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PRIMARY AND AFTERGLOW EMISSION FROM SUPERCOOLED NITROGEN EXCITED BY FAST ELECTRONS

by

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ABSTRACT

Measurements were made of the primary and afterglow emission lifetimes of some of the emitting species in an expanded nitrogen flow at 16° K and 30 microns Hg when excited by a 10 kV electron beam. Both the first negative system of N_2^+ and the second positive system of N_2 were observed in the afterglow to persist in the order of 2×10^{-6} seconds. The afterglow was swept downstream of the beam by the high velocity nitrogen stream so that it could be observed independent of the primary emission. The origin of the afterglow is explained by the possible transfer of energy from ground state N_2^+ ions and secondary electrons to ground state N_2 molecules. This is substantiated by observations of the departure from a Boltzmann distribution of the rotational energies in the N_2 molecules. In air, the afterglow was greatly quenched by the O_2 molecules and in nitrogen at a temperature above supersaturation no afterglow was observed.

INTRODUCTION

The technique of energetic electron excitation of gases including nitrogen has been investigated at some length[1,2] but the results were

[1] G. O. Langstroth: Proc. Royal Soc. A146,166, 1934.

[2] G. Davidson and R. O'Neil: AFCRL Report 64-466, 1, 1964.

generally limited to gas temperatures at or above room temperature. Since a determination of the characteristics of the radiated spectra from the excited gas is basic to an understanding of the energy transfer processes involved, this investigation was undertaken to extend these measurements to supercooled gaseous nitrogen (16° K at 30 microns Hg) where an afterglow was observed. The method used is unique in that the low temperature was achieved by expanding compressed nitrogen through a convergent-divergent nozzle into an evacuated chamber where the afterglow was separated from the primary emission due to the high directed velocity of the nitrogen stream. Both the primary and afterglow emission spectra were recorded independently from 3100 Å to 4300 Å and the radiative lifetimes of the afterglow was measured.

Collision processes are postulated to explain the afterglow by reason of a departure from a Boltzmann distribution of the rotational energies found in the N_2 molecule. No afterglow was observed in electron excited nitrogen at 60° K which is above the supersaturated region and the afterglow in electron excited air at 16° K was greatly quenched by the O_2 present. An application for the observed phenomena such as flow field visualization studies is demonstrated.

EXPERIMENTAL METHODS

A diagram of the apparatus used for this investigation is shown in figure 1. The electron beam device has been described previously[3] and has the capacity to produce a constant electron beam current of up to 500 microamps or be pulsed to measure lifetimes on the order of 10^{-8} seconds.

[3]D. I. Sebacher: Jour of Chem. Phys. 31, 1368, 1965.

The emission spectrum from the beam or from the afterglow could be scanned independently by proper allignment of the spectrograph and light stops shown in figure 1. The sensing element was a 1P28 photomultiplier, the spectrograph was a 2.25-m Ebert with a 30,000 line/inch grating and the output from the phototube was fed to a micromicroammeter whose output was displayed on a strip recorder.

Direct measurements of the radiative lifetimes were obtained by exciting the gas molecules by electron bombardment and then observing the photon emission as a function of time after the electron beam was cut off. This method of measuring radiative lifetimes has been explained in detail[3] and as described a 6810-A photomultiplier was used along with a narrow bandpass interference filter. The response of the lifetime detection system was in the order of a few nanoseconds and a quartz optical system was used throughout.

The nitrogen flow system shown in figure 1 consisted of a stagnation chamber which was maintained at a pressure of 2 atmospheres, a 5° half-angle convergent-divergent conical nozzle and a test section. The vacuum system consisting of a five-stage steam ejector could maintain the low pressure required in the test section at the flow rate used. In the diagram, the electron beam is coming out of the page and the light emitted by the excited gas molecules is viewed by the spectrograph and photomultipliers at a right angle to the well defined beam. The gas used was commercial grade nitrogen which was found to have an impurity content of 0.01 percent H_2O, but this impurity did not change the measured lifetime from these measured in research grade nitrogen.

