

# Energetics of Halogen Amine Reactions with Triplet Metastables: $\text{NFCl}_2$ with $\text{Ar}(^3\text{P}_{0,2})$ , $\text{He}(2^3\text{S})$ , and $\text{N}_2(^3\Sigma^+_{\text{u}})$ and $\text{NF}_2\text{Cl}$ and $\text{NCl}_3$ with $\text{Ar}(^3\text{P}_{0,2})$

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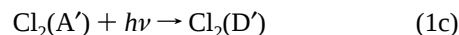
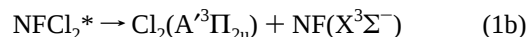
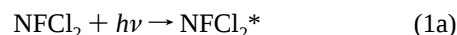
The collisions of  $\text{NFCl}_2$  with the metastable species  $\text{Ar}(^3\text{P}_{0,2})$ ,  $\text{He}(2^3\text{S}, 2^1\text{S})$ , and  $\text{N}_2(^3\Sigma^+_{\text{u}})$  and of  $\text{NF}_2\text{Cl}$  and  $\text{NCl}_3$  with  $\text{Ar}(^3\text{P}_{0,2})$  were carried out using a discharge flow system, and diatomic product channels were identified on the basis of emission from the fragments. The mechanisms for these reactions were determined from the emission spectra of the products, the energy available in the reacting species and released in the fragments, and the conservation of spin angular momentum. To carry out the energy analysis, the  $\Delta H_{\text{form}}$ 's of  $\text{NF}_2\text{Cl}$ ,  $\text{NFCl}_2$ , and  $\text{NCl}_3$  were calculated using G1 and G2 methods with Gaussian 94, yielding average theoretical values of  $-5.3$ ,  $23.0$ , and  $48.3$  kcal/mol, respectively. These values are compared to estimated experimental  $\Delta H_{\text{form}}$ 's which have been reported for  $\text{NF}_2\text{Cl}$  and  $\text{NCl}_3$ .

## Introduction

Halogen amines are a fascinating class of compounds that have been studied in our laboratory for several years. In particular, the series  $\text{NCl}_3$ ,  $\text{NFCl}_2$ , and  $\text{NF}_2\text{Cl}$  have been of interest to us because of the changes observed in stability as chlorine atoms are replaced with fluorine atoms and because of the ease with which excited state fragments can be generated both chemically and photolytically from the parent amines (for example, the  $a^1\Delta$  and  $b^1\Sigma^+$  states of  $\text{NF}$  and  $\text{NCl}$  and the  $D'$  states of  $\text{Cl}_2$  and  $\text{ClF}$ ).<sup>1–5</sup> It has been observed that conservation of spin angular momentum directs the product formation in the photolytic and chemical processes of these compounds studied to date.

Pertinent to the work presented here are the results from the gas phase and low-temperature matrix photolysis experiments of  $\text{NFCl}_2$ ,  $\text{NF}_2\text{Cl}$ , and  $\text{NCl}_3$ .<sup>1,3,5,6</sup> The UV absorption spectra of these compounds consist of structureless features, characteristic of dissociated electronic states.  $\text{NFCl}_2$  has two maxima at 275 and 190 nm,<sup>3,7</sup> which are accessible with  $\text{KrF}$  (249 nm, 4.98 eV) and  $\text{ArF}$  (193 nm, 6.42 eV) excimer laser wavelengths. When gas mixtures of  $\text{NFCl}_2$  in argon were photolyzed at 249 nm, both UV and visible emissions were observed, with features at 258, 284, and 440 nm.<sup>3</sup> The UV emission peaks were assigned to the  $D' \rightarrow A'$  transitions in  $\text{Cl}_2$  and  $\text{ClF}$ , respectively. The weak visible emission at 440 nm observed in the 249 nm photolysis study was tentatively assigned to  $\text{NFCl}$ , an assignment that was later confirmed by low-temperature matrix isolation experiments.<sup>8</sup> Photolysis of  $\text{NFCl}_2$  at 193 nm resulted in UV emission bands at 201, 209, 216, 225, 234, and 284 nm, with no emission in the visible region.<sup>3</sup> The 284 nm band was assigned to  $\text{ClF}(D' \rightarrow A')$ . When the pressure of argon was increased from 2 to 26 to 54 Torr, the bands between 200 and 235 nm were quenched and  $\text{Cl}_2(D' \rightarrow A')$  emission at 258 nm emerged, indicating that these were emission from high-lying electronic states of  $\text{Cl}_2$  (electronic states above the  $D'$  state). For both photolysis wavelengths, the species responsible for the emission were determined to be initially formed photofragments, and an energy balance analysis indicated that a two-photon process was responsible for the formation of the ion pair states of  $\text{Cl}_2$  and  $\text{ClF}$ . The proposed mechanism is shown here for the formation of  $\text{Cl}_2(D')$  at 249 nm, but analogous

