CHAPTER III

AFTERGLOW SPECTRA OF NITROGEN AT DIFFERENT TEMPERATURES AND PRESSURES

III.1. Introduction

The importance of studying nitrogen afterglow has been discussed in detail in the first chapter. The afterglow spectrum gives the relative intensity distribution of vibrational peaks corresponding to various electronic states of the molecule. The study of the vibrational intensity in the afterglow spectra at different pressures, temperature and with different diluent gases contributes to the knowledge of population mechanisms of the emitting states and also about quenching of emitting state by the carrier gas.
In this chapter the nitrogen afterglow spectra from 1900 to 8000 Å have been reported at two temperatures, 300 K and 77 K, using experimental system discussed in detail in the second chapter. Relative vibrational intensity for the first positive system have been computed at both the temperatures. The pressure dependence of intensities of various bands has been investigated at pressures between 2 and 7 Torr while the effect of diluent like argon has been studied at a fixed argon pressure of 5 Torr and varying nitrogen pressures from 0.2 to 3 Torr. Finally, the results are discussed in detail.

111.2. Results

111.2.1. Afterglow Spectra

Afterglow spectra of molecular nitrogen was studied from 1900 to 8000 Å at two temperatures, 300 K and 77 K. The spectra observed included, the well known first positive system of nitrogen from around 5000 to 7800 Å, a few Vegard-Kaplan bands from 2300 to 3400 Å and some bands belonging to infra-red afterglow system of nitrogen from 6800 Å to 7400 Å. The beta and gamma bands of nitric oxide, found to be very weak at 300 K but very predominant at 77 K, were observed in the spectral range from around 2000 Å to 4300 Å. Also, some CN bands and bands belonging to second positive system of nitrogen (only at 77 K) were observed in the afterglow spectra of nitrogen. The NI emission line at 3466 Å was observed both at 300 K and 77 K but the OI emission line at 5577 Å was observed in the spectrum at 77 K only.
The afterglow spectrum of nitrogen from 1900 to 4800 Å at 300°C is shown in Fig. III.1. Weak Vegard-Kaplan bands of molecular nitrogen could be identified at the same wavelength as reported by Pearse and Gaydon (1965). Only (0,6), (0,7) and (0,9) bands of the $A \, ^3\Sigma_u^+ \rightarrow X \, ^1\Sigma_g^+$ (Vegard-Kaplan) system were predominant to some extent while other bands were relatively weaker. Some of the beta bands of NO ($B \, ^2\Pi \rightarrow X \, ^2\Pi$) were also observed as impurity spectra. The (0,4) to (0,11) bands were relatively weak and the strongest of these bands was about 25 times less intense than the (11,7) band of first positive system of nitrogen at 300°C (Fig. III.2). The impurity CN bands ($B \, ^3\Sigma \rightarrow \Lambda \, ^2\Pi$) corresponding to $\Delta v = 0$ and 1 were also observed and were found to be relatively intense. Some other bands were also observed which could not be identified. The NI emission line at 3466 Å corresponding to N($^2P$) → N($^4S$) transition was observed to be as intense as some of the CN bands.

The afterglow spectrum of nitrogen at 7 Torr from 4800 to 8000 Å at 300°C is shown in Fig. III.2. The spectrum covers the first positive system ($B \, ^3\Pi_g \rightarrow A \, ^3\Sigma_u^+$) of nitrogen corresponding to $\Delta v = 6, 5, 4, 3, 2$ respectively. The band system corresponding to $v' = 12$ to 5 for $\Delta v = 4$, $v' = 12$ to 3 for $\Delta v = 3$ and $v' = 7$ to 2 for $\Delta v = 2$ are nicely resolved while some bands for $\Delta v = 6$ and 5 are barely resolved. The infra-red afterglow system corresponding to (8,2) and (8,3) bands have been observed to be very weak with band heads at 6896 Å and 7780 Å, respectively. These bands were observed to be very predominant at 77°C (Fig. III.6).
Fig. III.1 Afterglow spectra of nitrogen at 300°K from 1900 to 4800 Å.
Fig. III.2  Afterglow spectra of nitrogen at 300°K from 4800 to 8000 Å.
Ung (1976, 1980) observed the vibrational level \( v' = 13 \) of \( \text{N}_2(B \, ^3\Pi_g) \) state, in the first positive system of Lewis-Rayleigh afterglow of nitrogen, at higher pressure range (from 0.5 to 20 Torr). He also reported the detection of higher vibrational levels of the \( B \, ^3\Pi_g \) state up to \( v' = 26 \). Since \( v' = 13 \) lies just above the dissociation limit, it was interpreted as being populated from two-body recombination of \( \text{N}(^4S) \) atoms involving inverse predissociation via the \( \text{N}_2(5 \, \Sigma^+_g) \) state. Later on, Brennen and Shuman (1977) in a similar experiment failed to observe emissions from \( v' > 13 \) levels in the first positive system of nitrogen afterglow. In the present experiment, at both 300 \( ^0 \)K (Fig. III.2) and 77 \( ^0 \)K (Fig. III.6), we did not observe any emission corresponding to \( v' > 13 \) level. It appears that in Ung's experiment, there was a likely leakage of light from direct excitation into the afterglow chamber and this leaked light mixed with the afterglow emissions to produce wrong results. Our results therefore, favour the mechanism that \( \text{N}_2(B \, ^3\Pi_g) \) state is populated through collision-induced transition from a precursor state of nitrogen in the presence of a third body.