RESULTS AND DISCUSSION

Afterglow

The afterglow present in the beam excited cold nitrogen flow is easily visible to the eye in a darkened room. This is demonstrated in figure 2 where photographs are shown of the light emission produced by the electron beam at room temperature where no afterglow was observed, and in the cold flowing N_2 where the afterglow is blown downstream of the beam. A search was also made for afterglow at higher pressures and at room temperature such that the nitrogen density was equivalent to that in the cold temperature experiments. However, since no afterglow was found at these conditions, this indicates that the phenomena is temperature dependent. The freestream temperature and pressure of 16° K at 30 microns Hg were calculated from the ratio of the throat area to the area of the expanded stream made visible by the electron beam and assuming a perfect gas expansion (see figure 2(b)). This was in substantial agreement with pitot pressure measurements.

Emission spectrums were measured from the beam and from the afterglow and these are shown in figure 3. Figure 3(a) is a trace taken from the beam in stagnant N_2 at 297° K and 30 microns Hg, where it is seen that the (0,0) vibrational band of N_2^+ (3914 Å) is dominant over the wavelength range measured. The intensities shown have not been corrected for the wavelength sensitivity of the 1P28 photomultiplier. Figure 3(b) is a trace taken from the beam of the cold expanded N_2 and it shows a considerable change in the vibrational intensity distribution between the first negative system of N_2^+ and the second positive system of N_2 with the N_2 bands gaining in relative strength.

Figures 3(c) and 3(d) are traces at approximately 1/2-inch downstream of the beam in the afterglow and at 1-1/2-inches downstream of the beam in the afterglow with the light from the beam completely blocked out. From these traces it can be seen that both the first negative system of N_2^+ and the second positive system of N_2 are found in the afterglow and that the N_2 vibrational bands now dominate the N_2^+ vibrational bands. This is opposite to the case found in the primary emission of the beam. This dominance of the N_2 bands is seen to increase at increasing distance away from the primary source. There was no observable changes in the relative intensities of the bands within the given systems measured.

ROTATIONAL INTENSITY DISTRIBUTION

The traces in figures 3(c) and 3(d) show an obvious divergence of the rotational intensity distribution in the afterglow for the N_2 bands which is not present in the N_2^+ bands. This divergence is seen by the tailing toward the lower wavelengths for each N_2 band taken in the afterglow. This tailing indicates that the intensities of the higher rotational levels are greater than they should be at 16° K if the rotational energies can be described by a Boltzmann distribution.

Measurements were made of the rotational intensity distribution of both the first negative (0,0) band of N_2^+ at 3914 Å and the second positive (0,0) band of N_2 at 3371 Å from the electron beam and from the afterglow. These intensity distributions are presented in figure 4 and figure 5 in the usual manner of a plot of $\log (I/K')$ against $(K'(K'+1)$, where I is the rotational line relative intensity and K' is the rotational

quantum number of the upper state in transition. The rotational lines in these vibrational bands were not resolved so that the slope of the plots indicates too high a temperature. Despite this, the figures are useful in that a straight line plot indicates a Boltzmann distribution of the rotational energies while a curving line indicates a non-Boltzmann distribution.

Figure 4 shows a straight line slope for the 3914 Å band of N_2^+ in both the electron beam and the afterglow. Figure 5 shows a straight line slope for the 3371 Å band of N_2 in the electron beam but a curve that strongly diverges from a straight line in the afterglow.

This divergence observed in the rotational energy distribution of the 3371 Å band of N_2 can be explained in terms of changes in the internal motion of the nitrogen molecule assuming slow heavy molecules are the exciting particles. In this case, the collision duration will be significantly longer than for fast electron impact, and the Frank-Condon principle is no longer applicable. This effect is in agreement with previous experiments[3,4]. The straight line slope for the 3914 Å band of N_2^+ in the afterglow indicates that secondary electrons must be the exciting particles causing this emission in the afterglow. These secondary electrons would require energies greater than 18.7 ev to excite ground state N_2 molecules or 3.1 ev to excite ground state N_2^+ ions to the upper level of the 3914 Å transition. The most likely excitation path is a direct excitation from the $N_2 X^1\Sigma$ state to the $N_2^+ B^2\Sigma$ state. This is reasoned because of the observed relative ease by which even low energy electrons (20 ev) can ionize the ground

[4]F. M. Reeves and R. W. Nicholls: Proc. Phys. Soc. (London) 78,588 (1961)

state N_2 molecule[5] and the much greater population of N_2 ground state molecules.

