

## THE EXCITATION OF CHLORINE IN ACTIVE NITROGEN

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(Received May 24, 1977; in revised form August 3, 1977)

### Summary

Excitation of the 258 nm emission of chlorine in active nitrogen has been studied. The intensity was shown to be proportional to  $[N]^2$  over an order of magnitude variation of  $[N]$ . In  $N_2$  carriers within the pressure range 0.1 - 1.5 kPa the intensity increased smoothly with increasing  $[Cl_2]$ , finally reaching a limiting plateau; at a pressure of 0.83 kPa the limiting 258 nm photon yield was measured as  $(9.0 \pm 3.0) \times 10^2 [N]^2$  einstein  $dm^{-3} s^{-1}$ , with  $[N]$  in  $mol\ dm^{-3}$ : this corresponded to only about 0.2% of N atom recombinations. The variation of intensity with total pressure indicated that the  $N_2$  energy-donating species was populated mainly by a pressure independent process, while an  $[N_2]$  dependent process competed with  $Cl_2$  in its removal. When the nitrogen carrier was progressively replaced with argon, the limiting 258 nm intensity divided by  $[N]^2$  was invariant up to 70% argon but was substantially enhanced with further increase of the argon mole fraction, the enhancement factor being about 2 at 95% argon.

On the basis of known kinetic behaviours in active nitrogen, none of the energetically feasible species  $N_2(A^3\Sigma_u^+)$  ( $v' \geq 6$ ),  $N_2(B^3\Pi_g)$  or  $N_2(B'^3\Sigma_u^-)$  could have been acting as the donor species to  $Cl_2$ . Accordingly we advance a tentative mechanism for the excitation of the 258 nm emission with  $N_2(W^3\Delta_u)$ , apparently the only remaining possibility, as the donor species. The kinetic behaviour of  $N_2(W^3\Delta_u)$  itself in active nitrogen is unknown since no emission from this state has been detected. Hence this study may provide the first insight into this.

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### Introduction

Studies of the excitation of  $Cl_2$  in active nitrogen date back to 1912 [1, 2]. The most recent investigation [3] was carried out in 1970; in that

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paper, Provencher and McKenney (hereafter referred to as PM) concluded that the continuum emission of  $\text{Cl}_2$  peaking strongly at 258 nm (hereafter referred to as the 258 nm emission) was excited by energy transfer from both the lowest vibrational levels of  $\text{N}_2(\text{A}^3\Sigma_u^+)$  and vibrationally excited  $\text{N}_2(\text{X}^1\Sigma_g^+)$  formed by recombination of  $\text{N}(^4\text{S})$  atoms. However, since that time it has been established [4] that the energy of the upper state associated with the 258 nm emission is  $7.21 \pm 0.05$  eV compared with the 6.22 eV excitation energy of  $\text{N}_2(\text{A}^3\Sigma_u^+, v' = 0)$ . Hence the donor species cannot be  $\text{N}_2(\text{A}^3\Sigma_u^+)$  molecules with vibrational quantum numbers less than 6.

PM also concluded that  $\text{N}_2$  quenching of the emitting chlorine molecules  $\text{Cl}_2(^3\Pi(0_g^+))$  was more important than radiative decay for  $\text{N}_2$  pressures above 1.33 kPa (10 Torr). The radiative lifetime of  $\text{Cl}_2(^3\Pi(0_g^+))$  has recently been determined [5] as  $10 \pm 1$  ns. Hence quenching by  $\text{N}_2$  would have to occur on almost every collision for this conclusion to be correct. This cannot be the case since spectral scans of the  $\text{Cl}_2$  258 nm continuum produced by photodissociation of  $\text{OCCl}_2$  using krypton lines at 123.6 nm and 116.5 nm in the presence and absence of 4 kPa of  $\text{N}_2$  show little variation in emission efficiency [4].

In view of the doubt cast on the PM conclusions by these more recent findings, we decided to repeat the study of the  $\text{Cl}_2$  excitation in active nitrogen. We find evidence that the principal donor species is  $\text{N}_2(\text{W}^3\Delta_u)$  — a postulate advanced earlier [6] solely on the basis of energetic considerations.

## Experimental

Active nitrogen was generated in a conventional fast-flow system; the Pyrex glass observation vessel was 0.25 m long and 26 mm in internal diameter, and the emission passed out through a quartz window attached to the downstream end of the tube. The cell was mounted on the entrance slit of a McPherson model 218 grating monochromator. The  $\text{Cl}_2$  emission intensity was measured with the monochromator set to 258.0 nm (the peak of the emission) using a 2400 grooves  $\text{mm}^{-1}$  grating blazed at about 250 nm and an EMI 6256B photomultiplier. Slit widths of both 200 and 400  $\mu\text{m}$  were used (band passes of 0.27 and 0.53 nm respectively). The detection circuitry was the same as that used by Campbell and Neal [7], and the signals were ultimately displayed on a pen recorder (Honeywell Electronik 194).

