PRELIMINARY STUDIES OF NF3 + H2 PRODUCTION OF N2(A3 SIGMA++) IN A SUPERSONIC FLOW(U) AIR FORCE WEPNONS LAB KIRTLAND AFB NM Y D JONES ET AL. FE 88

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PRELIMINARY STUDIES OF NF₃ + H₂ PRODUCTION OF N₂(A³ Σ⁺ U) IN A SUPersonic FLOW

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The NF₄ has been used in reaction with H₂ and H₂O to produce NF₃(A¹Σ⁺), NF₃(B¹Σ⁺) and N₂(A³Σ⁺U). The NF₄ is shock sensitive and not commercially produced. Nitrogen trifluoride, NF₃ has been used in HF lasers as a fuel. By operating a conventional HF laser combustor at lower temperatures and less fuel, this study was designed to investigate the use of NF₃ as a replacement for NF₄ in NF₃(A¹Σ⁺) and N₂(A³Σ⁺U) production. Both of these energy transfer agents are of interest in the area of chemical lasers as an energy pump for a suitable species such as IF or NO. The NF₃ was not only used in the combustor and injected into an H₂ stream, but was also injected directly into the flow field.

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1.0 INTRODUCTION

The reaction between $\text{N}_2\text{F}_4$ and $\text{H}_2$ has been studied extensively (Refs. 1-4). Because of the hazard of working with the shock-sensitive $\text{N}_2\text{F}_4$ and the lack of commercial production of $\text{N}_2\text{F}_4$, an alternate means of producing the required $\text{NF}_2$ was investigated. The $\text{NF}_3$, nitrogen trifluoride, has been used frequently as a fluorine source for hydrogen fluoride (HF) and deuterium fluoride (DF) lasers.* The handling of ND$_3$ is substantially easier than N$_2$F$_4$ (Refs. 5,6). The NF$_3$ combustor method used in HF(DF) lasers to produce F atoms was assumed to work, except that a lower temperature in the combustor would be required to retain the NF$_2$ intact. Combustion of the NF$_3$ should provide the NF$_2$ and F source for the following reactions to produce NF(a$^1\Delta$) and N$_2$(A$^3\Sigma$).

\[
\text{NF}_3 \xrightarrow{\Delta} \text{NF}_2 + \text{F} \quad (1)
\]

\[
\text{H}_2 + \text{F} \rightarrow \text{H} + \text{HF} \quad (2)
\]

\[
\text{NF}_2 + \text{H} \rightarrow \text{NF}(a^1\Delta) + \text{HF} \quad (3)
\]

\[
\text{NF}(a^1\Delta) + \text{H} \rightarrow \text{N}(^2\text{D}) + \text{HF} \quad (4)
\]

\[
\text{NF}(a^1\Delta) + \text{N}(^2\text{D}) \rightarrow \text{N}_2(\text{B}) + \text{F} \quad (5)
\]

\[
\text{N}_2(\text{B}) \rightarrow \text{N}_2(\text{A}) + h_v \quad (6)
\]

The NF(a$^1\Delta$) and N$_2$(A) have been considered as energy storage molecules to be used in the transfer of energy to atoms or molecules suitable for lasing. Both NF(a$^1\Delta$) and N$_2$(A) have long lifetimes which makes them unsuitable for lasing (Refs. 7,8).

*Communications with operators of the RACHL device at AFWL and Mr. Chuck Lorenzen, Rocketdyne, KAFB, NM.
2.0 DEVICE

The experimental device has been described in Ref. 9; however, Fig. 1 is provided to show the overall layout. The NF₃ was injected where the fluorine port is indicated for the first series of tests. The later test series involved injecting NF₃ through the trip jets directly into the cavity. The device was constructed of 316L stainless steel. All flow systems were made of stainless steel because of the corrosive nature of the gases.

The nozzle used was the BCL-16. The supersonic nozzle has been studied for HF/DF laser applications (Ref. 10). The nozzle assembly consisted of a combustor section leading into the primary jets. The combustor portion of the nozzle assembly was operated (as it had been designed) to produce F atoms. The hydrogen or deuterium and flourine or NF₃ were injected into the combustor along with helium diluent at a molar ratio of F₂: D₂: He: NF₃ of approximately 3: 5.5: 1: 4.3 to begin testing, and was then optimized.

