# Vibrational Relaxation and Quenching in the Yellow Nitrogen Afterglow

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CAMPBELL and THRUSH[1] recently suggested a mechanism for the yellow nitrogen afterglow which involves electronic quenching of the $B^3\Pi_g$ state by carrier-gas molecules. Inclusion of a quenching process explains the observed pressure independence at high pressures of the $B^3\Pi_g$ vibrational distribution[2] and the overall emission intensity from $B^3\Pi_g$. At high pressure, the rate of quenching, which is proportional to the carrier concentration [M], is greater than the rate of radiative decay. Since the rates of vibrational relaxation in $B^3\Pi_g$ and of collision-induced transfer from the precursor state are also proportional to [M], it can be shown that the vibrational distribution and total concentration of $B^3\Pi_g$ in this case should be independent of [M]. If [M] is sufficiently small, however, the distribution should revert to that initially produced on transfer from the precursor state and the overall emission intensity should become proportional to [M]. A small shift in the distribution toward higher levels with decreasing pressure has been observed by Young[3] at pressures around 0·1 torr in a system having M = $N_2$. Because

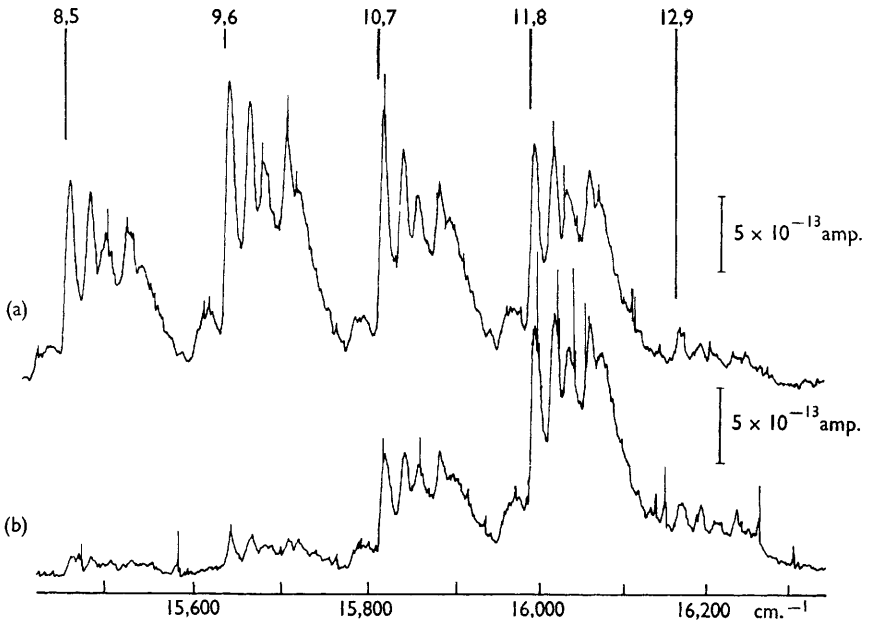


FIGURE. *Photoelectric recordings of first positive bands from active nitrogen produced by a pulsed discharge. The photomultiplier had an* S–20 *cathode and was cooled with dry ice.*

(a) Pressure = 2·2 torr; $[N] = 3 \times 10^{13}$ cm.$^{-3}$; $[N_2] = 4 \times 10^{13}$ cm.$^{-3}$; $[Ar] = 7{\cdot}8 \times 10^{16}$ cm.$^{-3}$, (b) Pressure = 0·32 torr, $[N] = 4 \times 10^{13}$ cm.$^{-3}$; $[N_2] = 9 \times 10^{13}$ cm.$^{-3}$; $[Ar] = 1{\cdot}1 \times 10^{16}$ cm.$^{-3}$. At 2 torr, the amount of $N_2$ in the mixture passing through the discharge was reduced from 1 to 0·07% so that [N] and $[N_2]$ would be about the same as for the trace at 0·3 torr. This change in composition affected the 2 torr distribution only slightly.

the quenching of $B^3\Pi_g$ by Ar or He appears to be less than by $N_2$,[1] pressure effects should become noticeable at a higher pressure if M = Ar or He.

We report here preliminary results of photoelectric intensity measurements of first-positive bands in a $N_2$–Ar system in the pressure range 0·3 to 4 torr. Nitrogen atoms were generated by passing a mixture of 1% or less $N_2$ in Ar through an electrodeless microwave discharge or through a pulsed discharge. Discharge products were pumped through a glass reaction tube 120 cm. long, 9·5 cm. internal diameter. The afterglow was viewed end-on with a low resolution grating monochromator (4 Å band-pass, *f*/11). The Ar flow was varied from 1 to 6 c.c./sec. (at 23° and 1 atm.). The N atom concentration [N] was measured by titration with NO.

We obtained the following results:

(a) When the pressure was lowered from 2 to 0·3 torr, the vibrational distribution in $B^3\Pi_g$ shifted to higher levels such that it almost resembled that normally observed[4] for M = $N_2$. This change is shown in the Figure.

(b) When the pressure was changed from 2 to 0·3 torr, the ratio of the sum of the intensities of the bands shown in the figure to $[N]^2$ decreased by a factor of approximately 4.

(c) Addition of 4% $N_2$ downstream from the discharge, with [N] and total pressure constant (at 1·5 torr), produced a small shift to higher levels, and slightly decreased the overall afterglow intensity, in agreement with previous observations.[1,4]

(d) The distribution at constant $[N_2]$ and [Ar] also depended somewhat on [N]. Decreasing [N] shifted the distribution slightly to lower levels.† For example, at 1·5 torr, changing [N] from $2{\cdot}5 \times 10^{14}$ to $0{\cdot}5 \times 10^{14}$ cm.$^{-3}$ decreased the ratio of the 11—8 band intensity to that of 8—5 by a factor of 1·6. This result suggests that N atoms also quench $B^3\Pi_g$.

† To facilitate dissociation of the $N_2$, either 0·01% $H_2O$ or $O_2$ was added to the gas upstream from the discharge. The concentrations of $H_2O$ or $O_2$ discharge products were probably too small to be responsible for the effect attributed here to nitrogen atoms. However, possible influence of these impurities on the distribution has not yet been excluded.

Except for a quenching step involving N atoms, these results seem to be consistent with the Campbell and Thrush mechanism. As a consequence vibrational relaxation in $B^3\Pi_g$ appears to be surprisingly rapid, occurring roughly once in every 100 $B^3\Pi_g$–Ar collisions.

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