Measurements of the nitrogen first positive (1+) emission intensities in the near-infrared region were also made. In these an EMI 9659 B (extended S-20 photocathode) was mounted on the exit slit of the monochromator, which was fitted with a 1200 grooves  $\text{mm}^{-1}$  grating blazed at 1000 nm. The dark current of this photomultiplier tube was reduced to negligible proportions by enclosing it in a housing unit (Products for Research, Model TE-114) cooled to about 230 K. The detection circuitry and procedures were the same as those used by Campbell and Mason [8] in their study of

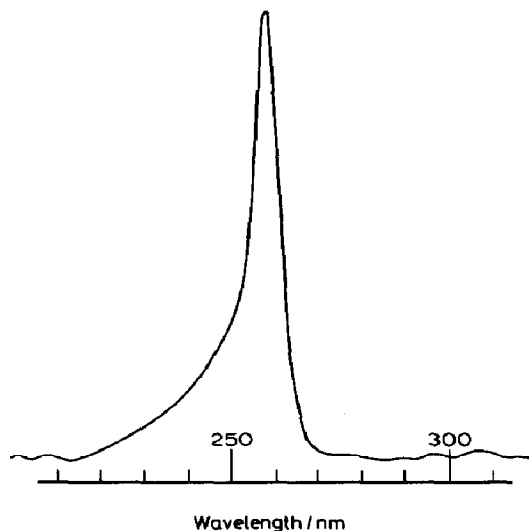


Fig. 1. Spectral scan across the  $\text{Cl}_2$  emission observed in active  $\text{N}_2$  in the  $\text{N}_2$  carrier. The total pressure was 0.52 kPa with  $[\text{N}] \approx 2 \times 10^{-6} \text{ mol dm}^{-3}$  and  $[\text{Cl}_2] \approx 10^{-6} \text{ mol dm}^{-3}$ . A trace of methane was added to the discharge to suppress the production of  $\text{O}(^3\text{P})$  atoms and hence NO emissions.

the nitric oxide Ogawa band emissions in the same spectral region. Here the  $\text{N}_2(1+)$  intensity measurements were made with  $400 \mu\text{m}$  slits (bandpass 1.06 nm).

Chlorine was taken from a BDH Chemicals lecture bottle (99.96% min.) and was distilled from bulb to bulb, rejecting the first and last fractions. The flow rate of this gas was measured using a capillary flowmeter with concentrated sulphuric acid as the manometer fluid; this had been pre-calibrated in the usual manner by measuring the rate of fall of the pressure of  $\text{Cl}_2$  in a standard volume. The flow rate was regulated by an Edwards stainless steel needle valve (Model OS1D) and the chlorine was added to the active nitrogen at the entry to the Pyrex cell using a pepper-pot jet to achieve rapid mixing. The concentrations of  $\text{N}(^4\text{S})$  atoms were measured by nitric oxide titration at the same jet (prior to addition of  $\text{Cl}_2$ ) and also at a jet in the exit tubing from the cell, as described before [8]. Total pressures in the cell were measured with a silicone oil manometer backed by a running vacuum. The flow system was pumped by an NGN PSR 12 pump; with the  $6 \text{ dm}^3 \text{ s}^{-1}$  pumping speed the typical residence time of gas in the cell was about 20 ms. The methods of flow rate measurement and purification of other gases were as described before [7, 8].

## Results

Figure 1 shows a scan across the  $\text{Cl}_2$  emission continuum, peaking at 258 nm, which was produced on adding  $\text{Cl}_2$  to active nitrogen. In contrast

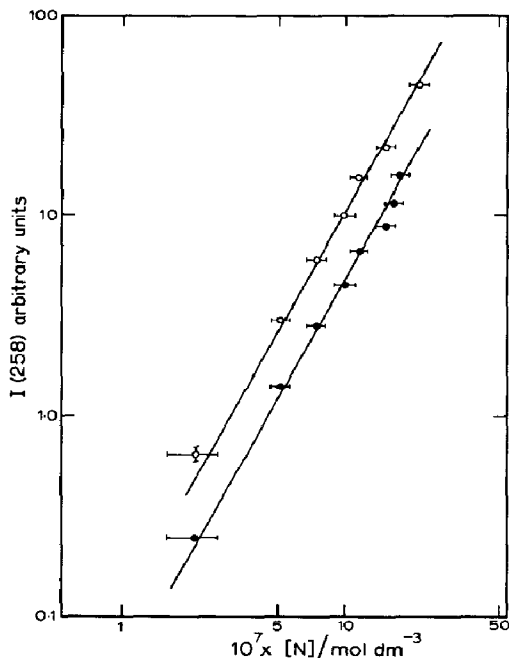


Fig. 2. Plots of the dependence of the 258 nm emission intensity ( $I(258)$ ) on nitrogen atom concentration in the  $N_2$  carrier at a total pressure of 0.51 kPa:  $\circ$  obtained with  $[Cl_2] \approx 4.3 \times 10^{-6} \text{ mol dm}^{-3}$ ;  $\bullet$  obtained with  $[Cl_2] \approx 7.0 \times 10^{-7} \text{ mol dm}^{-3}$ .