mechanisms can be written for the formation of  $\text{ClF}(D')$  and for the formation of the high-lying electronic states in the 193 nm experiments.



These data complement the results obtained from photolysis studies of  $\text{NFCl}_2$  in low-temperature argon matrices, where the formation of  $\text{NF}$  was observed.<sup>1</sup>

The UV absorption spectrum of  $\text{NF}_2\text{Cl}$  contains two broad structureless features with maxima at 185 and 235 nm.<sup>1,7</sup> Photolysis at 193 nm was used to probe the 185 nm feature, and emission was observed at 284 nm, the  $D' \rightarrow A'$  emission of  $\text{ClF}$ , and at 215 nm, emission from  $\text{ClF}$  originating from an ion pair state above the  $D'$  state.<sup>5</sup> A two-photon mechanism, analogous to the mechanism of reactions 1a–1c was proposed for the 193 nm photolysis in which  $\text{ClF}(A'^3\Pi)$  and  $\text{NF}(X^3\Sigma^-)$  were formed via the absorption of the first photon, with the second photon promoting  $\text{ClF}$  to the high-lying excited triplet ion pair states.

The UV absorption spectrum of  $\text{NCl}_3$  displays an intense maximum at 220 nm and a somewhat weaker feature at 260 nm with a red tail that extends weakly into the visible.<sup>2,9</sup> When  $\text{NCl}_3$  was photolyzed at 308 nm (4.03 eV) and 249 nm (4.98 eV) with  $\text{XeCl}$  and  $\text{KrF}$  excimer lasers, respectively,<sup>6</sup> no emission from diatomic fragments was observed, in contrast with  $\text{NFCl}_2$  and  $\text{NF}_2\text{Cl}$ .<sup>1,29</sup> Visible emission was observed and has since been assumed to be from  $\text{NCl}_2$  generated in the photolysis pulse. The excited electronic states of  $\text{NF}_2\text{Cl}$ ,  $\text{NFCl}_2$ , and  $\text{NCl}_3$  generated in the photolysis experiments were assigned as singlets since the ground state is a singlet, and in the case of the first two, they are easily observed in absorption.

This paper describes a set of experiments in which  $\text{NFCl}_2$ ,  $\text{NF}_2\text{Cl}$  and  $\text{NCl}_3$  were reacted with triplet metastable species.  $\text{NFCl}_2$  was reacted with metastables  $\text{Ar}(^3\text{P}_{0,2})$ ,  $\text{He}(2^3\text{S})$ , and  $\text{N}_2(^3\Sigma^+_{\text{u}})$  to examine the product formation as a function of metastable energy.  $\text{NF}_2\text{Cl}$  and  $\text{NCl}_3$  were reacted with  $\text{Ar}(^3\text{P}_{0,2})$  to compare the product channels with those of  $\text{NFCl}_2$ . Spectroscopic studies have shown that reactions between singlet