The only known heavy particles which exist in the flow that possess the required energy and lifetime to excite the upper state of the second positive system of N_2 in the afterglow are the ground state N_2^+ ions (15.6 ev). These excited particles are left over from the 3914 Å transition caused by both the primary electrons (10 Kev) and the secondary electrons in the afterglow. This concept is substantiated by the relative increase in the intensity of the second positive system in relation to the first negative system in the later afterglow, figure 3(d), than in the nearer afterglow, figure 3(c). The relative population of ground state ions to secondary electrons possessing the required energy would therefore increase causing the N_2 positive bands to gain in relative strength.

LIFETIMES

It has been shown previously[3,5] that the lifetimes of a particular vibrational state can be measured from a recording of the emission intensity time history of one of the observable transitions, if no additional molecules are added to this state.

The radiative lifetimes of the upper state of the 3914 Å transition of N_2^+ and the 3371 Å transition of N_2 have been measured[3,5] and are known to be in the order of 10^{-8} seconds. If these vibrational bands are observed in the afterglow at times greater than their lifetimes, then it is apparent that additional molecules are populating the upper state after the original excitation source has been removed.

[5] T. G. Bennett and F. N. Dalby: Jour. Chem. Phys. 31,439 (1959)

Figure 6 shows some typical oscilloscope traces of the buildup and free decay of light from the beam and from the afterglow along with a trace of the excitation pulse. The logarithms of the relative intensities of the decay taken from these traces were plotted against time to obtain the radiative lifetimes. For N_2 at 297° K, the lifetime was 6.5×10^{-8} seconds which corresponds to the lifetime of the 3914 Å transition since this band is dominant at this temperature over the spectral range of the 6810-A.

Figure 6(b) shows the buildup and decay of the total light from the beam and afterglow in the cold expanded nitrogen and from this trace it can be seen that the afterglow peaks about 10^{-6} seconds after the beam has been cut off and then decays with a lifetime of 2.7×10^{-7} seconds. In order to determine any difference in the lifetime characteristics of the different bands found in the afterglow, a measurement was made of only the 3914 Å transition by placing a narrow band pass interference filter in front of the photomultiplier. This trace, shown in figure 6(c), indicates that the 3914 Å transition peaks at the same time with less intensity but has the same radiative decay as the total afterglow. It would appear that the afterglow lifetime is dependent on both the rate of collisions between the secondary electron and N_2^+ ions with N_2 molecules and the ionic recombination rate.

HIGHER TEMPERATURES AND AIR

The temperature of the expanded N_2 in the test chamber was raised to the range from 60° to 170° K by heating the gas in the stagnation chamber with an electric arc heater. The above procedure was then repeated but no afterglow was detected downstream of the electron beam. Because of the difficulties in varying the range of test section stream temperature, the

limiting temperature for obtaining the afterglow was not found.

Unheated air was then expanded and a similar afterglow was detected but with a much less relative intensity. The oxygen molecules in the air are thought to be efficient quenchers of N_2 afterglow because of the large cross section between N_2^+ ions and O_2 molecules.

In both expanded nitrogen and air at 16° K and 30 microns of Hg the gases are considered to be in the extreme supersaturated state[6,7]. The gas has expanded to this condition because of the non-equilibrium existing between the freestream pressure and the vapor pressure predicted at the freestream temperature. At 30 microns of Hg the limiting temperature for supersaturation of air and N_2 is about 40° K so that the arc-heated expansions are well above this region.

AN APPLICATION

Aside from the general desire to understand molecular collisions and their associated energy transfers, the observed afterglow can be used to make visual flow field studies in low density wind tunnels. This is of interest to aerodynamicists since schlieren systems became inadequate at low densities.

Figure 7 indicates the simplicity of the technique in that the only equipment needed is an electron beam passed upstream of the flow field under study and a camera. The afterglow sweeps downstream in a sheet so that a discreet region of the field in only two dimensions can be observed, thus allowing for studies of such flow phenomena as shock interactions.