to the excitation of  $Cl_2$  by metastable argon atoms [9] the continuum peaking at 306.3 nm is not observed in active nitrogen. (The upper state of  $Cl_2$  of this transition has an excitation energy of  $7.93 \pm 0.03 \text{ eV}$  [4].) Under typical operating conditions small concentrations of  $O(^3P)$  atoms are present in the active nitrogen and give rise to weak  $\beta$ ,  $\gamma$  and  $\delta$  emission bands of NO as background in the 200 - 300 nm region. However, these emissions were generally much weaker than the  $Cl_2$  emission at 258 nm and, furthermore, no relatively strong NO band occurs in the vicinity of 258 nm so that no significant interference with our measurements of  $Cl_2$  emission intensities, made with the monochromator set to this wavelength, can be expected. At the same time the NO emissions were attenuated upon addition of  $Cl_2$ , owing to the removal of  $O(^3P)$  atoms by the reactions



Rate constants at 298 K are  $k_1 = 2.5 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $k_2 = 3.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [10], so that these rates are significant within the residence time (about 20 ms) in the observation cell in terms of  $O(^3P)$  consumption. However, removal of  $N(^4S)$  atoms by direct reaction with  $Cl_2$  is at least an order of magnitude slower [6, 11]. Because of the small, but finite, removal rate of  $N(^4S)$  atoms by this reaction, some experiments were carried out

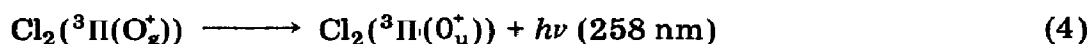
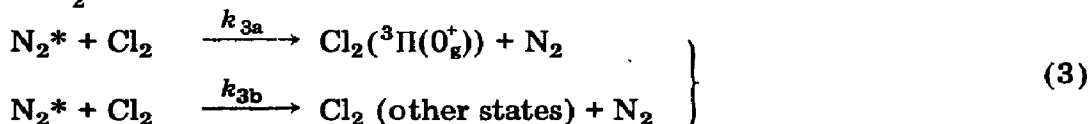
with the full pumping speed reduced by three to measure any effect on the results. The effect was found to be less than experimental error for  $\text{Cl}_2$  partial pressures below 20 Pa (with the full pumping speed).

Over the range of  $\text{N}_2$  pressures used in these experiments spectral scans showed that the shape of the 258 nm emission was essentially unchanged (half-width,  $6.5 \pm 0.5$  nm). Thus measurements of the peak height with the monochromator set at 258 nm were proportional to the total emission intensity in the continuum.

The dependence of the emission intensity at 258 nm ( $I(258)$ ) on  $[\text{N}]^2$  previously reported [3] was confirmed, as is shown by the logarithmic plot shown in Fig. 2 which has a gradient of 2 for  $[\text{N}]$  varied over an order of magnitude with two widely different partial pressures of  $\text{Cl}_2$ .

For these and subsequent experiments  $[\text{N}]$  was determined both before and after the observation cell, and the average was used because of the small (not more than 15%) decay of N atoms during transit through the cell.

Revealing experiments for elucidating the excitation mechanism were those where the variation of  $I(258)$  was measured as a function of  $[\text{Cl}_2]$  at various  $\text{N}_2$  pressures. Figure 3 shows the results of an experiment performed at 1.37 kPa pressure. A smooth increase of  $I(258)$  with increasing  $\text{Cl}_2$  addition is observed, rather than the two linear segments reported by PM [3]. With decreasing total pressure, for the same range of increasing  $\text{Cl}_2$  addition, the increase in  $I(258)$  was more rapid and a plateau was reached eventually. The attainment of a plateau intensity will occur when all of the excited  $\text{N}_2^*$  donor species which is capable of exciting the  $\text{Cl}_2$  emission is being removed by the  $\text{Cl}_2$ . On the basis of the mechanism



the prediction is

$$I(258) = \frac{k_{3a} [\text{Cl}_2] P}{k_3 [\text{Cl}_2] + A} \quad (I)$$

where  $P$  is the production rate of  $\text{N}_2^*$ . The plateau then occurs when  $k_3 [\text{Cl}_2] \gg A$ , where  $A$  is the rate of loss of  $\text{N}_2^*$  in the absence of  $\text{Cl}_2$ .

Equation (I) rearranges to the form

$$\frac{[\text{Cl}_2]}{I(258)} = \frac{k_3 [\text{Cl}_2] + A}{k_{3a} P} \quad (II)$$

The points shown in Fig. 3 are shown plotted in the form indicated by eqn. (II) in Fig. 4. The predicted straight line is clearly observed. The ratio of intercept to slope is predicted to be  $A/k_3$  and corresponds to  $2.4 \times 10^{-6}$