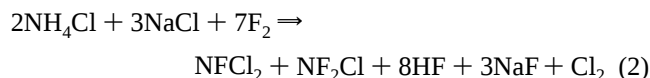
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ground state molecules and triplet metastables usually excite the molecule to the triplet state manifold.<sup>10</sup> Consequently, triplet states of the halogen amines should be accessed in these reactions, and the dissociation products will be different from those of the singlet states produced in the photolysis work. Similar studies were carried out by Zhao and Setser with PF<sub>3</sub>, and emission from PF and from the PF<sub>2</sub> radical was observed, indicating diatomic and triatomic dissociation channels.<sup>11</sup> In a separate set of experiments, Zhao and Setser generated NCl(b<sup>1</sup>Σ<sup>+</sup>) via the reaction of NFCl<sub>2</sub> with He metastables and measured its radiative lifetime and several quenching rate constants.<sup>12</sup> For the experiments reported here, it was anticipated that similar products would be formed, and while no emission from triatomic radicals was detected, there was identifiable emission from diatomic fragments NF, NCl, and Cl<sub>2</sub> in the NFCl<sub>2</sub> and NF<sub>2</sub>Cl studies and from NCl and Cl<sub>2</sub> in the NCl<sub>3</sub> studies. Mechanisms for the formation of these fragments are proposed on the basis of the electronic states of the fragments identified via their emission spectra, the energetics of the systems for which the  $\Delta H_{\text{form}}$ , using G1 and G2 methods with Gaussian 94, were calculated,<sup>13–17</sup> and the spin constraints of the system.

## Experimental Section

The discharge-flow method described by Zhao and Setser<sup>11</sup> was used to study the reactions of gaseous NFCl<sub>2</sub>, NF<sub>2</sub>Cl, and NCl<sub>3</sub> with the various metastables. The flow of metastables was produced by passing Ar, N<sub>2</sub>, or He gas through the high-voltage zone of the discharge cell. A 180 kohm resistor was placed in series with the discharge, and the voltage between the two tantalum electrodes was 400, 450, and 890 V to generate N<sub>2</sub><sup>\*</sup>, Ar<sup>\*</sup>, and He<sup>\*</sup>, respectively. Passing pure N<sub>2</sub> gas through a dc discharge generates what is known as “active nitrogen”, which contains reactive species in addition to N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>), including atomic nitrogen, N<sub>2</sub>(C<sup>3</sup>Π<sub>u</sub>), N<sub>2</sub>(B<sup>3</sup>Π<sub>g</sub>), and vibrationally excited N<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>). The effect of these other species in the flow system will be addressed.

NFCl<sub>2</sub> and NF<sub>2</sub>Cl were synthesized and purified as described in ref 1 and 4. Briefly, a stainless steel reactor tube (30 cm long and 1.8 cm o.d.) was filled with 14 g each of NH<sub>4</sub>Cl and NaCl and clean, dry copper shot. The charged reactor was heated to 110 °C for 4 h while passing dry N<sub>2</sub> gas through it to completely dry the contents. The reactor was cooled (to 55 °C to optimize the NFCl<sub>2</sub> production or to 35 °C to optimize the NF<sub>2</sub>Cl production), and the synthesis was started by passing a 20% mixture of F<sub>2</sub> in helium (Spectra Gases) through the reactor. The net chemical reaction has been proposed to be<sup>18</sup>



The reaction products were collected in a Teflon U-trap submerged in liquid N<sub>2</sub>. NFCl<sub>2</sub> or NF<sub>2</sub>Cl was separated from the other products by vacuum distillation techniques, and Pyrex bulbs containing between 5 and 10% NFCl<sub>2</sub> or NF<sub>2</sub>Cl in argon were prepared. UV absorption spectra, taken with a 7.5 cm Pyrex cell equipped with fused quartz windows and a Milton Roy Spectronic 3000 array spectrometer, were used to verify the presence of NFCl<sub>2</sub> or NF<sub>2</sub>Cl in the prepared bulbs.