From Fig. III.2, the relative populations for the different vibrational levels of the \( B \, ^3\Pi_g \) state were measured. Only peak heights were measured and it was assumed that under normal circumstances, the peak heights of different bands were proportional to the areas covered by the peaks. These peak heights were then corrected for the quantum efficiency of the photocathode of EMI 9558 QB photomultiplier, shown in Fig. III.3, which varied with wavelength of the emitted radiation. The vibrational population of the most intense peak ((11,7) in this case)
Fig. III.3  Spectral response curve for S-20 type (EMI 9558QB) photomultiplier tube from 5000 to 8000 Å.
was normalized to 100% and the population for other peaks were calculated accordingly. The vibrational populations thus calculated are shown in Fig. III.4. Also shown in this figure are vibrational intensities of the various bands of first positive system of nitrogen as observed from emission spectroscopy (Pearse and Gaydon (1965)). These are normalized in the similar way as in the case of afterglow data. The results for emission spectroscopy show a maxima at \( v' = 12, 11, 10 \) levels of the \( B^3\Pi_g \) state for \( \Delta v = 5 \), at \( v' = 10, 9, 8 \) for \( \Delta v = 4 \), at \( v' = 8, 7 \) for \( \Delta v = 3 \) and at \( v' = 4, 3 \) for \( \Delta v = 2 \) bands, in accordance with the Franck-Condon principle. In case of afterglow spectra as reported in Fig. III.4, the population maxima occur at \( v' = 11 \) for \( \Delta v = 5 \), at \( v' = 11, 6 \) for \( \Delta v = 4 \), at \( v' = 11, 6 \) and 4 for \( \Delta v = 3 \) and at \( v' = 6 \) and 2 for \( \Delta v = 2 \). This is because the emitting states of these two types of emissions are populated by different mechanisms.

Afterglow spectra of nitrogen was also studied at 77°K in the spectral range between 1900 and 8000 Å. These spectra are shown in Fig. III.5 and Fig. III.6, respectively. In Fig. III.5 is shown the afterglow spectrum observed at 5 Torr nitrogen pressure from 1900 to 4800 Å. Well-defined and very intense bands of nitric oxide have been observed corresponding to \( B^2\Pi + X^2\Pi \) and \( A^2\Sigma^+ + X^2\Pi \) transitions. The most intense \((0,6)\) band of NO \( (B^2\Pi + X^2\Pi) \) is almost 1.6 times as intense as \((11,7)\) band of the first positive system of nitrogen observed at 300°K. The doubly degenerate character of NO beta bands was observed in only some bands like \((0,8), (0,9), (0,10), (0,11)\) etc. Most of the bands corresponding to gamma system of NO have also been identified and
Fig. III.4: The relative intensities of vibrational bands corresponding to first positive system of nitrogen at 300°K. Also shown are intensities of these bands as obtained from emission spectroscopy.
Fig. III.5  Afterglow spectra of nitrogen at 77°K from 1900 to 4800 Å.
Fig. III.6  Afterglow spectra of nitrogen at 77°K from 4800 to 8000 Å.
have been shown in Fig. III.5. The NO bands observed as impurity bands. At 300°K, these bands are very weak as is evident from Fig. III.1, but at 77°K, such bands are highly intense. The reason is that any trace of NO formed gets solidified at the chamber temperature of 77°K. After some time, the large amount of solid NO is in equilibrium with its vapour at around 77°K. The temperature would not be exactly 77°K as it would vary slightly depending upon the pressure of molecular nitrogen gas in the afterglow tube. The large amount of NO in the experimental chamber gives rise to very intense beta and gamma bands. The other impurity afterglow spectra is of CN. A direct comparison at 77°K and 300°K clearly shows that the $B^3Σ + Λ^2Π$ bands of CN are much more intense at 77°K than at 300°K. The weak Vegard-Kaplan bands of nitrogen observed at 300°K are conspicuously absent in the afterglow spectra at 77°K. Some of the members of the Vegard-Kaplan bands are very close in wavelength to some gamma bands of nitric oxide with the result that they may be merged to show a single peak. A new set of bands corresponding to second positive system of molecular nitrogen ($C^3Π_u + B^3Π_g$) which were completely absent at 300°K (Fig. III.1) have been observed at 77°K (Fig. III.5). These are moderately intense bands.