[6] F. L Daum: AIAA Jour. Vol. 1, No. 5, 1043, May 1963.

[7] B. J. Griffith, H. E. Deskins and H. R. Little: AEDC-TDR 64-35,20, Feb. 1964.

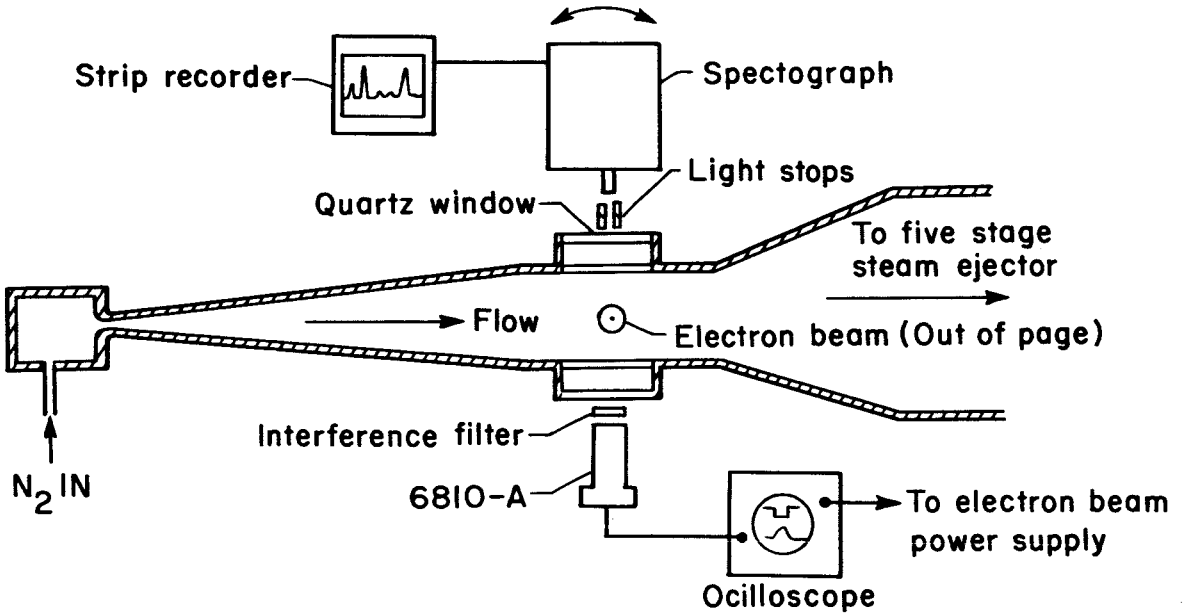
This method has been demonstrated in earlier investigations[8] but little has been indicated of its temperature limitations. Despite this handicap, a large number of existing aerodynamic facilities operate in the proper temperature range.

CONCLUDING REMARKS

The data presented describes an afterglow associated with very low temperature supersaturated gaseous nitrogen when excited by energetic electrons. The interaction of N_2^+ ions and secondary electrons with N_2 molecules left over from the primary excitation, is postulated as the source of the afterglow. Measurements of the departure from a Boltzmann distribution of rotational energies in the N_2 molecules in the afterglow is offered as verification. The radiative lifetime which was measured shows an afterglow peak intensity at 10^{-6} seconds and then a decay of 2.7×10^{-7} seconds for the observed vibrational bands which have a normal radiative lifetimes on the order of 10^{-8} seconds. A low density flow field visualization technique using the afterglow is suggested and demonstrated.