NCl<sub>3</sub> was synthesized following the method described in ref 6 in which a gaseous mixture of Cl<sub>2</sub> and argon was passed through an aqueous solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in 1M H<sub>2</sub>SO<sub>4</sub>. Due to its high vapor pressure and low solubility in water, NCl<sub>3</sub> was swept out of the solution with the argon and the excess chlorine and was condensed as an amber-colored liquid in a cold trap

submerged in a methanol/dry ice bath. The cold bath was removed, and any condensed Cl<sub>2</sub> was allowed to evaporate. Then, the NCl<sub>3</sub> vapor was carried by the flow of argon through 1/4 in. black Teflon tubing to the discharge flow cell. Black tubing was used to minimize the photodecomposition of NCl<sub>3</sub>. A Teflon metering valve, placed before the cell, allowed a small fraction of the NCl<sub>3</sub>/Ar gas mixture to enter the gas discharge system, and the rest was returned to the hood. It should be noted that NCl<sub>3</sub> can explosively decompose and should be used with adequate safety precautions.

Halogen amine/Ar or halogen/Ar gas mixtures were admitted to the stream of metastables through a perforated circular Pyrex ring placed inside the dc discharge-flow cell and located 1 cm below the lower electrode. The pressure in the system was monitored with an MKS Baratron gauge (Model 122A), and for the data presented here, the total pressure in the flow dc discharge cell was 5.8 Torr for the Ar<sup>\*</sup> and N<sub>2</sub><sup>\*</sup> experiments and 15 Torr for the He<sup>\*</sup> experiments. Reagent (with the exception of NCl<sub>3</sub>, which decomposes upon passing through a flow meter) and carrier gas mass flows were measured with calibrated MKS mass flow meters, and the linear flow velocity of the system was 200 cm s<sup>−1</sup> at the pressures used in these experiments. The reagent densities in the flow cell were calculated from the reagent flows, the carrier gas flow, and the total pressure. The NFCl<sub>2</sub> or NF<sub>2</sub>Cl density varied between 0.56 × 10<sup>14</sup> and 1.1 × 10<sup>14</sup> molecules/cm<sup>3</sup>, and the density of metastables in the dc discharge was assumed to be 0.01% of the total density of Ar, He, or N<sub>2</sub>.<sup>10</sup>

A circular 2.54 cm o.d. fused quartz viewing port was located 4 cm below the Pyrex ring on the side of the dc discharge flow tube (2.54 cm o.d.). For a second series of experiments, the circular viewing port was removed, a rectangular opening extending from 1 to 5 cm below the Pyrex ring was cut into the side of the Pyrex tube, and a fused quartz window was glued over the rectangular opening. Ultraviolet and visible emissions were dispersed by a Jarrell Ash 0.275 m monochromator with a 2 nm band-pass, and detected with a cooled GaAs photomultiplier tube (Hamamatsu R943-02). A cooled indium detector was used in place of the photomultiplier tube to look for infrared emission. The signal from the detector was transformed into a voltage signal with an electrometer (Keithley Instruments, Model 610C) and visualized with a strip-chart recorder (Alltech Associates). In some experiments, a yellow glass filter was placed between the viewing port of the discharge cell and the entrance slit of the monochromator to block second-order UV emission lines in the visible region.