The afterglow spectra of nitrogen at 77°K in the wavelength region from 4800 to 8000 Å, has been shown in Fig. III.6. The bands (12,7), (12,8) and (12,9) were observed to be much more intense than bands (11,6), (11,7) and (11,8). In comparison, the vibrational level $v' = 11$ for the $B^3Π_g$ state was found to be much more populated than the vibrational level $v' = 12$ in the afterglow spectra at 300°K. Also, the most intense band at 77°K ((12,8) in this case) was observed to be
about 2.2 times more intense than the most intense band (11,7) at 300°K. In general, the intensity of all bands observed at 77°K is much larger than for bands studied at 300°K. The Infra-red afterglow bands (8,2) and (8,3) were also very predominant in the spectra at 77°K. Some relatively weak bands in the spectral region from 4850 to 4980 Å, from 5080 to 5300 Å and around 8070 Å were also observed but these could not be identified in an unambiguous manner. Another special feature of the spectra was the presence of OI emission line at 5577 Å. This emission line was very intense in the afterglow spectrum at 77°K but was completely absent in the spectrum at 300°K. It appeared that both at 300°K and 77°K, an appreciable though small concentration of O(1S) atoms was produced by the three body volume recombination of O(3P) atoms which in turn, were produced because of discharge of small quantity of impurity oxygen present in the system. The strong quenching agents of O(1S) atoms were N₂, N and O₂ (¹Δg). It may be noted that O₂ (¹Δg) concentration would be appreciable, though small. We have observed that at a pressure of 1 Torr of oxygen, O₂ (¹Δg) and O (3P) produced by microwave discharge were about 24% and 10% respectively of parent molecule.

O₂ (¹Δg), though small in concentration, has large quenching rate of about 1.7 x 10⁻¹⁰ cm³ sec⁻¹ for O(1S) as reported by Slanger and Black (1981). Thus all the three quenching agents are effective at 300°K where collisions are large. But at 77°K, the number of collisions are appreciably reduced and therefore, the O(1S) → O(1D) transition emitting 5577 Å radiation, could be observed.

The oxygen atoms in O(1S) state could alternatively be produced by the following reaction...
An approximate rate constant of $3.2 \times 10^{-12}$ cm$^3$ sec$^{-1}$ as measured in a discharge flow tube, was reported by Meyer et al. (1969). A linear correlation between the intensities of any Vegard-Kaplan band ($\Lambda_3^+ \rightarrow \Lambda_1^+$) and that of 5577 Å emission would confirm the presence of this reaction. In the present experiment, as stated previously, most of the vibrational bands of Vegard-Kaplan system are masked by NO gamma and beta bands in the afterglow spectra at 77°K. Thus the intensity correlation between the two emissions cannot be studied. In light of the above arguments, it is strongly felt that $0 (^1S)$ could be produced by both the reactions mentioned above.

From Fig. III.6, the relative population for the different vibrational levels of the $B^3 \Pi_g$ state were measured in the same manner as in the case of measurement of vibrational intensities at 300°K. The vibrational populations were corrected for the quantum efficiency of the photocathode used and were normalized for the most intense peak (12,8) in this case) to 100%. The populations for the other peaks were computed accordingly. The vibrational populations at 77°K, thus computed are shown in Fig. III.7 along with those at 300°K. Intensity maxima were observed at $v' = 12$ for $\Delta v = 5$, at $v' = 12$ and 6 for $\Delta v = 4$, at $v' = 12$, 9, 6 and 4 for $\Delta v = 3$ and at $v' = 7$ and 3 for $\Delta v = 2$.

III.2.2. Pressure Dependence

The afterglow spectra of nitrogen was studied at various pressures ranging from 1 to 7 Torr, both at 300°K and 77°K. All members
Fig. III.7 The relative intensities of vibrational bands corresponding to first positive system of nitrogen at 77°K. Also shown are intensities of these bands at 300°K.
of the first positive system could be observed at pressure from 2 to 7 Torr but at 1 Torr, spectra corresponding to (12,8) and (11,7) bands could only be observed. At pressures less than 1 Torr, the wall-recombinations increased drastically with the result that no afterglow spectra could be observed at these two temperatures.

The spectra at 300°K and at various pressures have been shown in Fig. III.8 and Fig. III.9. The spectra correspond to $$\Delta v = 4$$ and $$\Delta v = 3$$ respectively. The peak intensities of the various bands were computed as a function of pressure of molecular nitrogen.

To ascertain whether the peak intensities of bands in the first positive system of nitrogen, had direct [N] dependence or direct [N]² dependence, it became essential to measure the absolute atomic nitrogen concentration as a function of pressure. As has been explained in Chapter II, such measurements were made using Wrede-Harteck gauge fixed on the observation vessel near the point from where discharged products entered into the observation vessel. The dissociation efficiency of nitrogen, as defined by equation II.3, was measured at various pressures and has been shown in Fig. III.10. It varied from about 8 to 14% at pressures ranging from 7 Torr to 0.2 Torr. Knowing dissociation efficiency, the atomic nitrogen concentrations at various nitrogen pressures could be easily calculated. Our values of dissociation efficiencies are higher than those obtained by nitric oxide titration method. The values by titration method were reported to vary from 1 to 3%.

However, it was observed by Ding et al. (1977) that the atomic concentrations measured by Wrede-Harteck gauge and mass spectrometric techniques
Fig. III.8  Afterglow spectra of some vibrational bands of first positive system of nitrogen at 300°K corresponding to Δν = 4. The spectra have been obtained for various pressures ranging from 7 to 2 Torr.
Fig. III,9  Afterglow spectra of some vibrational bands of first positive system of nitrogen at 300°K corresponding to Δν = 3. The spectra have been obtained for various pressures ranging from 7 to 3 Torr.
Fig. III.10 Dissociation efficiency of molecular nitrogen as a function of pressure of the parent gas from 0.2 to 7 Torr.
respectively, were relatively larger as compared to those observed by any other technique. However, a direct comparison as to which technique was superior was not possible.

