacent monochromator channels—one represented by the solid triangle in Fig. 4 and the other by the open circles. Short lines are used to connect the two intensity measurements obtained for each run.

The theoretical lines superimposed on the experimental points are obtained using the theory outlined in reference (1), and are based upon the concentration of species in the absorbing state, the spectral distribution function averaged over the wavelength interval observed, the absolute temperature and the electronic f-number. The solid segmented line is the theoretical spectral distribution based on f-numbers reported elsewhere[1] for the N_2^+ (1−) and N_2 (1+) systems. The dashed segmented line is the theory using the f-number

reported by BENNET and DALBY[5] for the N_2^+ (1—) system. The discrepancy in the 0·52 μ region was attributed to a small amount of scattered radiation.

C. Shock speed dependence

The problem of extrapolating the equilibrium radiation to obtain the spectral distribution at a given temperature as well as understanding attenuation effects makes the optical

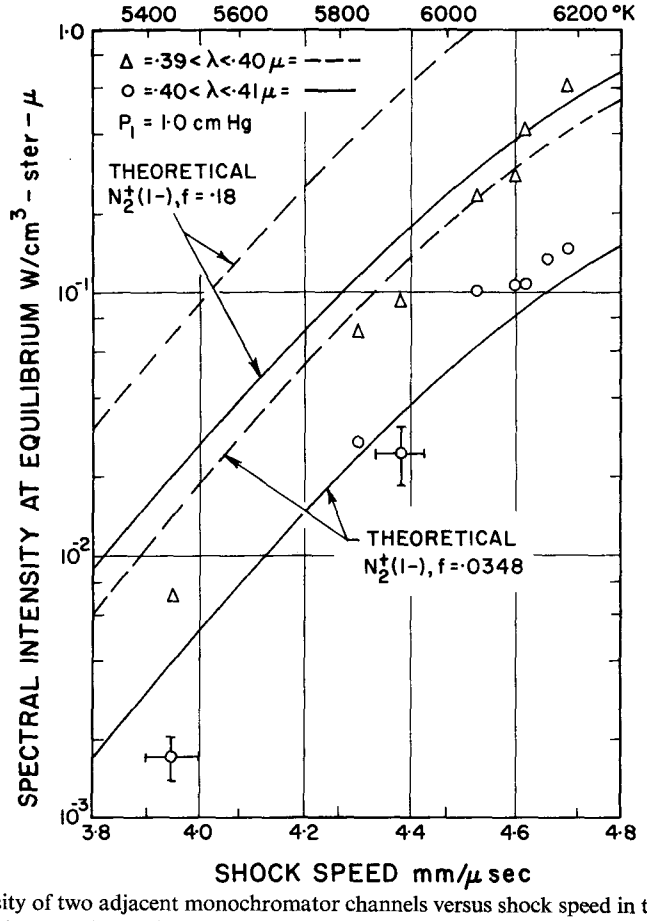

FIG. 5. Intensity of two adjacent monochromator channels versus shock speed in the N_2^+(1—) region comparing experimental observations with theoretical predictions based on the *f*-number of the N_2^+(1—) system reported by KECK *et al.*[1] (0·18) and BENNET and DALBY[5] (0·0348).

intensity dependence on shock speeds of interest. Shocks with the same monochromator setting were run at various shock speeds and are displayed in Fig. 5. Theoretical lines are constructed using the *f*-numbers for the N_2^+ (1—) system reported by both Keck *et al.* and Bennet and Dalby. It is upon these theoretical curves that the extrapolation in Fig. 4 is based. From this curve it can be seen that 1 per cent change in shock speed produces approximately 19 per cent change in radiant intensity of the N_2^+ (1—) system.

D. Effect of impurities

The presence of CN contamination has always been a problem in shock tube experiments and there has been much effort to eliminate it by such measures as using a pyrex shock tube

initially evacuating to low pressure and incorporating a flow system with a liquid N_2 trap to minimize impurities from outgassing. Under these conditions the CN radiation from shocks in pure nitrogen as observed spectroscopically (Fig. 3) is confined to the shock tube walls.