[8] A. E. Grun, E. Shopper and B. Schumacher: Jour Appl. Phys. 24, 1527 (1953)

LIST OR FIGURE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Spectograph
Light stops
Quartz window
To five stage
steam ejector
Flow
Electron beam (Out of page)
Interference filter
6810-A
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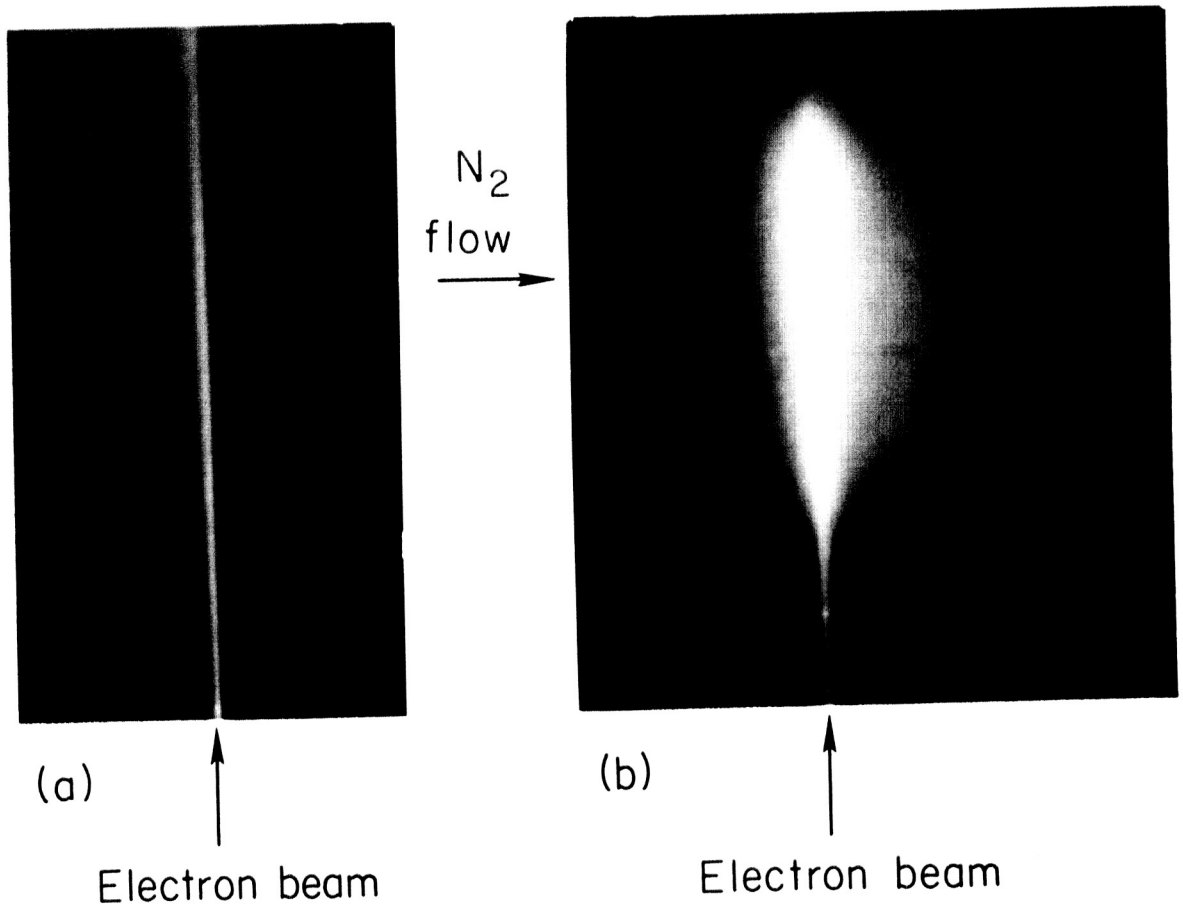
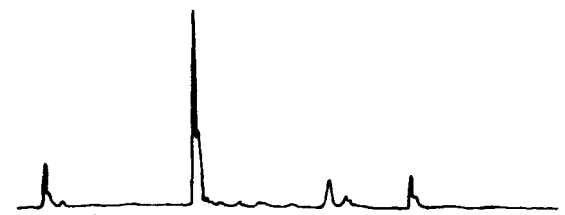
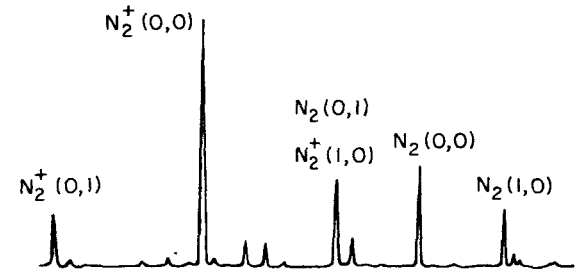
To electron beam
power supply
Ocilloscope

