

**REACTIONS FORMING ELECTRONICALLY EXCITED FREE RADICALS**  
**III: FORMATION OF EXCITED MOLECULAR STATES IN THE**  
**H + NF<sub>2</sub> REACTION**

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**Summary**

The reaction (1) of H(<sup>2</sup>S) atoms with NF<sub>2</sub> radicals forms metastable excited NF(a<sup>1</sup>Δ) molecules with a branching ratio greater than 0.9:



Subsequent reactions form also the b<sup>1</sup>Σ<sup>+</sup> state of NF; the strong 0-0 bands of the a-X and b-X transitions of NF are near 874 and 528 nm and their emission intensities were used to follow the excited state concentrations.

The secondary reaction (2a) of H + NF(a<sup>1</sup>Δ) forms excited N(<sup>2</sup>D) atoms, whilst ground state N(<sup>4</sup>S) atoms are formed by reaction (2b) of hydrogen atoms with ground state NF:



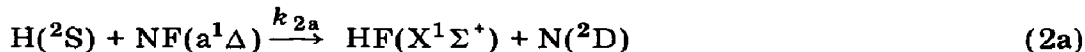
N(<sup>2</sup>D) atoms are the precursors of the intense emission of N<sub>2</sub> both in the First Positive system B<sup>3</sup>Π<sub>g</sub>-A<sup>3</sup>Σ<sub>u</sub><sup>+</sup> and in the Lyman-Birge-Hopfield system a<sup>1</sup>Π<sub>g</sub>-X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>. Excited N(<sup>2</sup>D) atoms also are the precursors of the singlet c<sup>1</sup>Π-a<sup>1</sup>Δ and triplet A<sup>3</sup>Π-X<sup>3</sup>Σ<sup>-</sup> transitions of NH, which are emitted from the H + NF<sub>2</sub> reaction in the presence of H<sub>2</sub>. It is believed that ground state NH(X<sup>3</sup>Σ<sup>-</sup>) radicals first are formed in the reaction N(<sup>2</sup>D) + H<sub>2</sub> → NH + H and are subsequently excited by energy transfer.

**1. Introduction**

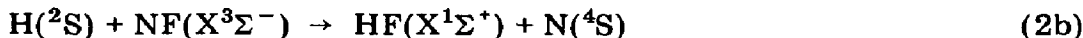
In previous work [1, 2] we have confirmed the hypothesis [3] that the rapid reaction of H(<sup>2</sup>S) atoms with NF<sub>2</sub> radicals leads mainly, if not exclusively, to metastable excited NF(a<sup>1</sup>Δ) radicals:



We were able to show that the formation of  $\text{NF}(a^1\Delta)$  in reaction (1) accounts for at least 90% of the product channels [2]. This conclusion was reached through the direct detection of excited  $\text{N}(^2\text{D})$  and ground state  $\text{N}(^4\text{S})$  atoms by resonance fluorescence [2] which showed that only  $\text{N}(^2\text{D})$  atoms are formed as primary products of reaction (2a):



Initial formation of  $\text{N}(^4\text{S})$  was not found, thus excluding the state-selective reaction (2b) as a major channel when  $\text{NF}$  radicals were formed in reaction (1):



In independent work done concurrently with this study Malins and Setser [4] came to the same conclusion regarding the products of reaction (1) using a different approach based on the measurement of the a-X emission intensities of  $\text{NF}$ . Also, they determined a value of 5.6 s for the radiative lifetime of the  $a^1\Delta$  state of  $\text{NF}$ .

The  $\text{H} + \text{NF}_2$  reaction emits chemiluminescence not only in the a-X transition of  $\text{NF}$ , the 0-0 band of which is near 874 nm, but also in the b-X transition of  $\text{NF}$ , the 0-0 band of which is near 528 nm. The resulting green chemiluminescence is very intense. The  $b^1\Sigma^+$  state of  $\text{NF}$  is believed to be formed by energy transfer in collisions of  $\text{NF}(a^1\Delta)$  with  $\text{HF}(v'' \geq 2)$  [3, 5].

Under conditions favouring the production of  $\text{N}(^2\text{D})$  atoms, namely when  $[\text{H}]_0 > [\text{NF}_2]_0$ , the  $\text{NF}$  chemiluminescence is dominated by the intense visible and vacuum UV emission in the First Positive  $\text{B}^3\Pi_g - \text{A}^3\Sigma_u^+$  and Lyman-Birge-Hopfield  $a^1\Pi_g - X^1\Sigma_g^+$  systems respectively of  $\text{N}_2$ . In addition, triplet and singlet emissions of  $\text{NH}$  are observed with moderate intensity.

In this work the emissions of  $\text{N}_2$  and  $\text{NH}$  were characterized, the vibrational (and, where possible, rotational) distributions were determined and possible precursors for these emissions were evaluated. To complement the study of the emissions of  $\text{N}_2$  and  $\text{NH}$  the time dependence of the  $\text{NF}(a^1\Delta)$  state was considered.

## 2. Experimental

Most of the observations described in this work were photometric measurements of chemiluminescence intensities supplemented by spectral observations of the molecular chemiluminescence emissions at moderate resolution (0.05 - 0.5 nm). As described previously [2] measurements of resonance fluorescence intensities in the vacuum UV region also were made in order to determine the time dependences of the concentrations of  $\text{N}(^4\text{S})$ ,  $\text{N}(^2\text{D})$  and  $\text{H}(^2\text{S})$ . These measurements are not described again here.

## 2.1. Photometric measurements

For convenience the same spectrometer was used for the atomic fluorescence measurements and for the photometric measurements of the molecular emission spectra. A large-aperture 1.5 m Fastie monochromator ( $f/8$ , Jarrell-Ash 75-100) accommodated two exit slits in its focal plane. The grating was a 1200 line  $\text{mm}^{-1}$  replica blazed at 500 nm in first order and overcoated with  $\text{MgF}_2$ . It was used in the first or second orders for measurements from 300 to 880 nm in conjunction with exit slit 1 and a thermoelectrically cooled GaAs photomultiplier tube (RCA C31034, fewer than 5 counts  $\text{s}^{-1}$  at 253 K). For photometric work on the 0-0 band of the  $\text{a}^1\Delta - \text{X}^3\Sigma^-$  system of NF near 874 nm the temperature of the photocathode was critical, since cooling drastically reduces the quantum efficiency of the photomultiplier at wavelengths above 850 nm.