The effect of CN contamination was further investigated by introducing 2 per cent C_2H_2. One channel of the monochromator was set on the 3888 CN band head; the other on N_2^+ (1—) radiation. A Dumont K1292 photomultiplier was used as the monitor with an appropriate filter so that it monitored essentially only the N_2^+ (1+) radiation. Several runs at identical shock speeds were made with and without C_2H_2 contamination. The results for the equilibrium radiation are displayed in Table 1 and normalized to the pure N_2 run. It can

TABLE 1. SHOWING EFFECT OF 2% C_2H_2 CONTAMINATION ON EQUILIBRIUM INTENSITY MEASUREMENTS—ALL RESULTS BEING NORMALIZED TO THE RESULTS FOR THE PURE NITROGEN RUN. CN CONTAMINATION PRODUCES NO NOTICEABLE EFFECT EXCEPT IN THE CN VIOLET REGION WHERE THE RADIATION IS GREATLY ENHANCED.

Gas $P_1 = 1$ cm Hg	Us $\frac{\text{mm}}{\mu\,\text{sec}}$	$0{\cdot}38 < \lambda < 0{\cdot}39\,\mu$ [CN band head] $I/I_{100\%N_2}$	$0{\cdot}39 < \lambda < 0{\cdot}40\,\mu$ [N_2^+ (1—) band head] $I/I_{100\%N_2}$	$0{\cdot}55 < \lambda < 1{\cdot}1\,\mu$ [N_2 (1+) system] $I/I_{100\%N_2}$
100% N_2	4·93	1	1	1
2% C_2H_2	4·98	8·05	1·01	1

be seen that the CN 3883 band radiation increased by a factor of 8 while there was no apparent change in the adjacent channel observing part of the N_2^+ (1—) system or in the N_2 (1+) radiation in the 0·55–1·1 μ wavelength interval. Since the CN red system radiates in the 0·55–1·1 μ region, this indicates that the red system is much less intense than the violet system and is, therefore, unlikely to effect the results of experiments carried out in the red region of the spectrum even though the CN contamination may be appreciable.

If there were NO present in the test gas excess electrons would be produced by its dissociating to NO^+ and e^- as reported by LAMB and LIN[6]. Since excess electrons would tend to suppress the N_2^+ concentration a false determination of the f-number for the N_2^+ (1—) system would be produced by the existence of electron contamination. To investigate this effect known amounts of oxygen up to 5 per cent were introduced into the test gas and the radiation across the 3914 N_2^+ (1—) band head was observed. The difference between the two adjacent channels versus O_2 contamination is displayed in Fig. 6. By taking the difference between the two channels, the possibility of a small contribution from impurity radiation is eliminated. The theoretical lines are based upon the chemistry of the hot gas at an equilibrium temperature of 6100°K. The results of these oxygen contamination runs show the N_2^+ (1—) radiation sensitiveness to electron concentration and also demonstrates that the nitrogen runs are reasonably pure.

E. Density dependence

"Collision limiting" of radiation occurs when the depopulation of an excited state of a molecule by radiation becomes significant compared with the depopulation of that state by collision. When this condition occurs one may have steady state radiation at a value considerably less than the equilibrium value. In this study the equilibrium radiation of the N_2 (1+) and N_2^+ (1—) systems was observed not to be "collision limited". This was deduced from the fact that there was no lowering in the apparent f-numbers for runs made

with initial pressures of 0·1 cm Hg as compared with runs made with initial pressures of 1·0 cm Hg. With the observation that these runs at 0.1 cm Hg were not collision limited, a minimum limiting value for the collisional deactivation cross-section can be determined based on the relations given by KECK *et al.*[1]. The results show that collisional deactivation cross-section is greater than or equal to 10^{-15} cm for the N_2^+ (1—) system and 10^{-16} cm for the N_2 (1+) system.