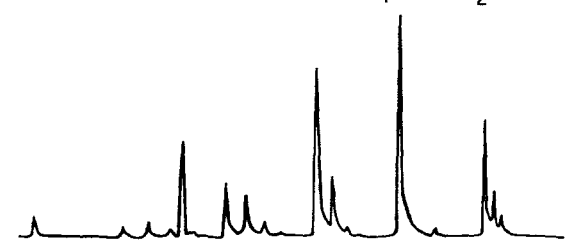

N_2
flow
(a)
Electron beam
(b)
Electron beam



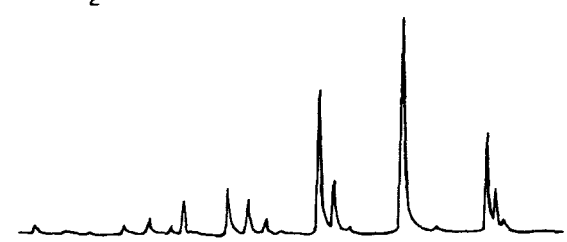
(a) From electron beam at room temperature.



(b) From electron beam in expanded N_2.



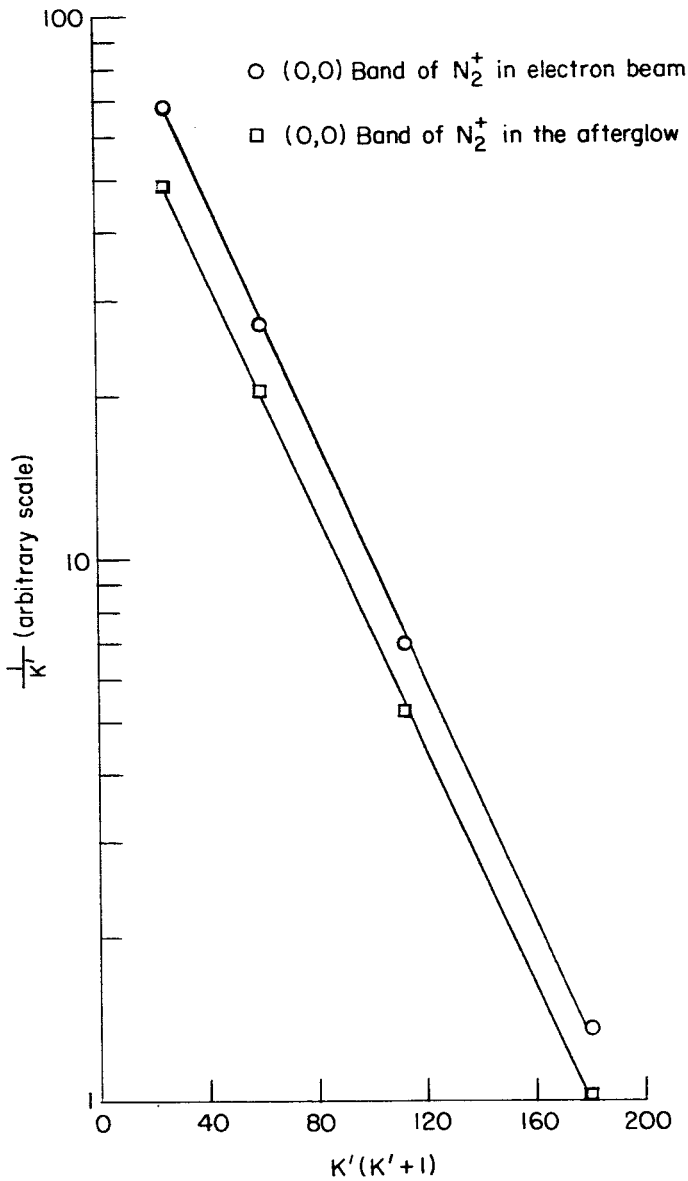
(c) $\frac{1}{2}$ inch downstream of beam in the afterglow.