In Fig. III.11 and Fig. III.12 are shown the peak intensities of various vibrational bands of the first positive system of nitrogen at 300°K, as a function of the square of atomic nitrogen concentration i.e. \([N]^2\). The vibrational bands studied include (11,7), (12,8), (10,6), (9,5), (11,8), (10,7), (12,9), (5,2), (7,4), (9,6), (8,5) and (3,0). A linear relationship between the peak intensity and \([N]^2\) has been observed for all these bands in the pressure range 4 to 7 Torr. Between 2 and 4 Torr, \([N]^2\) dependence does not seem to hold good. Some different type of dependence may be possible in this intermediate pressure region. Our results include very few data points in this region and thus, we are not in a position to give even a qualitative picture about the type of dependence. It is suggested that this region should be re-investigated with greater care so as to yield large number of data points, using the afterglow tube of such a size that the wall-recombinations in this pressure region are appreciably reduced.

At 77°K, the dissociation efficiencies at various pressures could not be measured because of some technical problems. It is assumed that without any serious ambiguity, the dissociation efficiency of nitrogen should be the same both at 300 and 77°K. The peak intensities for various vibrational bands of the first positive system of nitrogen at 77°K were plotted against square of the atomic nitrogen concentration i.e. \([N]^2\). The results are shown in Fig. III.13 for only a few
Fig. III.11 Peak intensities of (11,7), (12,8), (10,6) and (9,5) vibrational bands of the first positive system of nitrogen at 300°C as a function of square of the nitrogen atom concentration.
Peak intensities of (11,8), (10,7), (12,9), (5,2), (7,4), (9,6), (8,5) and (3,0) vibrational bands of the first positive system of nitrogen at 300°K as a function of square of the nitrogen atom concentration.

Fig. III.12
Fig. III.13 Peak intensities of (12,8), (11,7), (12,9), (11,8), (10,6) and (10,7) vibrational bands of the first positive system of nitrogen at 77°K as a function of square of the nitrogen atom concentration.
vibrational bands. A clear \([N]^2\) dependence is observed in the pressure region between 4 and 7 Torr. Again, in the pressure region between 2 and 4 Torr, \([N]^2\) dependence does not seem to hold good. Thus, it is concluded that 2 to 4 Torr pressure region has entirely different type of dependence, irrespective of the temperatures at which the afterglow spectra are studied.

III.2.3. Effect of Diluent

It was reported in Section III.2.2 that no afterglow spectrum for the first positive system of nitrogen, was observed at pressures below 1 Torr in the present work. Even at 1 Torr, very weak (12,8) and (11,7) bands were observed. It was found that when nitrogen along with some carrier gas or diluent like argon was discharged, an afterglow spectrum of first positive system of nitrogen was observed even at very low pressures of nitrogen. In the present experiment, a fixed pressure of 5 Torr of argon was used while the nitrogen pressure was varied from 0.2 to 3 Torr. In all cases, the afterglow spectra could be observed. In Fig. III.14 is shown the first positive system for nitrogen at 300°K obtained at 5 Torr of argon and 1 Torr of nitrogen. Similar investigations at 77°K were not undertaken. From Fig. III.14, it was clear that in this case the various vibrational levels of the \(B^3\Pi_g\) state were populated in different proportions than those observed in the afterglow spectra without diluent at 300°K. Firstly, the most intense band, (11,7) was about 2.3 times more intense than that without diluent at 7 Torr pressure and 300°K temperature. Also, the intensities of all bands are, in general, larger. In this spectrum, the vibrational levels
Fig. III.14 Afterglow spectra of first positive system of nitrogen at 300 K obtained at a 5 Torr pressure of argon and 1 Torr of nitrogen.
\( v' = 12 \) and \( 10 \) were equally populated for \( \Delta v = 4 \) and also for \( \Delta v = 5 \), but in case of \( \Delta v = 3 \), the level corresponding to \( v' = 10 \) was more populated than level at \( v' = 12 \). The pattern for the population of vibrational level \( v' = 11 \) to \( 8 \) for both \( \Delta v = 4 \) and \( 3 \) was entirely different than that reported for spectrum without diluent.

The existence of afterglow spectra below 1 Torr and that too with larger intensity obtained under the same experimental conditions, could only be attributed to production of large atomic nitrogen concentration in the presence of a diluent like argon. Under these conditions i.e. at 5 Torr fixed pressure of argon and nitrogen pressure varying from 0.2 to 3 Torr, the dissociation efficiency was measured by Wrede-Harteck method at entrance point of observational vessel. The results are shown in Fig. 11.15. The dissociation efficiency varied from about 33\% to 17\% at about 0.2 to 3.0 Torr nitrogen pressure. It was obvious that atomic nitrogen concentrations were much larger when argon was used as diluent with nitrogen.

The peak intensities for the different bands of the first positive system of nitrogen were computed as a function of pressure. The plot of peak intensity against \([N]^2\) has been shown in Fig. 11.16 to Fig. 11.18. It did not seem to follow the \([N]^2\) dependence but is more or less a third order dependence.