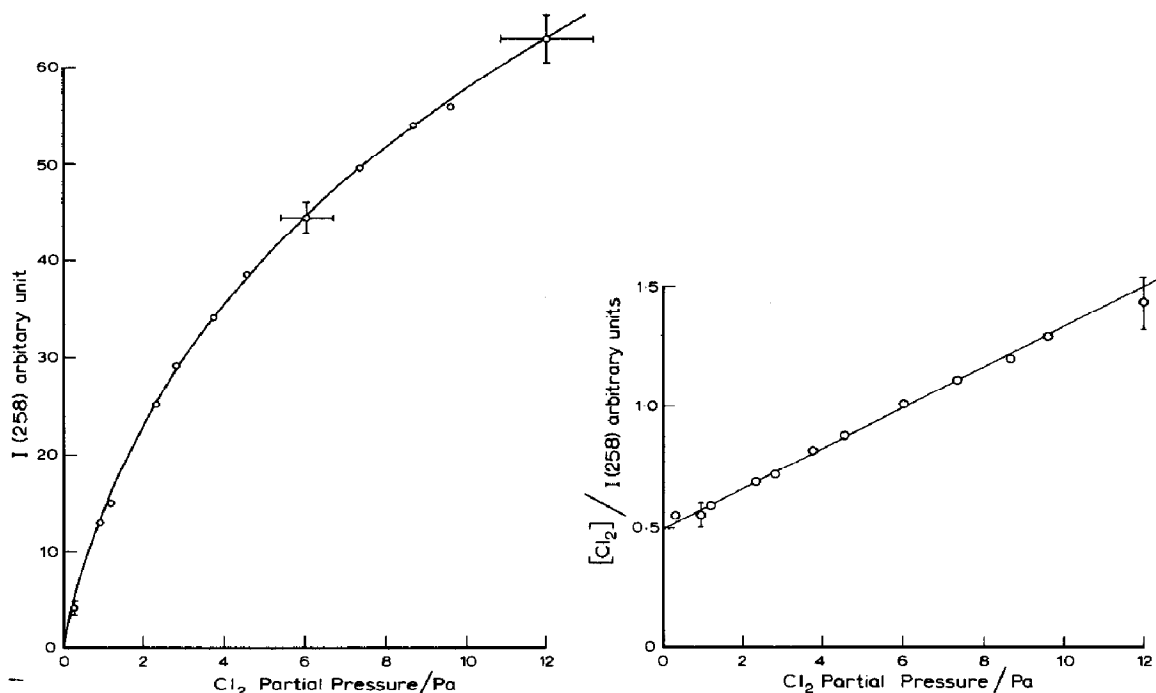


Fig. 3. Plot of  $I(258)$  vs.  $\text{Cl}_2$  partial pressure in the  $\text{N}_2$  carrier at a total pressure of 1.37 kPa and  $[\text{N}] = 1.6 \times 10^{-6} \text{ mol dm}^{-3}$ .

Fig. 4. Variation of  $[\text{Cl}_2]/I(258)$  with  $\text{Cl}_2$  partial pressure in the  $\text{N}_2$  carrier at a total pressure of 1.37 kPa and  $[\text{N}] = 1.6 \times 10^{-6} \text{ mol dm}^{-3}$ .

$\text{mol dm}^{-3}$  for a total pressure of 1.37 kPa of  $\text{N}_2$ . This value of  $A/k_3$  was found to be independent of  $[\text{N}]$  indicating that removal of  $\text{N}_2^*$  by nitrogen atoms was not significant. By carrying out measurements of  $I(258)$  versus  $[\text{Cl}_2]$  over a range of  $\text{N}_2$  pressures, the dependence of  $A/k_3$  on  $\text{N}_2$  pressure was determined as shown in Fig. 5. Clearly at low  $\text{N}_2$  pressure, the loss of  $\text{N}_2^*$  is dominated by collisional removal with nitrogen, a process which may be represented by the equation



From the slope of Fig. 5 at low  $\text{N}_2$  pressures, we derive  $k_6/k_3 = 1.0_5 \times 10^{-2}$ . Also included in Fig. 5 is a point for a  $\text{N}_2$  (4.5%) in Ar carrier at a total pressure of 0.47 kPa. This is only displaced by a comparatively small amount from the results for  $\text{N}_2$  carriers for the same  $[\text{N}_2]$ , showing that removal of  $\text{N}_2^*$  by argon is much slower than by  $\text{N}_2$  (argon is at least 10 times less efficient). The evident deviation of the plot in Fig. 5 from a straight line in the higher  $\text{N}_2$  pressure range and its effect on the previous reasoning will be discussed later.

The dependence of the production rate  $P$  of  $\text{N}_2^*$  on  $\text{N}_2$  pressure was derived from the plateau values of  $I(258)$  and the results are shown in Fig. 6.

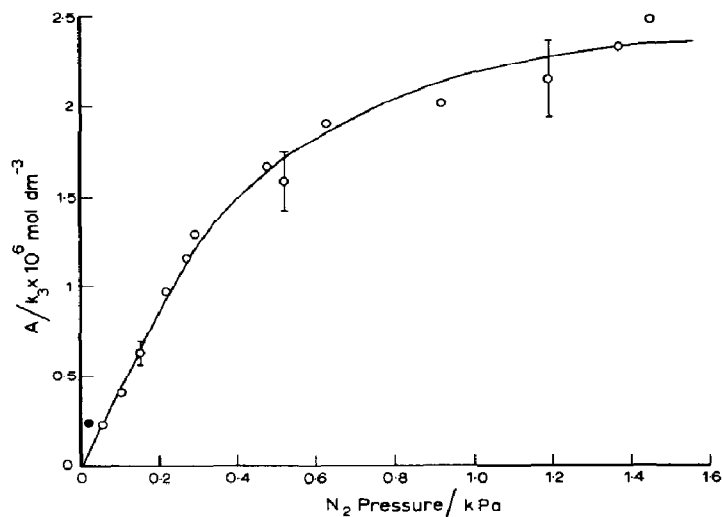


Fig. 5. Plot of the parameter ratio  $A/k_3$  (see text) vs. total pressure:  $\circ$  in the  $N_2$  carrier;  $\bullet$  in approximately 95% argon carrier (referred to  $N_2$  partial pressure).