Atomic resonance and other vacuum UV spectrometry was performed by using the grating in the third or fourth orders for work in the range 120 - 250 nm with exit slit 2 and a solar-blind CsI photomultiplier (EMR-541G-08-18), which had a dark count of less than 1 count  $\text{s}^{-1}$  at 298 K.

HF vibration-rotation transitions ( $v'' < 3$ ) in emission were observed as the 2-1 and 1-0 bands between 2 and 3  $\mu\text{m}$ . The detector was a PbS device (6 mm  $\times$  2 mm, Infra Red Industries Inc.) cooled to 198 K, and IR radiation was dispersed with a 30 cm monochromator giving a resolution of approximately 10  $\text{cm}^{-1}$  full width at half-maximum, *i.e.* adequate partially to resolve rotational structure in the HF bands.

### 2.1.1. Flow tube

The flow tube, which was used for the study of the  $\text{H} + \text{NF}_2$  and  $\text{H} + \text{NF}$  reactions, was made of Pyrex (26 mm in internal diameter) and was coated with Teflon. The flow tube passed through a cuboidal brass block and was provided with 25 mm holes directly opposite the  $\text{MgF}_2$  windows, one of which admitted light to the spectrometer entrance slit (ref. 2, Fig. 1). The block was provided with 25 mm  $\text{MgF}_2$  windows; its dimensions were designed to minimize the dead volume.

The flow tube was provided with several inlet jets and could be evacuated continuously, giving a maximum linear velocity of 1600  $\text{cm s}^{-1}$ . The total pressure was determined with a capacitance manometer (M.K.S. Baratron model 222, accuracy  $\pm 2\%$ ) and reagent flows were determined with transducer flowmeters (Hastings-Raydist) or with silicone oil capillary flowmeters (for the carrier gases only).

The production of hydrogen atoms was by means of a microwave discharge in hydrogen (less than or equal to 10 mol.%) using argon or helium as the carrier gas.  $\text{NF}_2$  radicals were produced as described previously [1] by the thermolysis of  $\text{N}_2\text{F}_4$  at 500 K.

### 2.1.2. Reagents

Helium, hydrogen and argon (BOC high purity grade) were dried and purified by passing them over an outgassed molecular sieve at a temperature

below 198 K. The tetrafluorohydrazine (Air Products or Hercules Research Grade) was stated to be greater than 99.8% pure.

### 3. Results and discussion

#### 3.1. Detection of $NF(a^1\Delta)$

The emission spectrum of the 0-0 band of the  $a^1\Delta-X^3\Sigma^-$  system of  $NF$  near 874 nm is shown in Fig. 1 using the  $H + NF_2$  chemiluminescence reaction as the source of  $NF(a^1\Delta)$ . The identification was readily made by comparison with the work of Jones [6]. The intensity was sufficient to give at least partial rotational resolution in the  $S_R$ ,  $R_Q$ ,  $R_R$ ,  $P_Q$  and  $P_P$  branches, although the  $Q_Q$ ,  $Q_R$  and  $Q_P$  lines are largely overlapped and form the central intense maximum in Fig. 1.

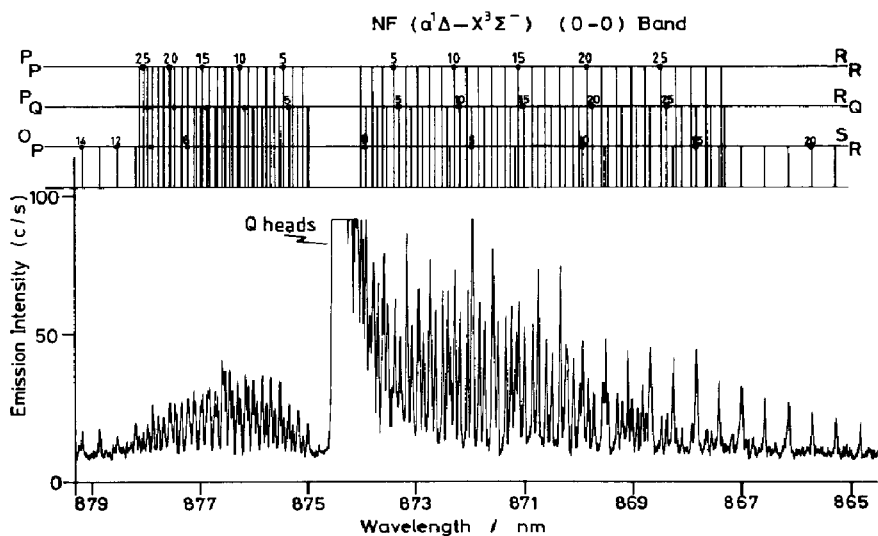
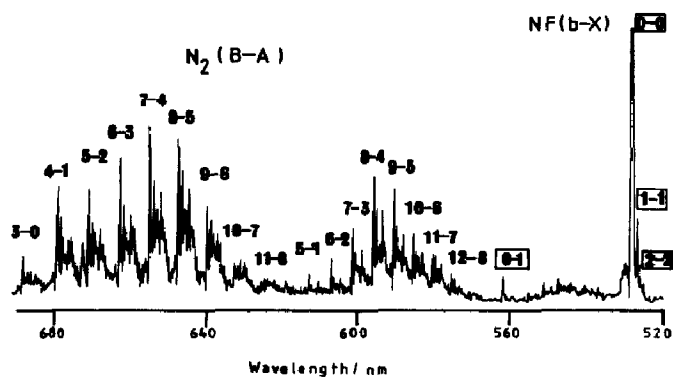
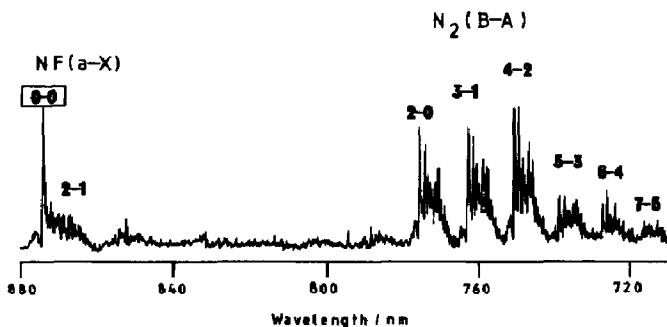


Fig. 1. Emission spectrum of the 0-0 band of the  $a^1\Delta-X^3\Sigma^-$  system of  $NF$  using the  $H + NF_2$  reaction as the source of  $NF(a^1\Delta)$ . Experimental conditions: excess  $NF_2$ ; total pressure, 1 Torr. There is an intense Q head region near the band centre.