In the pressure region from 0.2 Torr and above where the third order dependence on intensity of the vibrational bands has been found to exist, the quenching of \( N_2 (B \ ^3 \Pi_g) \) state by \( N_2 \) itself or by some
Fig. III.15 Dissociation efficiency of molecular nitrogen at a fixed pressure of argon (5 Torr) and at nitrogen pressure varying from 0.2 to 3 Torr.
Fig. III.16  Peak intensities of (11,7), (12,8), (11,6), (10,5) vibrational bands of 1+ system of nitrogen at 300°K in the presence of a diluent, argon, as a function of $[N]^2$. 

First Positive System of $N_2$ + Argon
Fig. III.17 Peak intensities of (10,6), (11,8), (10,7), (12,9) vibrational bands of 1+ system of nitrogen in the presence of a diluent, argon, as a function of $[N]^2$. 
Fig. III.18 Peak intensities of (9,5), (9,6), (8,4), (7,3) vibrational bands of 1+ system of nitrogen in the presence of a diluent, argon, as a function of \([N]^2\).
diluent, is, in general, appreciable. In the present experiment, the afterglow spectra at this low pressure region without diluent could not be studied because of constraints posed by certain experimental conditions. So quenching parameters for $N_2$ could not be obtained. But the quenching of $N_2\left(B^3Π_g\right)$ state by argon at these low pressures was studied in detail. Knowing quenching parameters of $N_2\left(B^3Π_g\right)$ state by nitrogen from experiments reported by other scientists, similar parameters for argon were obtained in the present experiment.

At low pressures of nitrogen with no diluent, the intensity of the afterglow for different vibrational levels of the $B^3Π_g$ state, obeyed a rate law (Brennen and Shane (1971)) of the form

$$\frac{1}{[N]^2} = \frac{K[M]}{kτ_B[M] + 1}$$  \hspace{1cm} \text{(III.2)}$$

where $K$ and $k$ are constants for a particular diluent, $τ_B$ is the radiative life time of the emitting state and $[M]$ is the concentration of the diluent. The half-quenching pressure is defined as $[M]_\frac{1}{2} = (kτ_B)^{-1}$. In this case, the diluent is pure nitrogen alone. At two pressures 1 and 2 in the flow system, equation (III.2) will be

$$\frac{1}{[N]^2} \cdot \frac{[M]^2}{[N]^2} = \frac{kτ_B[M]_2 + 1}{kτ_B[M]_1 + 1}$$  \hspace{1cm} \text{(III.3)}$$

When at low pressure of nitrogen, a diluent, argon is added, then $k$ becomes

$$k = k\,(Ar) \times (Ar) + k\,(N_2) \times (N_2)$$  \hspace{1cm} \text{(III.4)}$$
where $X$ is the mole fraction of the gas and is also pressure dependent. Substituting $k$ from equation 11.4 in equation 11.3, $k(\text{Ar})\tau_B$ could be obtained provided $k(N_2)\tau_B$ is known from other experiments. The value of $k(N_2)\tau_B$ was taken as $8.6 \pm 1.3 \text{ Torr}^{-1}$ (Brennen and Shane (1971)) for $v' = 12, 11, 10$ levels of the $B^3\Pi_g$ state and the values of $k(\text{Ar})\tau_B$ and $k(\text{Ar})$ were calculated. The results are shown in Table III.1.

### Table III.1

Half quenching pressures and quenching rates of argon for $v' = 12, 11, 10$ levels of the $B^3\Pi_g$ state of nitrogen

<table>
<thead>
<tr>
<th>Level $v'$</th>
<th>Vibrational bands studied</th>
<th>$k(\text{Ar})\tau_B$ in Torr$^{-1}$</th>
<th>$k(\text{Ar})$ in cm$^3$ mole$^{-1}$ sec$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>12, 9</td>
<td>0.56$\pm$0.15</td>
<td>$(3.61\pm0.98)\times10^{-12}$</td>
<td>Present work</td>
</tr>
<tr>
<td></td>
<td>12, 8</td>
<td></td>
<td>$12 \times 10^{-12}$</td>
<td>Jonathan and Petty (1969)</td>
</tr>
<tr>
<td>11</td>
<td>11, 6</td>
<td>0.86$\pm$0.13</td>
<td>$(5.48\pm0.82)\times10^{-12}$</td>
<td>Present work</td>
</tr>
<tr>
<td></td>
<td>11, 7</td>
<td></td>
<td></td>
<td>Bronnen and Shane (1971)</td>
</tr>
<tr>
<td></td>
<td>11, 8</td>
<td></td>
<td></td>
<td>Jonathan and Petty (1969)</td>
</tr>
<tr>
<td>10</td>
<td>10, 5</td>
<td>0.96$\pm$0.13</td>
<td>$(6.16\pm0.84)\times10^{-12}$</td>
<td>Present work</td>
</tr>
<tr>
<td></td>
<td>10, 6</td>
<td></td>
<td>$12 \times 10^{-12}$</td>
<td>Bronnen and Shane (1971)</td>
</tr>
<tr>
<td></td>
<td>10, 7</td>
<td></td>
<td>$12 \times 10^{-12}$</td>
<td>Jonathan and Petty (1969)</td>
</tr>
</tbody>
</table>
In all these calculations, \( \tau_B \) for \( v' = 12, 11 \) and \( 10 \) of the \( B^3\Pi_g \) state of nitrogen, was taken as \( 4.4 \times 10^{-6} \) sec as reported by Jeunehomme (1966). The values of \( k(\text{Ar}) \tau_B \) reported by Brennon and Shane (1971) and Jonathan and Petty (1969) were larger than those reported in the present work. This could be because of the fact that these scientists used a few overlapping interference filters for peak intensity measurements while in the present work, all the afterglow spectrum was scanned by grating of the monochromator, thus avoiding the cumulative effects so inherent in the interference filters.