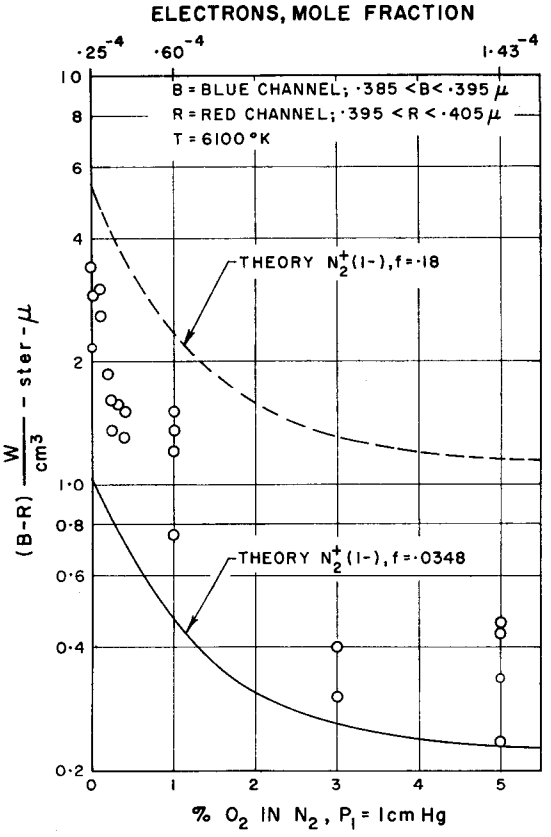

FIG. 6. Intensity difference across 3914 N^+ (1—) band head versus oxygen contamination. The two theoretical lines are based upon the *f*-number reported by KECK *et al.*[1] (0·18) and BENNET and DALBY[5] (0·0348). The depressing effect on the N_2^+ radiation by excess electrons is demonstrated here since NO readily dissociates to NO^+ and e^-.

F. Electronic f-*numbers*

Following the method outlined by KECK *et al.*[1], an electronic *f*-number of 0·09 ± 0·05 for the N_2^+ (1—) system was determined by fitting the data in Figs. 4, 5 and 6. Although some data were obtained in the wavelength region of the N_2 (1+) system, it was not considered sufficient to warrant a detailed analysis. As can be seen in Fig. 4, however, the data which were obtained are a little lower than expected for the *f*-number of 0·025 reported by Keck *et al.* which suggests that this value may be a little high. It was not possible to obtain any information on the N_2 (2+) radiation in these experiments due to the fact that the radiation from this band system is very small in the wavelength region covered.

The value of $0{\cdot}09 \pm 0{\cdot}05$ for the *f*-number of the N_2^+ (1−) system determined in this study lies between the values of $0{\cdot}18 \pm 0{\cdot}09$ reported by Keck *et al.* and $0{\cdot}0348 \pm 0{\cdot}002$ reported by Bennet and Dalby. It, therefore, does little to resolve the question as to which of the previous values is to be preferred. Since the method of this experiment is the same as that of Keck *et al.* the comparison of these two experiments does not give any information on the validity of the method but is primarily a check on the unfolding procedure used in the earlier experiments, and the general cleanliness of the shock tube. In this regard, it is felt that the most likely explanation of the larger *f*-number reported by Keck *et al.* is associated with the difficulty of eliminating impurity radiation from CN in the stainless steel shock tubes employed. With reference to the measurements of Bennet and Dalby we note that their method involves an observation of the decay time of the radiation from the N_2^+ (1−) system and is completely independent of the method employed here. Although it is difficult to find fault with their technique, there is the possibility that in a highly non-equilibrium situation, the population in the radiating state may be fed from higher states thus increasing the apparent lifetime and leading to a low *f*-number.

In concluding this discussion we should like to comment on a few of the problems associated with the use of the shock tube technique employed in this experiment for making *f*-number determinations.

First, there is the problem of precisely determining the gas temperature. The temperatures used in this study were obtained from FELDMAN'S tables[4] and are based on the continuity, momentum and energy equations across the shock front and an equation of state which assumes full thermodynamic equilibrium. PARKINSON and NICHOLLS[7], by spectroscopic methods and the use of "thermometric" molecules, obtained rotational temperatures in shock heated gases which are slightly lower (10–15 per cent) than the gas kinetic temperatures calculated from the shock velocities. Although it is our opinion that the method employed by us is the more accurate, we should like to point out that the assumption of a lower temperature would lead to higher apparent *f*-numbers further increasing the discrepancy between the shock tube measurements and those of Bennet and Dalby.

Second, there is the problem of accounting for effects of shock speed attenuation and boundary layer growth. The results of this study were relatively free of attenuation effects as indicated by the measured shock speeds and the flat region of radiation behind the shock front which rose only slightly until passage of the driver gas interface. This flat region of the equilibrium radiation and the fact that CN radiation in pure nitrogen shocks was observed to be confined along the shock tube walls also indicates that the test region was free of boundary layer effects.

Finally, there is the problem of dealing with impurities. By purposely introducing impurities, several possible sources of experimental error were found to be negligible. There was no CN red contribution to the N_2 (1+) radiation in a CN contaminated shock. Although the violet bands radiated strongly in the N_2^+ (1−) region, the N_2^+ (1−) radiation intensity could still be effectively measured in these contaminated runs by observing the radiation away from the CN violet bands. The depression of the N_2^+ (1−) radiation by excess electrons was studied by introducing small amounts of oxygen into the test gas. The observed effect was that which was predicted based on the equilibrium concentrations[8] of the various species and the gas kinetic temperature. The results indicate that the pure nitrogen runs were free of excess electrons.

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