Under the conditions used (low  $[H_2]$ , less than  $1 \times 10^{14} \text{ cm}^{-3}$ ) no vibration-rotation bands of  $HF$  ( $\Delta v = 3$ ), which overlap the spectral range of the 874 nm band of  $NF$ , could be observed. However, under different conditions, using excess free hydrogen atoms and with  $H_2$  present, a weak 3-0 overtone band of  $HF$  could be observed. Also, in the presence of free hydrogen atoms the First Positive  $B^3\Pi_g-A^3\Sigma_u^+$  bands of  $N_2$  were developed. (These were absent when hydrogen atoms were not present, see Fig. 1.) The development of the B-A bands of  $N_2$  in the presence of free hydrogen atoms is shown in Fig. 2. The 2-1 band of the B-A transition of  $N_2$  may be seen partially to overlap the 0-0 band of the a-X transition of  $NF$ . This illustrates the need in this work for adequate spectral resolution in photometric measurements of the transient species.



(a)



(b)

Fig. 2. Emission spectrum from the  $\text{H} + \text{NF}_2$  reaction in the presence of free hydrogen atoms: (a) 520 - 680 nm; (b) 720 - 880 nm. The B-A bands of  $\text{N}_2$  are strongly developed in addition to the a-X and b-X bands of NF.

### 3.2. Relaxation in $\text{NF}(a^1\Delta)$

The radiative lifetime of the  $a^1\Delta - X^3\Sigma^-$  transition of NF has been reported by Malins and Setser [4] to be  $5.6 \text{ s}^{-1}$  ( $\pm 50\%$ ). The observation of intense emission in the 0-0 band therefore indicates (1) that considerable steady state concentrations of  $\text{NF}(a^1\Delta)$  were present in the products of the  $\text{H} + \text{NF}_2$  reaction and (2) that electronic quenching of the  $a^1\Delta$  state of NF is relatively inefficient. The latter conclusion agrees with the small rate constants found for electronic quenching [7] of the highly metastable  $a^1\Delta_g$  state of  $\text{O}_2$ .

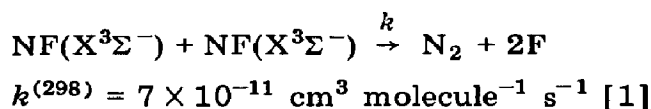
Emission spectra were observed after reaction times of 5 ms or longer. The absence of significant features arising from a 1-1 band in Fig. 1 is expected since vibrational relaxation of the initially formed distribution of states in  $\text{NF}(a^1\Delta)$  is likely to be extensive within 5 ms. We note that Malins and Setser [4], using the much shorter reaction time of approximately 0.2 ms, observed additional features in the  $a^1\Delta - X^3\Sigma^-$  spectrum of NF which they assigned to the 1-1 and 2-2 bands.

The measurement of the rotational line intensities of the 0-0 band of the  $a^1\Delta - X^3\Sigma^-$  system of NF (Fig. 1) gave a rotational temperature of  $306 \pm$

20 K for the excited state, *i.e.* essentially that of a thermal Boltzmann distribution at ambient temperature. Since vibrational equilibration in  $\text{NF}(a^1\Delta)$  evidently was rapid, it is not surprising that rotational relaxation was essentially complete under the conditions used.

### 3.3. Quenching of $\text{NF}(a^1\Delta)$

In view of the long radiative lifetime of the  $a^1\Delta$  state of  $\text{NF}$ , collisional deactivation of this state can be expected to be dominant under the conditions used in this work. This deactivation may be of two types: reactive collisions and electronic quenching collisions. A rapid bimolecular reaction between two ground state  $\text{NF}(X^3\Sigma^-)$  radicals has been inferred in previous studies [1] of the  $\text{H} + \text{NF}_2$  reaction in the presence of excess  $\text{H}_2$ :



A similarly rapid reaction between  $\text{NF}(a^1\Delta)$  and  $\text{NF}(a^1\Delta)$  or between  $\text{NF}(a^1\Delta)$  and  $\text{NF}(X^3\Sigma^-)$  may occur, although there is no direct evidence in favour of rapid bimolecular  $\text{NF} + \text{NF}$  disproportionation reactions involving excited  $\text{NF}$  radicals.

Typical data for the variation of the  $\text{NF}(a^1\Delta)$  concentration with reaction time, based on the observation of the 0-0 band intensity of the  $a$ - $X$  transition at 874 nm, are shown in Fig. 3. As was expected, the concentra-

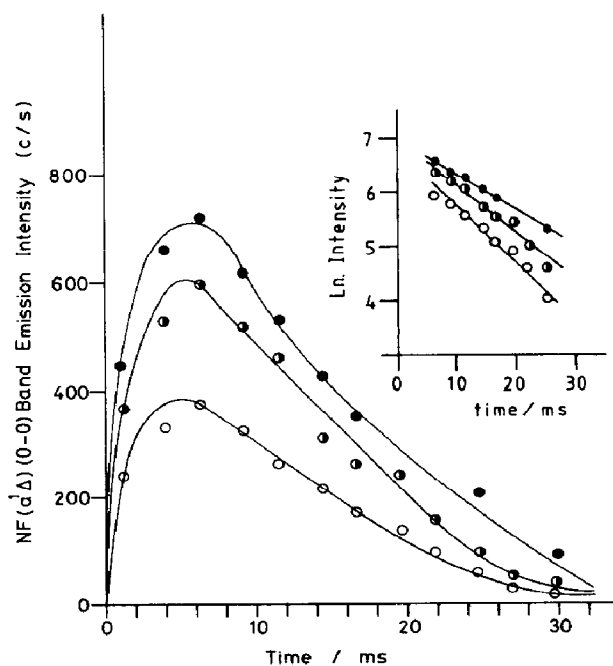
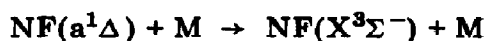