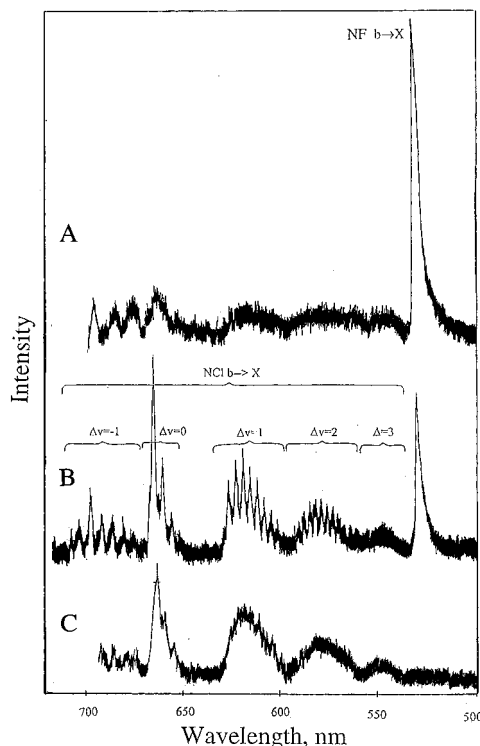
## Results

The energies of the excited metastables Ar(<sup>3</sup>P<sub>0,2</sub>), N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>), and He(2<sup>3</sup>S, 2<sup>1</sup>S) are listed in Table 1. Also included in Table 1 is a summary of the emitting products detected when NFCl<sub>2</sub> was admitted to a stream of each of these metastables. In the Ar metastable experiments, both visible and UV emission were observed. The visible emission appeared to the eye as a very intense orange flame, and its spectrum is shown in Figure 1B. To achieve the spectral resolution in Figure 1B, the bandwidth of the monochromator was reduced to 1 nm. The single blue degraded peak with a maximum at 530 nm is identified as the Δ*v* = 0 sequence band of the b<sup>1</sup>Σ<sup>+</sup> → X<sup>3</sup>Σ<sup>−</sup> transition in NF. The emission bands between 710 and 535 nm are assigned to the b<sup>1</sup>Σ<sup>+</sup> → X<sup>3</sup>Σ<sup>−</sup> transition in NCl. The most intense peak at 664 nm is part of the Δ*v* = 0 sequence band, and the other sequence bands are assigned as indicated in the figure, with the individual band maxima listed in Table 2. These data are in good agreement with previously reported NCl emission data

**TABLE 1: States and Energies (*E*) of He, Ar, and N<sub>2</sub> Metastable Species and the Emission Observed upon Reaction of These Metastables with NFCl<sub>2</sub>**

| species                     | state                        | <i>E</i> , cm <sup>-1</sup> | <i>E</i> , kcal/mol | <i>E</i> , eV | emission observed                                                                                  |
|-----------------------------|------------------------------|-----------------------------|---------------------|---------------|----------------------------------------------------------------------------------------------------|
| He <sup>a</sup>             | 2 <sup>1</sup> S             | 166 272                     | 475.3               | 20.6          | NF(b <sup>1</sup> Σ <sup>+</sup> →X <sup>3</sup> Σ <sup>-</sup> ); Δ <i>ν</i> = 0                  |
|                             | 2 <sup>3</sup> S             | 159 850                     | 457.0               | 19.8          | NCl(b <sup>1</sup> Σ <sup>+</sup> →X <sup>3</sup> Σ <sup>-</sup> ); Δ <i>ν</i> = 0                 |
| Ar <sup>a</sup>             |                              |                             |                     |               | Cl <sub>2</sub> emission at 258, 246, 236, 226, 216 nm                                             |
|                             | 3P <sub>0</sub>              | 94 554                      | 270.3               | 11.7          | NF(b <sup>1</sup> Σ <sup>+</sup> →X <sup>3</sup> Σ <sup>-</sup> ); Δ <i>ν</i> = 0                  |
|                             | 3P <sub>2</sub>              | 93 144                      | 266.3               | 11.5          | NCl(b <sup>1</sup> Σ <sup>+</sup> →X <sup>3</sup> Σ <sup>-</sup> ); Δ <i>ν</i> = -1, 0, +1, +2, +3 |
| N <sub>2</sub> <sup>b</sup> |                              |                             |                     |               | Cl <sub>2</sub> (D'→A') at 258 nm, secondary reaction                                              |
|                             | 3Σ <sub>u</sub> <sup>+</sup> | 50 934                      | 145.7               | 6.31          | Cl <sub>2</sub> emission at 198 nm, secondary reaction                                             |
|                             |                              |                             |                     |               | NF(b <sup>1</sup> Σ <sup>+</sup> →X <sup>3</sup> Σ <sup>-</sup> ); Δ <i>ν</i> = 0                  |