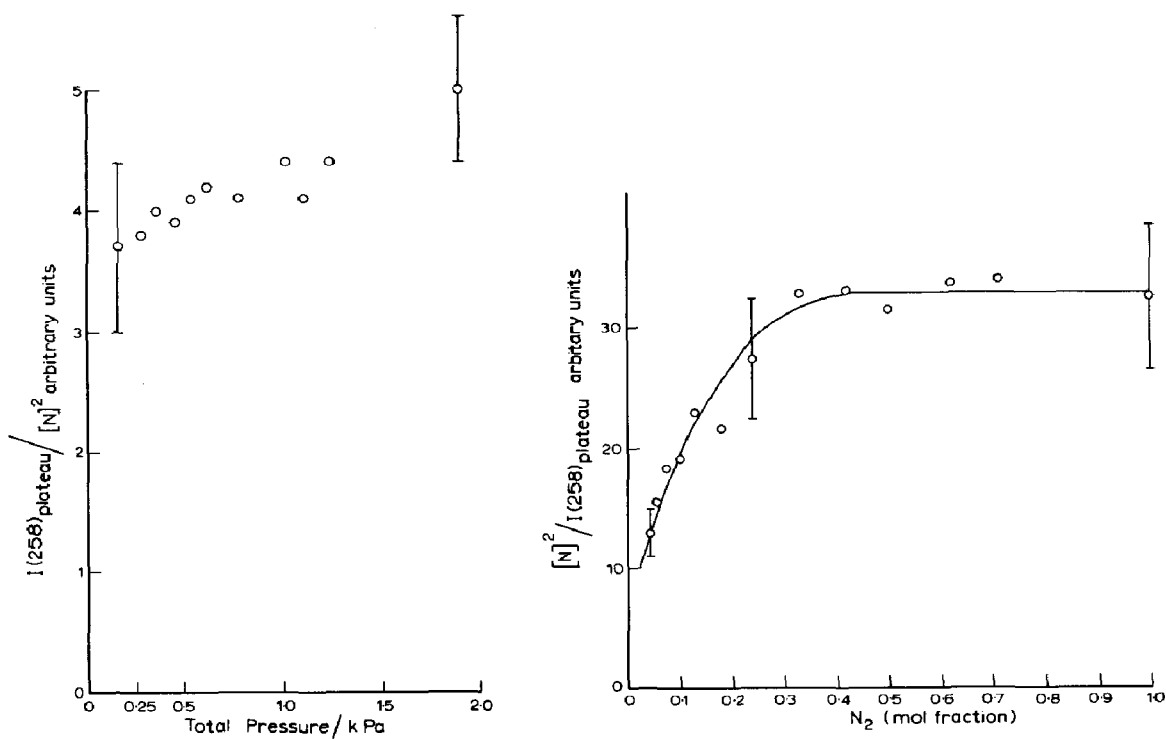


Fig. 6. Plot of the limiting efficiency of  $Cl_2$  emission (expressed as  $I(258)_{\text{plateau}}/[N]^2$ ) vs. total pressure in the  $N_2$  carrier.

Fig. 7. Plot of the inverse limiting efficiency of  $Cl_2$  emission (expressed as  $[N]^2/I(258)_{\text{plateau}}$ ) vs. mole fraction of  $N_2$  in argon carriers.

$P$  appears to increase slightly (about 20%) over an order of magnitude variation in  $N_2$  pressure, but the indicated error limits cannot exclude an invariance.

The effect on the plateau values of  $I(258)$  of replacement of the  $N_2$  carrier with argon is shown in Fig. 7 for a constant total pressure of 0.49 kPa. It is evident that there is a considerable effect, which is non-linear as a function of the mole fraction of  $N_2$ ; above 0.35 there is no change, but this marks the threshold of a considerable enhancement at lower mole fractions, amounting to more than a factor of 2 for 5%  $N_2$  carrier.

### Absolute intensity measurement

Since absolute emission rate coefficients are known [12, 13] for the  $NO(0,2)$   $\delta$  band at 206.1 nm and the  $NO(0,7)$   $\beta$  band at 303.9 nm, scans across these bands with established  $[N]$ ,  $[O]$  and  $[N_2]$  provided emission standards for comparison with the 258 nm  $Cl_2$  emission excited in subsequent experiments with established  $[N]$ . At an  $N_2$  carrier pressure of 0.82 kPa the integrated plateau intensity was given by  $(9.0 \pm 3.0) \times 10^{-2} [N]^2$  einstein  $dm^{-3} s^{-1}$ , with  $[N]$  expressed in  $mol dm^{-3}$ . The overall three-body rate constant for nitrogen atom recombination (third body  $M = N_2$ ) has been measured as  $(1.38 \pm 0.11) \times 10^9 dm^6 mol^{-2} s^{-1}$  [14]. This indicates that under the above conditions only about  $0.19 \pm 0.06\%$  of the N atom recombination events give rise to emission in the chlorine continuum with excess chlorine. Hence it follows that the donor species is only a minor energy carrier in active nitrogen or, if the donor is a major energy carrier, there must be a series of energy exchange channels with  $Cl_2$  of which that which excites the 258 nm continuum is only a minor component. Unfortunately we can only resolve this uncertainty by elimination.