Fig. 3. Variation of the  $\text{NF}(a^1\Delta)$  concentration with time. Initial concentrations of  $\text{NF}_2$  ( $\times 10^{13} \text{ cm}^{-3}$ ):  $\circ$ , 0.62;  $\ominus$ , 0.92;  $\bullet$ , 1.70.

tion of  $\text{NF}(a^1\Delta)$  reached a maximum at relatively short reaction times (of the order of 10 ms) and then diminished with increasing reaction times. A kinetic analysis of the decay curves gave satisfactorily linear first-order plots (Fig. 3). However, a contribution by a second-order decay at the highest concentration of  $\text{NF}(a)$  could not be excluded since the linearity of first-order plots is notoriously insensitive to small or moderate rates of concurrent second-order decay. A more detailed analysis of the decay kinetics of  $\text{NF}(a^1\Delta)$  is described elsewhere [8]. This analysis shows that the dominant elementary process removing  $\text{NF}(a^1\Delta)$  is electronic quenching by a molecular species M, which is kinetically first order:



Wall loss appeared to be unimportant [8]. In the present system such quenching species included  $\text{H}_2$ , HF, NF and any unreacted  $\text{NF}_2$ . Typical overall first-order rate constants for  $\text{NF}(a^1\Delta)$  quenching were in the range  $75 - 150 \text{ s}^{-1}$ , indicating that radiative loss of  $\text{NF}(a^1\Delta)$  (radiative lifetime  $\tau_R = 5.6 \text{ s}$  [4]) was negligible under these conditions.

#### 3.4. Reaction of H with $\text{NF}(a^1\Delta)$

Although quenching of  $\text{NF}(a^1\Delta)$  was the dominant reaction, appreciable reaction of this species with free  $\text{H}(^2\text{S})$  atoms occurred via reaction (2a). The rate constant  $k_{2a}$  has been estimated to be  $2.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. Typical values of  $[\text{H}]$  in the region of  $2 \times 10^{13} \text{ cm}^{-3}$  then gave a pseudo-first-order rate constant of approximately  $5 \text{ s}^{-1}$  for the removal of  $\text{NF}(a^1\Delta)$  in reaction (2a). This indicates that approximately 5% of the  $\text{NF}(a^1\Delta)$  depletion under typical conditions was accounted for by reaction (2a), the remaining 95% being lost by quenching.

#### 3.5. Decay kinetics of $\text{NF}(b^1\Sigma^+)$

The green emission bands of the b-X transition of NF [9] dominated the chemiluminescence from the  $\text{H} + \text{NF}_2$  reaction in the absence of free hydrogen atoms. A spectrum of the main bands observed at short reaction times (less than 5 ms) is shown in Fig. 4; these bands were assigned readily to a predominant 0-0 band with weaker 1-1, 2-2, 3-3 and 4-4 bands. Each band consists of an intense complex Q head with well-defined rotational side branches in which the  $^{\text{O}}\text{P}(\text{N})$  and  $^{\text{S}}\text{R}(\text{N})$  branches stand out clearly (Fig. 4).

The rotational temperature in the 0-0 band was estimated to be  $350 \pm 20 \text{ K}$ , *i.e.* slightly above the temperature of the bath gas (298 K). Thus, the  $b^1\Sigma^+$ ,  $v' = 0$  state of NF was mainly rotationally relaxed after 5 ms had elapsed. However, the vibrational distribution of  $\text{NF}(b^1\Sigma^+)$  was hot, as is shown clearly by the relative intensities of the 0-0, 1-1, 2-2 and 3-3 bands in Fig. 4, bearing in mind that the Franck-Condon factors for this band sequence decrease with an increase in  $v'$ . This non-thermal vibrational distribution relaxed rapidly along the flow tube, giving only very weak  $v' = 1$  emission after approximately 30 ms. The retention of initial vibrational energy at short times in  $\text{NF}(b^1\Sigma^+)$ , although not in  $\text{NF}(a^1\Delta)$ , can be readily

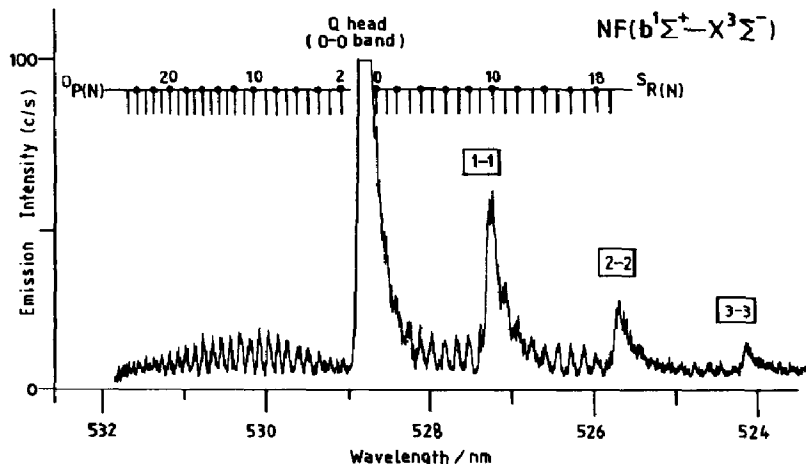


Fig. 4. Emission spectrum of the  $b^1\Sigma^+-X^3\Sigma^-$  system of NF from the  $H + NF_2$  reaction. The partial rotational resolution of the 0-0 band and the weaker band heads arising from the 1-1, 2-2 and 3-3 bands should be noted.

understood in terms of the more rapid quenching rate constants [8] and the much shorter radiative lifetime of the  $b^1\Sigma^+$  state, which is around 23 ns according to recent work [8, 10].