III.3. Discussion

The mechanisms for populating various vibrational levels from \( v' = 12 \) to \( 2 \) for the \( B^3\Pi_g \) state of nitrogen molecule would be discussed here on the basis of present results reported in the previous section as well as results from other experiments, on the afterglow spectra of first positive system at both 300 and 770K and on pressure dependence of the peak intensities with or without diluent. The energy level diagram shown in Fig. III.19 for \( B^3\Pi_g \) and \( A^3\Sigma^+ \) states is based on the work reported by Bonesch et al. (1965). Only vibrational levels have been shown in the diagram. Also shown in the figure are relative contributions from other excited states like \( B'_1^3\Sigma_u^- \) and \( C^3\Pi_g \) to \( B^3\Pi_g \) state. The weak afterglow emission corresponding to \((8,2)\) vibrational band of infra-red afterglow system \((B'_1^3\Sigma_u^- \rightarrow B^3\Pi_g)\) at 3000K is shown by dotted line while moderately intense infra-red afterglow emission, \((8,2)\) and \((8,3)\) bands and similar \((1,2) \ (1,4), \ (3,7), \ (4,3), \ (4,4)\) and \((4,8)\) vibrational bands of second positive system \((C^3\Pi_u \rightarrow B^3\Pi_g)\) at
Fig. III.19  Energy level diagram of B $^3\Pi_g$ and A $^3\Sigma_u^+$ states. Only vibrational levels have been shown in the figure. Also shown are radiative contribution from some vibrational bands of IRA system and second positive system of nitrogen, both at 77$^0$K and 300$^0$K.
77°K as reported in the present work are shown by full lines.

III.3.1. Mechanisms for populating \( v' = 12 \) to 9

In section III.2.2, we have reported that the intensity of vibrational bands with \( v' = 12, 11, 10, 9 \) --- is proportional to \([N]^2\) for the pressure range from 4 to 7 Torr and has third order dependence in the region 0.2 to 2 Torr. The intensity of vibrational bands with \( v' = 12, 11, 10 \) were found to be larger at 77°K than at 300°K as reported in section III.2.1. This means that first positive system of nitrogen afterglow shows negative temperature coefficient. As discussed in Chapter I, the three-body emission intensity should show a change from a second order to third order dependence at low pressures. Similar behaviour has been found for the first positive system of nitrogen afterglow. This indicates that \( B^3\Pi_g \) is populated via three-body recombination.

In Chapter I, four mechanisms were considered for populating the \( B^3\Pi_g \) state of nitrogen afterglow. The first mechanism, proposed by Benson (1968) is ruled out because it requires rate of vibrational relaxation at least one order of magnitude greater than collision rate (Becker 1972). Due to the position of the potential curves primarily, \( 5\Sigma_g^+ \) and \( 3\Sigma_u^+ \) have to be considered as precursor state for \( B^3\Pi_g \), \( v' = 9-12 \) in a stabilization mechanism. The simplest assumption, that a collision induced process

\[
N^2 \left( 5\Sigma_g^+ \right) + M \rightarrow N_2 \left( B^3\Pi_g \right) \quad v' = 12-9 + M
\]

III.5
populates the \( v' \) level of the B state is consistent with our results. A \( ^3\Sigma_u^+ \) state as precursor of B \( ^3\Pi_g \) state, as proposed by Campbell and Thrush (1967) is rejected on the following grounds:

1. Campbell and Thrush (1967) had chosen A \( ^3\Sigma_u^+ \) state as a precursor state as they felt that spin conservation was important in collision induced transitions between excited triplet and singlet state of nitrogen. But involvement of \( ^5\Sigma_g^+ \) in the preassociation of B \( ^3\Pi_g \), \( v' = 13 \) has clearly been established. This indicates that \( \Delta S = 0 \) selection rule is violated. In collisions, the selection rule \( g \leftrightarrow u \) for radiationless transition is not strictly valid; thus a collision induced transition \( ^5\Sigma_g^+ \rightarrow ^3\Pi_g \) might occur more readily than A \( ^3\Sigma_u^+ \rightarrow ^3\Pi_g \) transition.

2. Also, Campbell and Thrush (1967) mechanism failed to account for the observed change in the \( (v' = 11 / v' = 12) \) intensity ratio of B \( ^3\Pi_g \) state with change in temperature. Campbell and Thrush (1967) suggested that shift towards \( v' = 12 \) at low temperature was due to a reduction in the rate of predissociation of higher vibrational levels of A state. This explanation is in contradiction to what has been suggested by Golde and Thrush (1972).