### Effect of $Cl_2$ on $N_2(1+)$ emission

Using the near-infrared detection system, we examined the effect of the addition of  $Cl_2$  on the intensities of the bands in the  $N_2(1+)$  system. Figure 8 shows the effect of adding 0.45% of  $Cl_2$  to active nitrogen at 1.37 kPa pressure; this amount of  $Cl_2$  is sufficient to reduce the concentration of  $N_2^*$  by a factor of 2 on the basis of Fig. 5. It can be seen that there is very little quenching of the emission from high vibrational levels of the emitting  $N_2(B^3\Pi_g)$  state but that the extent of quenching increases as the vibrational quantum number  $v'$  decreases, being most noticeable for  $v' = 1$  ( $v' = 0$  emission lies above 1000 nm and could not be detected with our photomultiplier). However, even for  $v' = 1$  the quenching is not as large as a factor of 2. Further quenching experiments conducted on individual bands showed that even for much larger  $Cl_2$  additions only a part of the  $N_2(1+)$  emission was removed. The fraction which could be removed increased with decreasing  $v'$ .



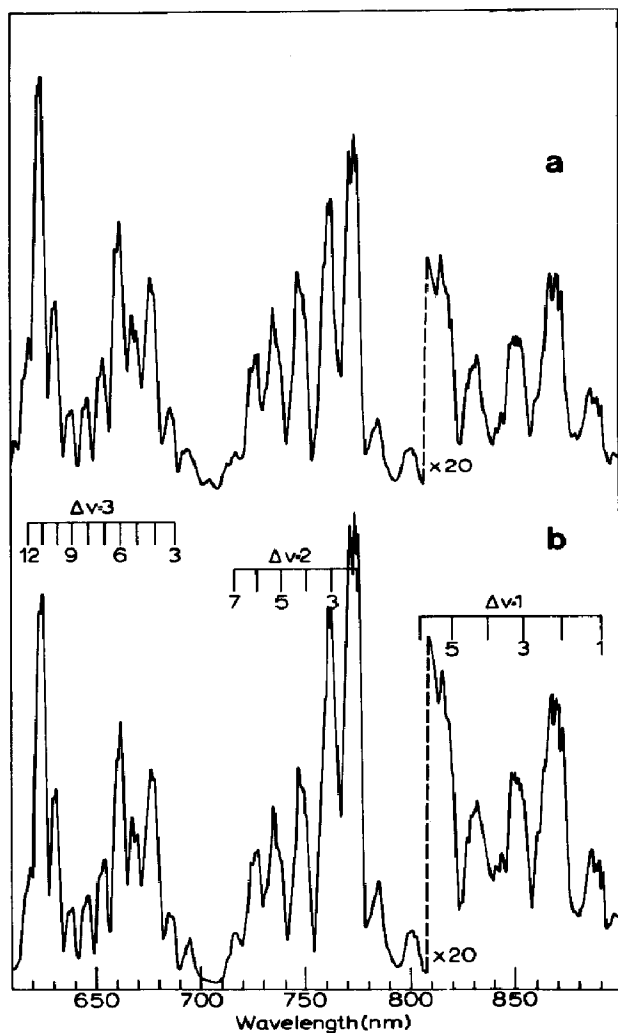


Fig. 8. Scans across the  $N_2(1+)$  emission in the near-infrared region with the  $N_2$  carrier at a total pressure of 1.37 kPa. Bands are indicated by  $\Delta v$  and the vibrational quantum number  $v'$  of the upper  $N_2(B^3\Pi_g)$  level. Spectrum (a) is for 0.45%  $Cl_2$  added; spectrum (b) is in the absence of  $Cl_2$ .

A further point with regard to the extent of dissociation of the  $Cl_2$  into Cl atoms can be made on the basis of Fig. 8. It is well known that three-body association of chlorine atoms gives rise to a reddish emission which extends into the near-infrared region with maximum intensity in the vicinity of 850 nm [15]. There is no indication of any such emission appearing between the  $N_2(1+)$  bands upon addition of  $Cl_2$ . It follows that  $[Cl]$  must be very low in our systems. The walls of our tube were not poisoned in any definite way and it is known that acid coating is required to inhibit chlorine atom destruction [16]; it is therefore possible that the chlorine dissociation rate in collisions with metastable nitrogen species could be quite large but

associated with a steady state [Cl] which is very low owing to efficient wall recombination. However, we can be certain that, for practical purposes, all the Cl<sub>2</sub> added to the active nitrogen is in the form of Cl<sub>2</sub> in our system.

## Discussion

The simplest excitation mechanism, *i.e.*



can be ruled out on a number of grounds, *e.g.* the plateau intensity is reached with very little removal of N atoms, competition with N<sub>2</sub> for the donor species at low N<sub>2</sub> pressures (Fig. 5) and the argon effect (Fig. 7).