Under similar conditions the true photon intensity of the b-X emission of NF was typically 10 times greater than that of the a-X emission of NF. However, we note that the ratio  $\tau[NF(a)]/\tau[NF(b)]$  of radiative lifetimes is large, namely of the order of  $5.6/0.023 \approx 300$ . Consequently the steady state concentration of the  $a^1\Delta$  state can be expected normally to dominate that of the  $b^1\Sigma^+$  state. For this reason it is believed that the  $b^1\Sigma^+$  state plays only a minor role in the production of excited (or ground) state nitrogen atoms in the  $H + NF$  reaction. However,  $N(^2D)$  atom formation (from  $H + NF(a^1\Delta)$ ) is postulated in this work to be the precursor of  $N_2$  and NH emissions. It seems unlikely, therefore, that  $NF(b^1\Sigma^+)$  can be a major precursor of  $N_2$  and NH emissions in the light of its relatively low concentration.

Before completing the consideration of the  $b^1\Sigma^+$  state of NF it is of interest to speculate on the possible products of the reaction  $H(^2S) + NF(b^1\Sigma^+)$ . In previous work [2],  $H(^2S) + NF(a^1\Delta)$  was found to give  $N(^2D) + HF$ , whilst  $H(^2S) + NF(X^3\Sigma^-)$  gives  $N(^4S) + HF$ . The spin correlation rules prohibit the formation of  $N(^4S)$  from  $H(^2S) + NF(a^1\Delta)$  although not the formation of  $N(^2P)$ . However, the formation of  $N(^2D)$  from  $H(^2S) + NF(X^3\Sigma^-)$  is not prohibited by the spin correlation rules, although it is forbidden by the  $L-\Lambda$  orbital angular momentum correlation rule.  $L-\Lambda$  correlation can be expected to be rigorous, of course, only when the transition complex  $[H-N-F]$  is linear [11].

Preferential formation of  $N(^4S)$  atoms from  $H(^2S) + NF(X^3\Sigma^-)$  [2] thus suggests that  $L-\Lambda$  correlation may be important. If this is so, it would be concluded that  $H(^2S) + NF(b^1\Sigma^+)$  would be unreactive since there is no energetically feasible exit channel giving a nitrogen atom that can simultaneously satisfy the spin and  $L-\Lambda$  correlation rules. However, the observation



[2] of small concentrations of  $N(^2P)$  atoms ( $[N(^2P)]/[N(^2D)] \approx 0.1$ ) from the reaction of  $H(^2S)$  with a mixture of the  $X^3\Sigma^-$ ,  $a^1\Delta$  and  $b^1\Sigma^+$  states of  $NF$  suggests that there is some relaxation of the  $L-\Lambda$  correlation rules.  $N(^2P)$  might then be formed with a small rate constant from reaction of  $H(^2S)$  with any (or all) of the three states of  $NF$ .

### 3.6. First Positive $B^3\Pi_g-A^3\Sigma_u^+$ emission system of $N_2$

In the presence of free hydrogen atoms following the  $H + NF_2$  reaction, excited metastable  $N(^2D)$  atoms were found to be formed at concentrations of the order of  $10^{11} \text{ cm}^{-3}$  and typically to persist for approximately 30 ms [2]. Under these conditions intense B-A bands of  $N_2$  (Fig. 2) were emitted along the flow tube and decayed at approximately the same rate as the  $N(^2D)$  atoms.

#### 3.6.1. Vibrational distribution within the $B^3\Pi_g$ state of $N_2$

The observed distribution of vibrational bands of the B-A emission of  $N_2$  is shown in Fig. 2, with the partial resolution demonstrating the several heads within the complex rotational structure of these triplet bands. Transitions with  $12 \geq v' \geq 2$  were identified readily; observed band intensities were converted to absolute intensities using the monochromator and detector response curves, and the corresponding relative vibrational populations  $N_{v'}$  were calculated by the application of the relevant Franck-Condon densities  $q_{v',v''}$  [12]:

$$N_{v'} \propto I_{v',v''} / \nu^3 q_{v',v''}$$

The resulting variation of the vibrational population  $N_{v'}$  with the vibrational quantum number  $v'$  in the excited  $B^3\Pi_g$  state is shown in Fig. 5(a) for

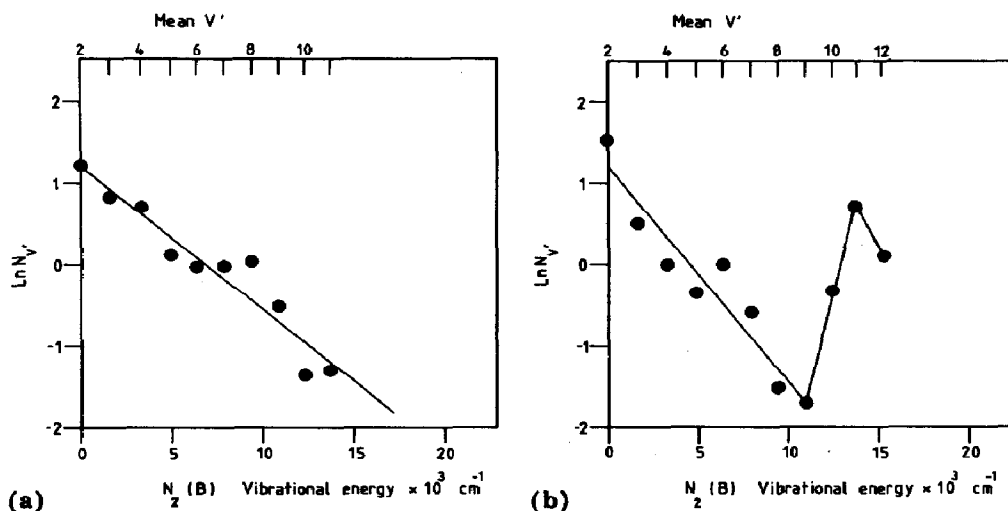


Fig. 5. Vibrational distribution within the B state of  $N_2$ : (a) distribution using the  $H + NF_2$  reaction as the source of  $N_2(B)$  for a pressure of 1 Torr; (b) distribution in the Lewis-Rayleigh afterglow from recombination of  $N(^4S) + N(^4S) (+M)$  for a pressure of 10 Torr.

typical conditions of 1.8 Torr total pressure (greater than 99 mol.% Ar). A monotonic fall in  $N_{v'}$  with increasing  $v'$  was obtained; the data could be fitted to an apparent Boltzmann vibrational temperature of 8200 K.