<sup>a</sup> See Table 1 in ref 10 for state assignments and energies. <sup>b</sup> N<sub>2</sub>(3Σ<sub>u</sub><sup>+</sup>) energy calculated from [*T<sub>e</sub>* + ω<sub>e</sub>/2] from ref 30.



**Figure 1.** Visible emission spectrum observed when (A) NF<sub>2</sub>Cl, (B) NFCl<sub>2</sub> and (C) NCl<sub>3</sub> were added to a stream of Ar(<sup>3</sup>P<sub>0,2</sub>) metastables. The bandwidth of the emission monochromator was 2 nm for (A) and (C), and 1 nm for (B).

by Colin et al.<sup>19</sup> and by Pritt and Coombe and co-workers.<sup>20,21</sup> When Cl<sub>2</sub> was reacted with the argon metastables, no such emission was observed.

Since the NFCl<sub>2</sub> + Ar(<sup>3</sup>P<sub>0,2</sub>) reaction generates the b<sup>1</sup>Σ<sup>+</sup> states of NF and NCl, the possibility that the a<sup>1</sup>Δ states of NF and NCl were also produced was explored. When the PMT was replaced with the cooled indium detector to probe the infrared region, the only emission that was observed was from the B<sup>3</sup>Π<sub>g</sub> → A<sup>3</sup>Σ<sub>u</sub><sup>+</sup> transition in N<sub>2</sub>,<sup>22</sup> with no evidence of the a<sup>1</sup>Δ → X<sup>3</sup>Σ<sup>-</sup> transitions in NCl (at 1080 nm) and NF (at 874 nm).<sup>20,23</sup> The nitrogen source was determined to be a small air leak.

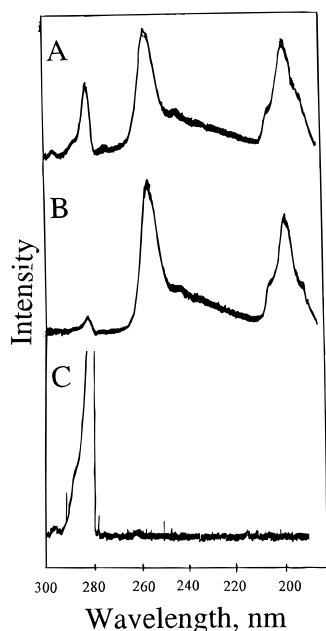
The spectrum of the UV emission, shown in Figure 2A, consists of two features with maxima at 258 and 198 nm. Both bands were also observed when a 5% mixture of Cl<sub>2</sub> in argon was admitted to the stream of argon metastables as shown in Figure 2B. The 258 nm band is the well-known transition between the D'(3Π 2g) and A'(3Π 2u) states of Cl<sub>2</sub>.<sup>24</sup> Cl<sub>2</sub> emission at 198 nm has been reported, and although the specific electronic states involved are debated, it is likely that this transition originates from an ion pair state at a higher energy than the D' state.<sup>25</sup> The C → A transition of ArCl has been observed in the 198 nm spectral region, and there is certainly a possibility of direct abstraction of Cl by an Ar(<sup>3</sup>P<sub>0,2</sub>) in these

systems.<sup>26</sup> However, at the pressures used in these experiments, this emission should be effectively quenched according to the data provided in ref 26. Consequently, this emission is assigned to Cl<sub>2</sub>. The D' → A' transition in ClF is a blue degraded band which is known to lie at 284 nm.<sup>27</sup> A band at 284 nm is observed in Figure 2A; however, it is red degraded and is also observed in Figure 2B and in Figure 2C (the spectrum of the emission from the argon discharge with no added reagents), so is associated with emission from the discharge. As is apparent in Figure 2, this emission is greatly attenuated when either NFCl<sub>2</sub> or Cl<sub>2</sub> is added to the system.