The triplet nature of the excited state of Cl<sub>2</sub> giving the 258 nm emission and the singlet nature of the ground state of Cl<sub>2</sub> rules out any singlet state of N<sub>2</sub> acting as donor on the basis of spin conservation rules. The potential donors are then N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>) (*v* > 6), N<sub>2</sub>(B<sup>3</sup>Π<sub>g</sub>), N<sub>2</sub>(B<sup>3</sup>Σ<sub>u</sub><sup>-</sup>) and N<sub>2</sub>(W<sup>3</sup>Δ<sub>u</sub>).

The principal problem in interpreting our data is that only the ratio  $A/k_3$ , which increases linearly with pressure below 0.25 kPa (Fig. 5) but shows decreasing gradient above, can be extracted. Process (6), the interaction of N<sub>2</sub>\* with N<sub>2</sub> in competition with the interaction(s) with Cl<sub>2</sub>, explains the low pressure portion. The higher pressure fall-off could reflect a change in the nature of N<sub>2</sub>\* (*e.g.* towards a more vibrationally relaxed species) with increasing pressure but this cannot be clarified with the present results. The kinetic behaviours of N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>) (*v*' > 6) [17, 18], N<sub>2</sub>(B<sup>3</sup>Π<sub>g</sub>) [19 - 24] and N<sub>2</sub>(B<sup>3</sup>Σ<sub>u</sub><sup>-</sup>) [25, 26] in active nitrogen are well established and known to involve pressure dependent population. This leaves only N<sub>2</sub>(W<sup>3</sup>Δ<sub>u</sub>), about which least is known since associated emission has only been detected in discharge sources [27] and never in active nitrogen itself. The radiative lifetime of W state levels is of the order of 10<sup>-4</sup> s [28], which would permit it the degree of metastability required for the above mechanism.

Although Fig. 8 shows that Cl<sub>2</sub> interacts with the lowest levels of N<sub>2</sub>(B<sup>3</sup>Π<sub>g</sub>), the N<sub>2</sub> half-quenching pressures of these are of the order of 50 Pa [24] so that under our conditions the populations will be controlled by collisional processes. The form of Fig. 6 shows that the population process of N<sub>2</sub>\* is substantially pressure independent which cannot allow N<sub>2</sub>(B<sup>3</sup>Π<sub>g</sub>) to fill this role. Further, the plateau of 258 nm intensity corresponding to only (0.19 ± 0.06)% of N atom recombinations is not consistent with the efficiency for population of the lower levels of N<sub>2</sub>(B<sup>3</sup>Π<sub>g</sub>) in N<sub>2</sub> carriers which is greater than 10% [24]. Also the very definite proportionality of *I*(258) to [N]<sup>2</sup> shown in Fig. 2 is inconsistent with the intensities of N<sub>2</sub>(1+) emission from low *v*' being governed by an [N]<sup>*x*</sup> relationship with *x* < 2 [24].

With N<sub>2</sub>\* identified with N<sub>2</sub>(W<sup>3</sup>Δ<sub>u</sub>), the pressure independent population could be accommodated by the observed N<sub>2</sub>(B → W) radiation involving

the higher  $v'$  levels of  $N_2(B)$  which have populations strongly proportional to  $[N]^2$  and independent of  $[M]$ . On the basis that about 50% of N atom recombinations populate  $N_2(B^3\Pi_g)$  [14] and that  $N_2$  quenches the higher  $v'$  levels at about one-tenth of the collision frequency [22], a radiative rate constant of about  $10^4 \text{ s}^{-1}$  for  $B \rightarrow W$  means that at 0.8 kPa only around 0.15% of the population rate of  $N_2(B)$  can reach  $N_2(W)$  by radiative decay. If the 258 nm emission plateau is to reflect this population rate, then an efficiency of less than 0.08% is indicated, rather lower than our measured value of  $0.19 \pm 0.06\%$  but not unreasonably so within the scale of approximation of the above estimation. Since the radiative lifetime of  $N_2(W)$  is about  $10^{-4}$  s, a rate constant  $k_6$  of the order of  $2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  would allow  $N_2$ -induced removal of  $N_2(W)$  to be dominant under our conditions; in this event our result of  $k_3/k_6 \approx 100$  suggests that  $Cl_2$  must be excited to the 258 nm emitting state at nearly every collision with  $N_2^*$ . It appears unlikely that the  $N_2$  interaction could involve vibrational relaxation down the W state since the separations are close to  $150\,000 \text{ m}^{-1}$  [29], as opposed to  $236\,000 \text{ m}^{-1}$  for  $N_2(X)$ .

If we are to regard  $N_2(W)$  as making a vertical transition down to  $N_2(X)$  in transferring its energy to  $Cl_2$ , then the transition from the point of maximum probability of  $v' = 0$  ends most probably near  $v'' = 5$ . The resultant 6.0 eV released cannot excite  $Cl_2$  to the 258 nm state and may point to the identification of  $N_2^*$  with  $N_2(W)$  ( $v' > 0$ ). This is a necessary feature of the mechanism since it appears that there are rapid collision-induced crossings between  $N_2(B)$  ( $v' = 0$ ) and  $N_2(W)$  ( $v' = 0$ ) [30]. The rapid divergence of both limbs of the B and W potential curves with increasing  $v'$  makes such crossings less likely.