It is particularly significant that no second maximum near  $v' = 11 - 13$  was present in the vibrational distribution curve for the  $N_2$  population formed from the  $H + NF_2$  reaction. However, this second maximum is observed for the  $N_2$  B state population from the Lewis-Rayleigh afterglow, which is characteristic of recombination of ground state  $N(^4S)$  atoms [13 - 15]:



The population maximum near  $v' = 12$  in the B state of  $N_2$  is ascribed to its formation by various mechanisms of preassociation of  $N(^4S)$  atoms at this energy level [13 - 15]. The observed vibrational population curve for the B state of  $N_2$  from the B-A emission in an  $N(^4S) + N(^4S)$  system is shown in Fig. 5(b) for a pressure of  $N_2$  of 10 Torr. The curve is in agreement with the finding of Becker *et al.* [15] that the maximum near  $v' = 12$  persists well above a pressure of 1 Torr when  $N(^4S)$  recombination is the precursor.

It is concluded that the vibrational distribution of the B-A emission of  $N_2$  from the  $H + NF_2$  reaction shows no evidence for the formation of the B state via preassociation of atoms, as is observed in the  $N(^4S)$  atom recombination. Furthermore, the intensity of emission in the B-A bands from the  $H + NF_2$  reaction was several orders of magnitude greater than could be accounted for by recombination of available nitrogen atoms.

### 3.6.2. Mechanism of formation of $N_2(B)$

For the reasons given in Section 3.6.1 it is likely that the precursor of  $N_2(B)$  in the  $H + NF_2$  system is a rapid (and highly exoergic) bimolecular reaction. We show in Fig. 6 typical data for the time dependence of the B-A emission of  $N_2$  ( $v' = 9$ ), as well as similar data for the other major excited states, namely  $N(^2D)$ ,  $NF(a^1\Delta)$ ,  $NF(b^1\Sigma^+)$ ,  $N_2(a^1\Pi_g)$  and the  $A^3\Pi - X^3\Sigma^-$  system of NH. The time evolutions of the  $N_2(B)$ ,  $N_2(a)$  and NH(A) states are quite similar and follow qualitatively those of the  $N(^2D)$  and  $NF(a^1\Delta)$  states. They do not follow the evolution of the  $N(^4S)$  state profile, which increases monotonically with reaction times up to and greater than 30 ms [1, 2].

Thus, it seems possible that  $N(^2D)$  and  $NF(a^1\Delta)$  are the major precursors of the  $N_2$  and NH emitters. In the cases of  $N_2(B)$  and  $N_2(a)$ , very large amounts of excitation energy must be transferred into the emitters: up to  $78\,700\text{ cm}^{-1}$  for  $N_2(B)$  ( $v' \leq 12$ ) and up to  $72\,250\text{ cm}^{-1}$  for  $N_2(a)$  ( $v' \leq 2$ ). Suitably exoergic reactions are



and



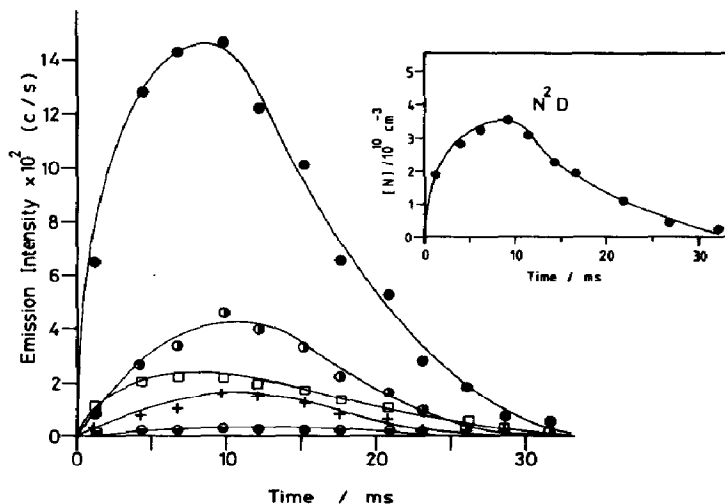


Fig. 6. Time variations of the concentrations of major excited species in the  $\text{H} + \text{NF}_2$  reaction:  $\bullet$ ,  $\text{NF}(b^1\Sigma^+)$ ;  $\circ$ ,  $\text{N}_2(\text{B})$ ;  $\square$ ,  $\text{NF}(a^1\Delta)$ ;  $+$ ,  $\text{NH}(A^3\Pi)$ ;  $\ominus$ ,  $\text{N}_2(a)$ . Relative concentrations from the relevant emission intensities are shown.

Reaction (3) is more probable than reaction (4) as a precursor for the  $\text{N}_2(\text{B}, a)$  excited states, since typical  $\text{N}(^2\text{D})$  concentrations were of the order of  $10^{11} \text{ cm}^{-3}$  whilst  $\text{NF}(a^1\Delta)$  concentrations were much greater (of the order of  $10^{13} \text{ cm}^{-3}$ ). Thus, the rate of reaction (3) assuming a collision efficiency of 0.1, *i.e.*  $k_3 \approx 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , typically would be approximately  $3 \times 10^{13} \text{ photons cm}^{-3} \text{ s}^{-1}$ , in agreement with the high observed intensity of the B-A emission.

### 3.7. Lyman-Birge-Hopfield $a^1\Pi_g - X^1\Sigma_g^+$ emission system of $\text{N}_2$

As in the case of emission from  $\text{N}(^4\text{S})$  recombination [15 - 18], the vacuum UV bands of the  $a^1\Pi_g - X^1\Sigma_g^+$  system of  $\text{N}_2$  were found to be emitted from the  $\text{H} + \text{NF}_2$  reaction under the same conditions as those favouring the emission of the B-A bands of  $\text{N}_2$ .