On the other hand, stabilized N\(_2\) \( (^5\Sigma_g^+, v = 0) \) molecules formed by reaction 111.6, as suggested initially by Bayer and Klistlakowsky (1960), can be depopulated by dissociation into atoms (111.7)

\[
N (^4S) + N (^4S) + M \rightarrow N\(_2\) (^5\Sigma_g^+, v = 0) + M \quad 111.6
\]

\[
N\(_2\) (^5\Sigma_g^+, v = 0) + M \rightarrow N (^4S) + N (^4S) + M \quad 111.7
\]
Molecules formed in stabilized $^5\Sigma_g^+$ state can also be depopulated by collision induced process

$$N_2\left( ^5\Sigma_g^+, v = 0 \right) + M \xleftrightarrow{\text{III.8}} N_2\left( ^3\Pi_g, v = 12 \right) + M$$

Crossing of $^3\Pi_g$, $v = 12$ with $^5\Sigma_g^+$ near $v = 0$ of latter, together with the observed inverse predissociation of $^3\Pi_g$, $v = 13$ at very low pressure (Becker et al. (1972)) from $^5\Sigma_g^+$ implies a perturbation of $(^3\Pi_g, v = 12)$ level by $(^5\Sigma_g^+, v = 0)$. It can be assumed that, because of the heterogeneous perturbation, the radiationless transition between $(^5\Sigma_g^+) \xrightarrow{\text{III.8}} (^3\Pi_g, v = 12)$ takes place over a range of rotational levels.

Rotational level analysis of this state corresponding to vibrational level $v' = 12$ as discussed in Chapter IV, also supports $^5\Sigma_g^+$ state as the precursor of $^3\Pi_g$ state.

According to perturbation theory, molecules in $^5\Sigma_g^+(v = 0)$ would undergo a collision-induced-radiationless transition into $v' = 12$ only and by no means into $v' = 11$ to 9 of the $^3\Pi_g$ state. This was clear from the energy level diagram (Fig. III.19) which showed practically no energy difference between $^5\Sigma_g^+(v = 0)$ and $^3\Pi_g(v' = 12)$ level and larger energy difference for other combinations. Callear and Williams (1966) have shown that the probability of collision-induced transfer of vibrational energy falls off approximately exponentially with the amount of energy that has been converted from the vibrational to the translational form. In this case, only $\Delta S = 0$ selection rule has been violated, which looks a weak selection rule in the presence of collisions. The level $v' = 12$ of $^3\Pi_g$ thus populated, could be depopulated to some
extent by collision-induced vibrational relaxation to lower vibrational level, collision-induced electronic quenching and radiative deactivation to $A^3\Sigma_u^+$ state.

The gas kinetic collision rate is defined as

$$Z = 4 \ n \ \sigma^2 \ (\frac{\pi k T}{m})^{\frac{1}{2}}$$

where $n$ is the number of molecules per c.c., $\sigma$ is the impact parameter and $k$, $T$, $m$ have their usual meaning. Lambert (1977) gives a value of $Z = 8.69 \times 10^9 \ sec^{-1} \ atm^{-1}$ for nitrogen molecules in the ground state and at 273K. It would be interesting to note that $Z$ has been computed for $N_2-N_2$ collisions for the ground state molecules. The collision rate for molecules in excited states would possibly be different than for those in the ground state. The value of quenching rate $k(N_2)$ has been reported as $6.6 \times 10^{-11} \ cm^3 \ molec^{-1} \ sec^{-1}$ for $v' = 12, 11$ and 10 levels of the $B^3\Pi_g$ state (Brennen and Shane (1971)) at very low pressures. This would give a high value of one collision in five for quenching the higher vibrational levels at 300K as against a value of one out of twenty as reported by Campbell and Thrush (1967).

As reported in section 11.2.2, at higher pressure, there is practically negligible quenching but at pressures below 1 Torr, the quenching becomes appreciable. Also, at low pressures, there are losses due to wall recombination. That is why no afterglow spectra could be observed below 1 Torr. The spectra at low pressure was observed only in the presence of a diluent like argon which helps to increase the atomic nitrogen concentration and also reduces the wall recombination. Again,
it could be seen by comparing the spectra with and without diluent that the population of vibrational level of the \( B^3\Pi_g \) state are different in the two cases.

It is clear from perturbation theory that \( v' = 11, 10 \) and \( 9 \) of \( B^3\Pi_g \) state cannot significantly be populated directly from \( 5\Sigma_g^+ \) state. The perturbation effect between \( 5\Sigma_g^+, \ v = 0 \) and \( B^3\Pi_g, v' = 11, 10 \) and \( 9 \) will be smaller than that between \( 5\Sigma_g^+, \ v = 0 \) and \( B^3\Pi_g, v' = 12 \) because the energy difference for \( v' = 11, 10, 9 \) are greater than that for \( v' = 12 \) and the energy difference appears in the denominator of the perturbation term. The only possibility of populating \( v' = 11 \) to \( 9 \) levels of \( B^3\Pi_g \) state is through vibrational relaxation from \( v' = 12 \) to \( 11, v' = 11 \) to \( 10 \) and \( v' = 10 \) to \( 9 \) respectively. It is possible that the probability of vibrational relaxations at high pressure is very large but no calculation has been done to prove this fact quantitatively. Similar mechanism was proposed by Anketell and Nicholls (1970) and Brennen and Shane (1971).