We cannot interpret the argon effect quantitatively as yet. Figure 7 does not show the linear enhancement for increasing the argon mole fraction expected if  $N_2(B)$  is involved in the precursor chain [14]. However, the spectacular enhancement above 0.7 mol fraction of argon almost parallels the observations of the change in vibrational distribution within  $N_2(B)$  made by Bayes and Kistiakowsky [31]. This may suggest a rather complex situation with different population channels to an array of  $N_2(W)$  levels, within which there could be significant variation of  $k_6$  and/or  $k_3$  rate constants.

In conclusion, we can claim to have made significant progress towards understanding the excitation of  $Cl_2$  emission in active nitrogen. Clearly, direct observation of  $N_2(W^3\Delta_u)$  emission in active nitrogen would provide the most direct way of testing the ideas presented here.

## Acknowledgments

One of us (G.B.) thanks the Science Research Council for the award of a Senior Visiting Fellowship. The assistance of Dr. R. S. Mason in setting up some of the experimental equipment is gratefully acknowledged.

## References

- 1 R. J. Strutt and A. Fowler, *Proc. R. Soc. London, Ser. A*, 86 (1912) 105.
- 2 A. N. Wright and C. A. Winkler, *Active Nitrogen*, Academic Press, New York, 1968.
- 3 G. M. Provencher and D. J. McKenney, *Chem. Phys. Lett.*, 5 (1970) 26.
- 4 H. Okabe, A. H. Laufer and J. J. Ball, *J. Chem. Phys.*, 55 (1971) 373.
- 5 G. Black, R. L. Sharpless and T. G. Slinger, unpublished results.
- 6 K. S. Raxworthy and L. F. Phillips, *Can. J. Chem.*, 42 (1964) 2928.
- 7 I. M. Campbell and S. B. Neal, *Discuss. Faraday Soc.*, 53 (1972) 72.
- 8 I. M. Campbell and R. S. Mason, *J. Photochem.*, 5 (1976) 383.
- 9 J. E. Velazco, J. M. Kolts and D. W. Setser, *J. Chem. Phys.*, 65 (1976) 3468.
- 10 D. L. Baulch, J. Duxbury, S. J. Grant and D. C. Montague, *Evaluated Kinetic Data for High Temperature Reactions*, Vol. 4, to be published.
- 11 M. R. Grigor and L. F. Phillips, *Proc. 11th Symp. Combustion*, Combustion Institute, Pittsburgh, Pa., 1967, p. 1171.
- 12 R. A. Young and R. L. Sharpless, *J. Chem. Phys.*, 39 (1963) 1071.
- 13 M. Mandelman, T. Carrington and R. A. Young, *J. Chem. Phys.*, 58 (1973) 84.
- 14 I. M. Campbell and B. A. Thrush, *Proc. R. Soc. London, Ser. A*, 296 (1967) 201.
- 15 L. W. Bader and E. A. Ogryzlo, *J. Chem. Phys.*, 41 (1964) 2926.
- 16 E. A. Ogryzlo, *Can. J. Chem.*, 39 (1961) 2556.
- 17 J. W. Dreyer and D. Perner, *J. Chem. Phys.*, 58 (1973) 1195.
- 18 J. W. Dreyer, D. Perner and C. R. Roy, *J. Chem. Phys.*, 61 (1974) 3164.
- 19 W. Brennen and E. C. Shane, *Chem. Phys. Lett.*, 2 (1968) 143.
- 20 N. Jonathan and R. Petty, *J. Chem. Phys.*, 50 (1969) 3804.
- 21 R. L. Brown, *J. Chem. Phys.*, 52 (1970) 4604.
- 22 A. W. Johnson and R. G. Fowler, *J. Chem. Phys.*, 53 (1971) 65.
- 23 K. H. Becker, E. H. Fink, W. Groth, W. Jud and D. Kley, *Discuss. Faraday Soc.*, 53 (1972) 35.
- 24 E. M. Gartner and B. A. Thrush, *Proc. R. Soc. London, Ser. A*, 346 (1975) 121.
- 25 M. F. Golde and B. A. Thrush, *Proc. R. Soc. London, Ser. A*, 330 (1972) 121.
- 26 E. M. Gartner and B. A. Thrush, *Proc. R. Soc. London, Ser. A*, 346 (1975) 103.
- 27 K. A. Saum and W. M. Benesch, *Appl. Opt.*, 9 (1970) 195.
- 28 R. Covey, K. A. Saum and W. Benesch, *J. Opt. Soc. Am.*, 63 (1973) 592.
- 29 W. M. Benesch and K. A. Saum, *J. Phys. B*, 4 (1971) 732.
- 30 R. F. Heidner, D. G. Sutton and S. N. Suchard, *Chem. Phys. Lett.*, 37 (1976) 243.
- 31 K. D. Bayes and G. B. Kistiakowsky, *J. Chem. Phys.*, 29 (1958) 949.