A typical spectrum of the a-X bands of  $\text{N}_2$  from the  $\text{H} + \text{NF}_2$  reaction is shown in Fig. 7 for a pressure of 1 Torr. The vibrational energy distribution was strongly relaxed with bands of the  $0-v''$  progression being predominant. However, weaker emission up to at least  $v' = 2$  can be discerned in the spectrum of Fig. 7. Strong vibrational relaxation in the  $a^1\Pi_g$  state of  $\text{N}_2$  by approximately 1 Torr of bath gas was observed in the  $\text{N}(^4\text{S})$  recombination, where the initially formed vibrational state of  $\text{N}_2(a^1\Pi_g)$  is  $v' = 6$  [16]. Similar relaxation is expected with other precursor reactions [17 - 20]. Rapid vibrational relaxation is to be expected in view of the metastability of the  $a^1\Pi_g$  state ( $\tau_R = 1.4 \times 10^{-4} \text{ s}$  [21]), which radiates to the ground state via a magnetic dipole transition.

Golde [19, 20] has shown that the formation of  $\text{N}_2(a^1\Pi_g)$  in flowing afterglows occurs through collisional curve crossing from the even more metastable  $a'^1\Sigma_u^-$  state of  $\text{N}_2$ . In the present  $\text{H} + \text{NF}_2$  system the spectra

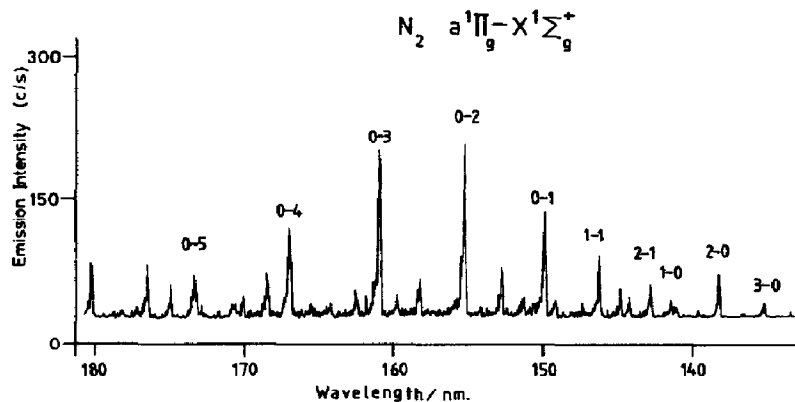


Fig. 7. Emission spectrum of the  $a^1\Pi_g-X^1\Sigma_g^+$  system of  $N_2$  from the  $H + NF_2$  reaction. Weak  $a'-X$  bands (not assigned) also are present in this wavelength region.

(Fig. 7) showed definite evidence of the forbidden  $a^1\Sigma_u^- - X^1\Sigma_g^+$  system of  $N_2$ ; thus, small concentrations of  $N_2(a')$  appear to be present.

### 3.8. Kinetics of formation of $N_2(B)$

We show in Fig. 8 typical data for the variation of the intensity  $I(B-A)$  of the B-A emission of  $N_2$  ( $v' = 9$ ) with the product  $[NF(a^1\Delta)][N(^2D)]$ . Three sets of runs are shown with initial concentrations  $[NF_2]_0$  of  $6.2 \times 10^{12} \text{ cm}^{-3}$ ,  $9.2 \times 10^{12} \text{ cm}^{-3}$  and  $1.7 \times 10^{13} \text{ cm}^{-3}$ , using a constant initial concentration  $[H]_0$  of approximately  $2 \times 10^{13} \text{ cm}^{-3}$ . The intensity of the B-A emission of  $N_2$  is a measure of the concentration of  $N_2(B^3\Pi_g)$ , whilst the intensity of the a-X emission of NF is a measure of the concentration of  $NF(a^1\Delta)$ . The concentrations of  $N(^2D)$  atoms were determined directly by resonance fluorescence at 149 nm [2]. Within experimental error the plot of Fig. 8 is a straight line through the origin. Thus, the observed concentration dependence of  $I(B-A)$  is consistent with the formation of  $N_2(B)$  through the bimolecular reaction (3). The present direct observations confirm the suggestion first put forward by Herbelin and Cohen [3], based on somewhat indirect evidence, that  $N_2(B)$  was formed by reaction (3).

### 3.9. $NH A^3\Pi - X^3\Sigma^-$ and $c^1\Pi - a^1\Delta$ emissions

The emission spectra of chemiluminescence that were observed between 324 and 345 nm from the  $H + NF_2$  reaction are shown in Figs. 9(a) and 9(b) with excess hydrogen atoms and undissociated  $H_2$  present. Two transitions of NH of medium intensity readily were identified; these were the 0-0 bands of the triplet  $A^3\Pi - X^3\Sigma^-$  system [22] (Fig. 9(a)) and the 0-0 bands of the singlet  $c^1\Pi - a^1\Delta$  system [23] (Fig. 9(b)). These transitions are well known in emission from flames and discharges as well as in the photodissociation of  $HN_3$  [24]. Furthermore, the A-X and c-a transitions were used in absorption or fluorescence to study the kinetic behaviour of  $NH(X)$  [25] and  $NH(a)$  [26]. Partial rotational resolution was obtained, sufficient to determine approximate rotational temperatures of 5500 K and 900 K in the

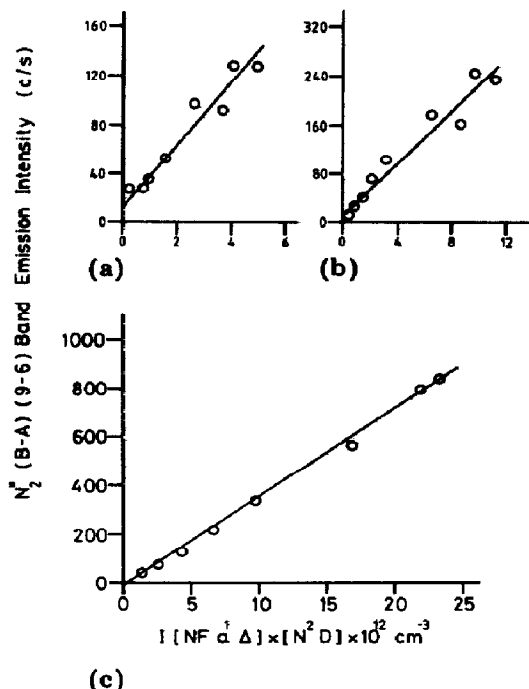


Fig. 8. Kinetics of formation of  $N_2(B^3\Pi_g)$ . The variation of  $I(B-A)$  with the product  $[NF(a^1\Delta)][N(2D)]$ . Initial concentrations of  $[NF_2]_0$  ( $\times 10^{12} \text{ cm}^{-3}$ ): (a) 6.2; (b) 9.2; (c) 17.0.