A one-half cross section of the nozzle is shown in Fig. 2. The nozzle is symmetric in the X-Y plane about the indicated X-axis. The He purge flow as indicated in Fig. 2 represents the He bleed plate which was an annular injector positioned on the gas input wall of the device. The bleed plate injection was used to confine the nozzle flame and kept the observation windows from direct contact with the flame. The BCL-16 contains three secondary nozzles through which either H₂ or D₂ could be mixed with the F atoms arriving through the two primary nozzles. Using NF₃ in the combustor involved starting the combustion with F₂ + D₂ and then mixing in NF₃. At lower NF₃ flow rates, a constant low flow of F₂ was required for sustained combustion.
3.0 DIAGNOSTICS

3.1 NF(a1A) AND NF(b1Σ) DIAGNOSTICS

The NF(a1A) diagnostic was an important part of the reaction analysis. The overall arrangement of the NF(a) and NF(b) diagnostics is shown in Fig. 3 and has been described in Ref. 11. The diagnostic as applied to the device is shown in Fig. 4. Figure 5a shows the result of a digitized photograph of the NF3 flame. The flame shape was less broadened than the N2F4 flame because of lower temperatures in the flow. Figure 5b illustrates the comparison. The actual width of the flame was used to determine the volume viewed by the diagnostic along the path of the scan. The spatial filter was mounted on a remotely operated translation stage with a linear voltage displacement transducer to accomplish scans across the flow field of the device with a known position. Sample scans of the NF(a1A) and NF(b1Σ) emissions are shown in Figs. 6 and 7.

Errors for the diagnostics were based upon the extent of interferences from other emissions and calibration errors. The error for the NF(b1Σ) diagnostic was determined to be ±10% with a range to 10^{11} to 10^{13} molecules/cm^3. For the NF(a1A) diagnostic, the error was larger due to the interferences from other emissions in the system and was estimated at ±20% with a range of 10^{14} to 10^{16} molecules/cm^3.

3.2 OPTICAL MULTICHANNEL ANALYZER (OMA)

The OMA III 1460R system (EG&G PAR) was used to monitor the change in emission over a wide wavelength range (usually 300-900 nm) at a fixed point within the device. The OMA III system consisted of a nonintensified diode array head (Model 1412) coupled to a Model 1233 polychromator. The triple grating polychromator was operated using the 150 l/mm or 600 l/mm grating. The emission from the device was delivered to the polychromator via a fused silica fiber optic matched to the entrance slit. The system using the 150 l/mm grating had a wavelength resolution of 0.6 nm/channel. Using the fiber optic with a spatial filter, the spatial resolution was about 4 cm.
4.0 OPTIMIZATION OF N₂(B)

4.1 COMBUSTOR INJECTION OF NF₃

The combustor flow rates were varied to obtain an intense N₂(B) visible spectra as a method of tracking N₂(A) production. After the combustor was optimized, the secondary H₂ was varied. Figures 8 through 11 show some of the results of the parametric NF₃ studies. The N₂(B) population was not as sensitive to NF₃ flow as might be expected. Table 1 summarizes several test conditions where high N₂(B) levels were achieved. The N₂(B) levels were as high as similar tests using N₂F₄. The NF(a¹Δ) production was lower than on tests with N₂F₄. A sample OMA III scan is shown in Fig. 12, using NF₃. A scan using N₂F₄ is shown for comparison in Fig. 13. The feature which is most striking is a peak around 670 nm. The possible problem is that the second order of the NH peak is causing the visible peak; however, the scans were also performed using ultraviolet blocking filters and the peak remained. The identity of the peak has not been determined. The marked lack of NF(a¹Δ) and NF(b¹Σ) when NF₃ is used is interesting in that large N₂(B) populations were still found. One conclusion may be that the reaction is occurring more rapidly in the NF₃ combustion. This is probably due to more complete mixing occurring between the NF₂ primary and H₂ secondary jets; although to confirm this, a mixing study should be performed. The lack of definition of the features in N₂(B-A) series in Fig. 12, may be due to greater broadening caused by slightly higher pressure in the NF₃ experiment.