There is another mechanism which may be giving additional contribution to the process of populating some of the vibrational levels in this group. Some vibrational levels in the B state are very close to some levels in the A state. According to perturbation theory, the system could go from one state to the other state at \( B^3\Pi_g (v' = 10) \) and \( A^3\Sigma_u^+ (v'' = 22) \) and also at \( B^3\Pi_g (v' = 11) \) and \( A^3\Sigma_u^+ (v'' = 24) \) where these levels have approximately the same energy (Fig. III.19). The energy difference for \( v' = 11 \) and \( v'' = 24 \) is only 0.005 eV while
that for \( v' = 10 \) and \( v'' = 22 \) is only 0.02 eV. Therefore, this process would also populate \( v' = 11 \) and 10 levels of the \( B^3\Pi_g \) state.

The picture is slightly different at 77\(^0\)K where \( v' = 12 \) is maximum populated. The three-body recombination of nitrogen atoms has a negative temperature coefficient (Campbell and Thrush (1967)) and also, the number of collisions energetically capable of predissociating \( N_2 ({}^5\Sigma_g^+) \) state at 77\(^0\)K is small (Berkowitz et al. (1956)). Also, the collision-induced vibrational relaxation to lower levels would again be small at this temperature. This would explain why the \( v' = 12 \) level is populated the maximum at 77\(^0\)K. The \( v' = 11 \) and 10 levels would be populated by the second mechanism reported above.

### III.3.2. Mechanism for populating \( B^3\Pi_g, v' = 8 \) to 5

The mechanism which populates the lower vibration level \( v' \leq 8 \) of \( B^3\Pi_g \) state obviously cannot involve \( {}^5\Sigma_g^+ \) state. It has been emphasised before, that the curves \( A^3\Sigma_u^+ \) and \( B^3\Pi_g \) intersect near \( v'' = 16 \) and \( v' = 6 \) respectively. The energy difference of those vibrational levels is about 0.032 eV. Thus, there is a significant probability for collision-induced radiationless transition from one level to the other. Also, the potential curves co-trace their paths above this energy along the repulsive part of the potential. There would also be collision-induced radiationless transition between \( A^3\Sigma_u^+ (v = 19) \) and \( B^3\Pi_g (v = 8) \), the energy difference being 0.014 eV between the two. (It may be important to note that we have taken energies of vibrational energy levels as
reported by Benesch et al. (1965) which are probably the latest. There is some difference between these values and those taken by Campbell and Thrush (1967). This way the levels corresponding to \( v' = 8 \) and 6 would be populated, \( v' = 6 \) being populated much more. There would be a collision-induced vibrational relaxation from levels \( v' = 8, 6 \) to \( v' = 7 \) and 5 respectively. The net effect would be that all levels in this group would be populated, though \( v' = 6 \) would be populated the maximum. The above picture corresponds well to the experimental results reported at 300\(^{\circ}\)K (section III.2).

At 77\(^{\circ}\)K, there would be less vibrational relaxation. But as shown in Fig. III.19, 8 and 7 levels of B state would have some contribution from the radiative transition \((C^{3}\Pi_u \rightarrow B^{3}\Pi_g})\), \((4,8)\) and \((3,7)\) vibrational bands of the second positive system of nitrogen.

III.3.3. Mechanisms for populating \( v' = 4 \) to 2

The first positive emission from \( v' = 4 \) to 0 levels of the \( B^{3}\Pi_g \) state covers the spectral range from 7000 to 11000 \( \AA \) but in our experiment, we could observe up to 8000 \( \AA \) only. This corresponds to emission from \( v' = 4 \) to 2 levels. At room temperature (300\(^{\circ}\)K), the levels \( v' = 4 \) to 2 could be populated through the following radiative transitions:

1. A weak \((8,2)\) band of infra-red afterglow system has been observed by us as reported in section III.2.1. Level \( v' = 2 \) could be weakly populated by this radiative transition.
The strong observed transition corresponding to (4,2), (5,2) and (6,3) bands of the $^3\Sigma_u^+ ightarrow B^3\Pi_g$ system have been reported by Wu and Benesch (1968). This would be another agency to populate $v' = 2$ and 3 levels of the $B^3\Pi_g$ state.

The (7,4), (7,3) bands of the $B^1\Sigma_u^+ ightarrow B^3\Pi_g$ system in the near infra-red region (not reported in our work) could moderately populate $v' = 4,3$ levels of $B^3\Pi_g$ state.

The net result of the three above processes would be to populate $v' = 4$ to 2 levels of the $B^3\Pi_g$ state. The extent of populating any level by one of these processes is not known to us. Also, the levels $v' = 3$ and 2 may be populated to some extent, by collision-induced vibrational relaxation from $v' = 4$ and 3 levels respectively.

At 77°K, the levels $v' = 2$ and 3 are intensely populated by emission corresponding to (8,2) and (8,3) bands of the infra-red afterglow system. Also, (1,4), (4,4), (1,3), (4,3) and (1,2) bands corresponding to second positive system contribute significantly to $v' = 2,3$ and 4 levels. All these transitions have been observed by us in the afterglow spectra of nitrogen at 77°K.