The spectra of Figures 2A,B appear to be nearly identical, and the question arose as to whether or not Cl<sub>2</sub> contamination in the NFCl<sub>2</sub> sample was responsible for the UV emission. Cl<sub>2</sub> is a product of the synthesis, as shown in reaction 2, and the separation of NFCl<sub>2</sub> from Cl<sub>2</sub> requires that the last step in the vacuum distillation procedure be repeated many times. It is judged to be complete when the Cl<sub>2</sub> absorption at 330 nm does not appear in the UV spectrum of the sample. The small extinction coefficient of Cl<sub>2</sub> (60 L mol<sup>-1</sup> cm<sup>-1</sup> at 330 nm)<sup>28</sup> and the fact that the tail of the NFCl<sub>2</sub> absorption peak at 270 nm extends weakly into the 330 nm region makes it possible, however, that some Cl<sub>2</sub> was present in all of the samples used in this study. To address this problem, experiments were run in which Cl<sub>2</sub>/Ar samples were admitted to the Ar metastables, and the emission intensity at 258 and 198 nm as a function of Cl<sub>2</sub> density was monitored. Calibration plots of the intensity vs Cl<sub>2</sub> density were prepared from these data, and the plot obtained for the 258 nm emission is shown in Figure 3A. Figure 3B is a plot of the Cl<sub>2</sub> emission observed when an NFCl<sub>2</sub>/Ar sample was added to the stream of argon metastables. (The Cl<sub>2</sub> + Ar(<sup>3</sup>P<sub>0,2</sub>) were performed on the same day as the NFCl<sub>2</sub> + Ar(<sup>3</sup>P<sub>2</sub>) experiments to reduce the possibility that the metastable density had changed for the Cl<sub>2</sub> and the NFCl<sub>2</sub> runs.) An upper limit on the Cl<sub>2</sub> contamination in the NFCl<sub>2</sub>/Ar sample was calculated from the UV absorption spectrum of the NFCl<sub>2</sub> sample, and the Cl<sub>2</sub> emission intensity expected for this density of Cl<sub>2</sub> was read from the calibration plots. It was assumed that this intensity could be subtracted from the total Cl<sub>2</sub> emission intensity observed in the NFCl<sub>2</sub>/Ar experiments. However, the decays observed in Figure 3 indicate that quenching of the Cl<sub>2</sub> emission becomes important when the reagent density gets larger than about 1.5 × 10<sup>13</sup> molecules cm<sup>-3</sup>, and this complicates the correction of the Cl<sub>2</sub> emission intensity in the NFCl<sub>2</sub> experiments for Cl<sub>2</sub> contamination. Consequently, only NFCl<sub>2</sub> data in the low-density regime, where the intensity increases with density, could be corrected for Cl<sub>2</sub> contamination. Curve A of Figure 4 shows the total Cl<sub>2</sub> emission intensity in the NFCl<sub>2</sub> experiment, and curve B shows the Cl<sub>2</sub> emission intensity corrected for the Cl<sub>2</sub> contamination. Clearly, some of the Cl<sub>2</sub> emission observed in the NFCl<sub>2</sub> experiment can be ascribed to the presence of Cl<sub>2</sub> contamination in the sample, but not all of it. For example, at NFCl<sub>2</sub> densities of 6 × 10<sup>12</sup> molecules/

**TABLE 2: Individual Band Maxima (in nm) for the NCl (b<sup>1</sup>Σ<sup>+</sup>→X<sup>3</sup>Σ<sup>-</sup>) Emission Shown in Figure 2**