$A^3\Pi$  and  $c^1\Pi$  states respectively under typical conditions. The difference in rotational temperatures clearly is not due to the difference in lifetime between the  $A^3\Pi$  state ( $0.46 \mu\text{s}$ ) [27 - 29] and the  $c^1\Pi$  state ( $0.43 \mu\text{s}$ ) [27, 29]. More probably, the initial rotational energy in the  $A^3\Pi$  state is much greater than that in the  $c^1\Pi$  state.

In order to identify the precursor of the NH emissions, the usual  $H_2 + H$  atom flow was replaced by a flow of  $D_2 + D$  atoms. The NH spectra were replaced by the corresponding A-X and c-a transitions of ND. The c-a transition of ND together with a short section of A-X transition of ND are shown in Fig. 9(c). Based on this evidence it seems likely that the initial step responsible for forming NH radicals is reaction (5):



It is noted that reaction (5) is exoergic by  $12\,200 \text{ cm}^{-1}$  with respect to the formation of ground state NH; the corresponding reaction of ground state  $N(^4S)$  atoms with  $H_2$  is endoergic by  $7030 \text{ cm}^{-1}$  and thus is negligibly slow at 298 K.

Collisions of ground state  $NH(X^3\Sigma^-)$  formed in reaction (5) with excited electronic states, probably  $N_2(A^3\Sigma_u^+)$  metastables, very likely are responsible for the formation of the excited  $A^3\Pi$  and  $c^1\Pi$  states of NH.

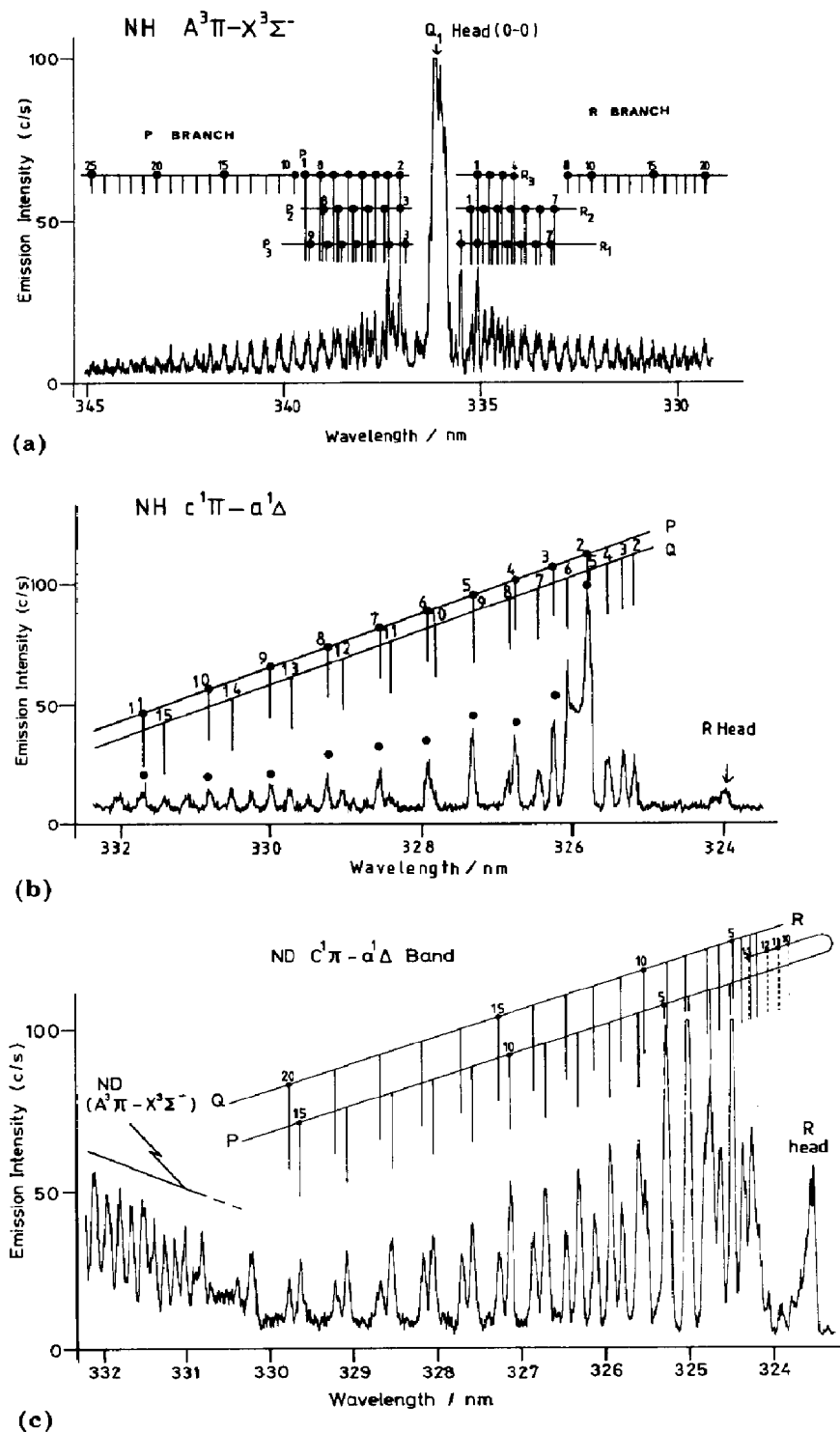


Fig. 9. Emission spectra of NH (ND) from the  $H(D) + NF_2$  reaction: (a) the  $A^3\Pi-X^3\Sigma^-$  system of NH; (b) the  $c^1\Pi-a^1\Delta$  system of NH; (c) the  $c^1\Pi-a^1\Delta$  system of ND and a short section of the  $A^3\Pi-X^3\Sigma^-$  system of ND. Free hydrogen atoms present; the same conditions as those used to obtain Figs. 2 and 7.

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