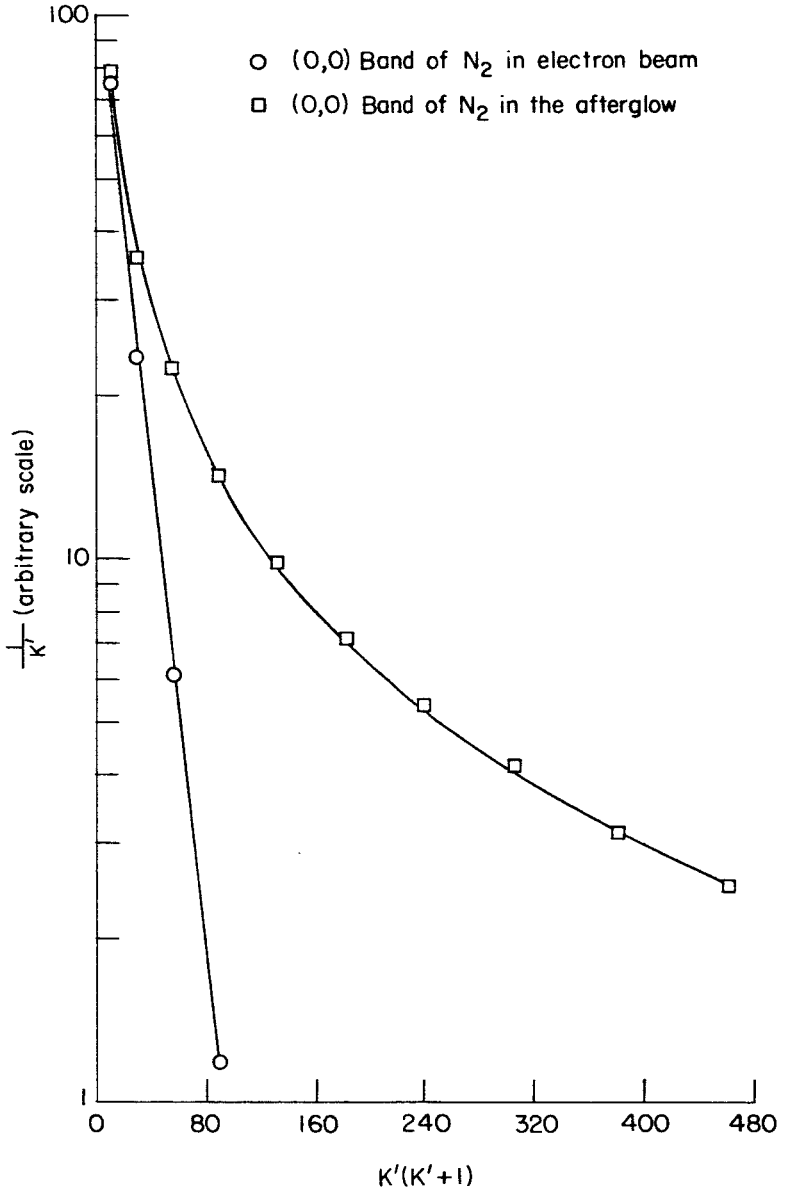


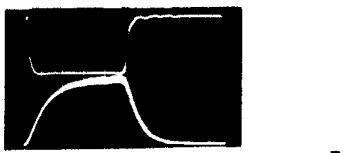
(d) $1\frac{1}{2}$ inches downstream of beam in the afterglow.

4000 3500 3000

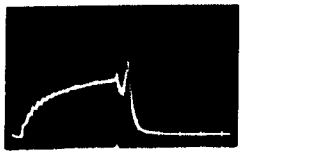
λ, angstroms


100
10
1
○ (0,0) Band of N_2^+ in electron beam
□ (0,0) Band of N_2^+ in the afterglow
$\frac{1}{K'}$ (arbitrary scale)
0
40
80
120
160
200
K'(K'+1)

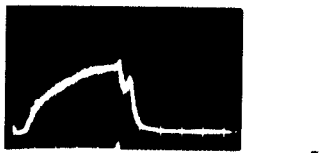

100
10
1
0
80
160
240
320
400
480
K'(K'+1)
$\frac{I}{K'}$ (arbitrary scale)
(0,0) Band of N_2 in electron beam
(0,0) Band of N_2 in the afterglow