4.2 TRIP JET INJECTION OF NF₃

Based upon the high temperature in the cavity with N₂F₄ and the known reaction of NF₃ with H₂, injection of NF₃ directly into the cavity was tried. Visible emission was seen via video cameras focused on the device. The measured emission using the NF(a) and NF(b) diagnostics were much lower than the NF₃ combustor studies. The NF(a) was two orders of magnitude lower and the NF(b) not detectable on several tests. Sample OMA III scans are shown in Figs. 14
to 17. Very little $N_2(B-A)$ is shown and mainly the HF ($\Delta v = 4$) sequence bands are apparent. The scans are at increasing distance from the NEP or the point of injection. By Fig. 17, one observes an increase in the $N_2(B-A)$ emission. This corresponds to 9 cm from the NEP. The $N_2(B-A)$ emission may increase downstream; however, the reaction of $NF_3 + H_2$ and the mixing combined is too slow for the supersonic application. More investigation of the system may provide a method for accelerating the reaction. Mixing can be improved by a new nozzle design; however, trip jet injection was discarded in favor of direct combustion with $D_2$ and $F_2$ until nozzle studies can be performed.
5.0 CONCLUSIONS

The direct injection of NF$_3$ into a stream of H atoms is insufficient at the temperature generated by reaction in the cavity. Combustion of NF$_3$ and D$_2$ provided an excellent source of NF$_2$ through control of the combustion mixture and thus the temperature. The production level of N$_2$(B) implies that NF$_2$, and perhaps NF, was formed in the combustion. The lower NF(a’A) production with NF$_3$ rather than with N$_2$F$_4$ is an unexpected result. This implies that NF is being formed in another state or that some N(2D) is being formed directly in the combustion. The large NH or ND peak seen when NF$_3$ is used may also indicate early N(2D) formation. Further exploration of the mechanism is required in order to explain these observations.

The question of whether complete mixing is occurring is present in this set of experiments as was reported with the N$_2$F$_4$ studies (Ref. 9). Detailed hot flow mixing studies will be required to answer the level of mixing question.

These experiments are only intended to be preliminary studies to determine the utility of using NF$_3$ in place of N$_2$F$_4$ in N$_2$(A) production. The results here indicate that the approach is promising. Further work must be accomplished in the areas of kinetics, mechanism and reactive flow mixing; however, it appears as if with some improvements N$_2$(A) production levels needed for energy transfer could be achieved.
Figure 1. Device Schematic and Flow Input.
Figure 2. Half cross section of the BCL-16 nozzle.
Figure 5. Digitized photograph of the flame (a) with NF_3 and (b) with N_2F_4.
Figure 7. NF(b₁Σ) sample scan.
Figure 8. Species variation with D₂ combustor flow.
Figure 9. Species variation with H₂ secondary flow.
Figure 10. Species variation, at increased combustor $D_2$, with $H_2$ secondary flow.
Figure 11. Species variation with \( \text{NF}_3 \) flow.
Figure 12. OMA III scan (uncorrected) of flow with NF₃.
Figure 13. OMA III scan (uncorrected) of flow with $N_2F_4$. 
Figure 15. OMA III scan at 3.8 cm
6.4 cm FROM NEP

Figure 16. OMA III scan at 6.4 cm.
Figure 17. OMA III scan at 9 cm.
### TABLE 1. NF₃ COMBUSTION DATA

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ᵃtorr = 1.33 x 10² pascal
REFERENCES

9. Jones, Y.D., et al., NF(a\textsuperscript{1}A) Production in a Supersonic Flow Using N\textsubscript{2}F\textsuperscript{+} + H\textsubscript{2} in a BCL-16 Nozzle, AFWL-TR-87-24, Kirtland AFB, New Mexico, January 1988.
11. Jones, Y.D., An Absolute Scanning NF(a\textsuperscript{1}A) and NF(b\textsuperscript{1} ) Diagnostic for the N\textsubscript{2}F\textsuperscript{+} + H\textsubscript{2} system, AFWL-TR-86-99, Kirtland AFB, New Mexico, July 1987.
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