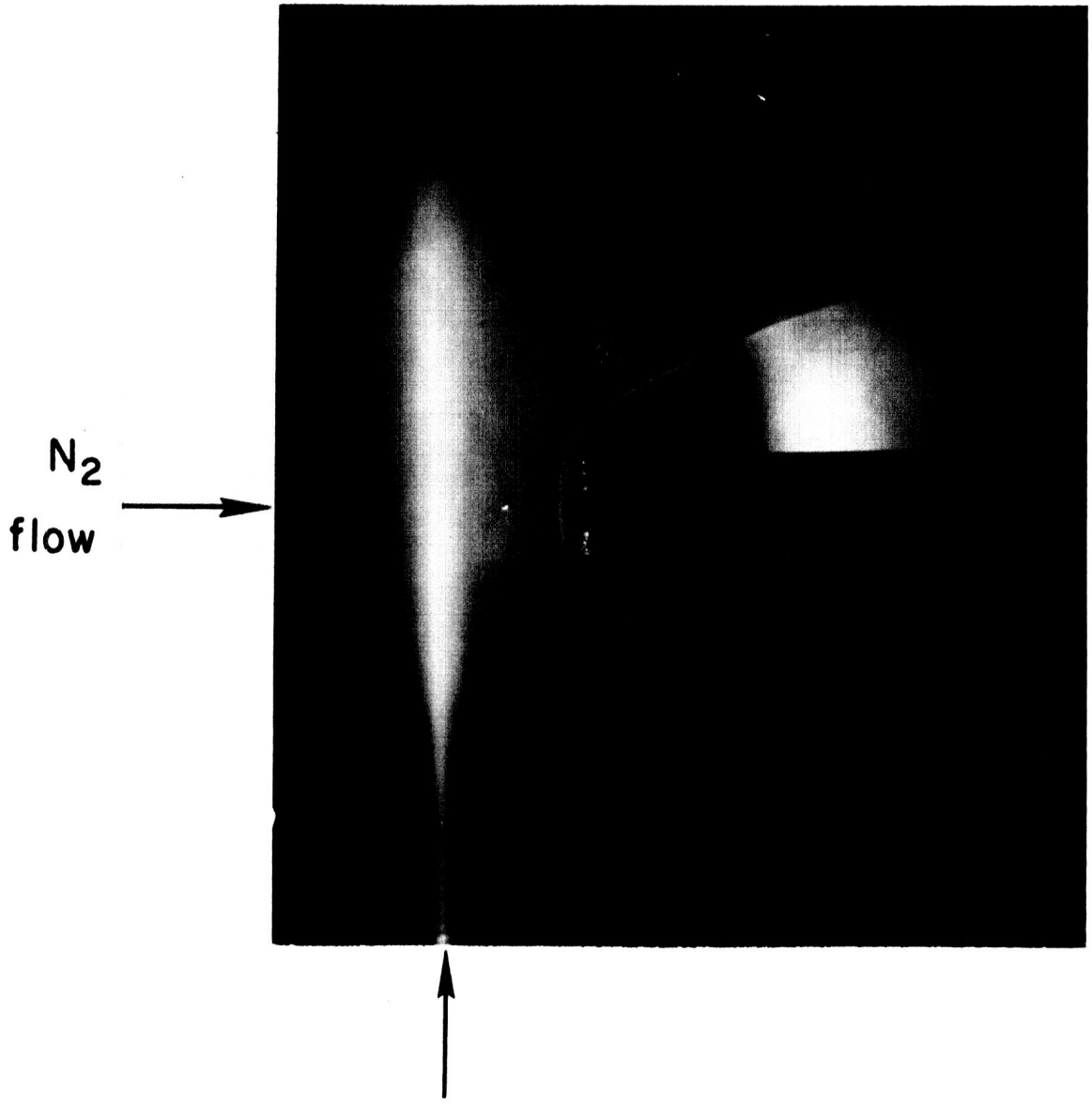
(a) Total emission from N_2 at room temperature.



(b) Total emission from expanded N_2.



(c) 3914 Å emission from expanded N_2.


N_2
flow
Electron beam