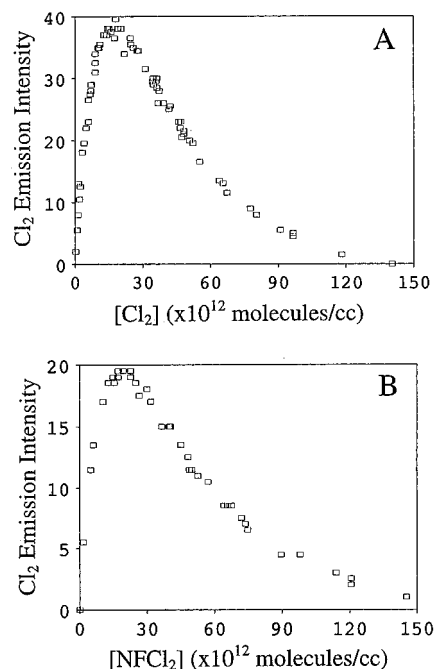
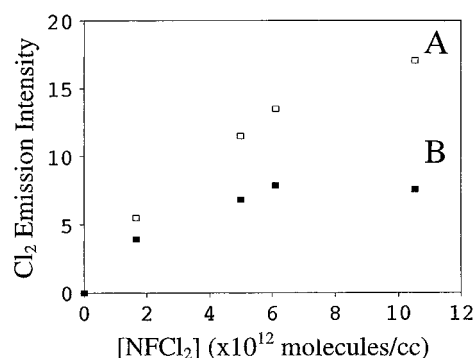
| sequence<br>Δv = -1 | assignment<br>v', v'' | sequence<br>Δv = 0 | assignment<br>v', v'' | sequence<br>Δv = +1 | assignment<br>v', v'' | sequence<br>Δv = +2 | assignment<br>v', v'' |
|---------------------|-----------------------|--------------------|-----------------------|---------------------|-----------------------|---------------------|-----------------------|
| 703                 | 0, 1                  | 664                | 0, 0                  | 626                 | 1, 0                  | 589                 | 3, 1                  |
| 697                 | 1, 2                  | 660                | 1, 1                  | 619                 | 2, 1                  | 587                 | 4, 2                  |
| 691                 | 2, 3                  | 665                | 2, 2                  | 619                 | 3, 2                  | 584                 | 5, 3                  |
| 686                 | 3, 4                  |                    |                       | 615                 | 4, 3                  | 581                 | 6, 4                  |
| 680                 | 4, 5                  |                    |                       | 611                 | 5, 4                  | 578                 | 7, 5                  |
| 674                 | 5, 6                  |                    |                       | 608                 | 6, 5                  | 575                 | 8, 6                  |
|                     |                       |                    |                       | 604                 | 7, 6                  | 572                 | 9, 7                  |
|                     |                       |                    |                       | 600                 | 8, 7                  | 569                 | 10, 8                 |
|                     |                       |                    |                       |                     |                       | 566                 | 11, 9                 |
|                     |                       |                    |                       |                     |                       | 563                 | 12, 10                |

**Figure 2.** UV emission spectra observed upon the addition of (A) NFCl<sub>2</sub> and (B) Cl<sub>2</sub> to a stream of Ar(<sup>3</sup>P<sub>0,2</sub>) metastables. The bands at 258 and 198 nm are assigned to Cl<sub>2</sub>. (C) UV spectrum of the Ar discharge.

cm<sup>3</sup>, one-half to two-thirds of the Cl<sub>2</sub> emission is from NFCl<sub>2</sub> and the remainder is attributed to the Cl<sub>2</sub> contamination. The same analysis was performed for the 198 nm emission feature, with a similar result. Since the Cl<sub>2</sub> density calculations were upper limits, these analyses give lower limits on the contribution that NFCl<sub>2</sub> gives to the Cl<sub>2</sub> emission at both 198 and 258 nm.

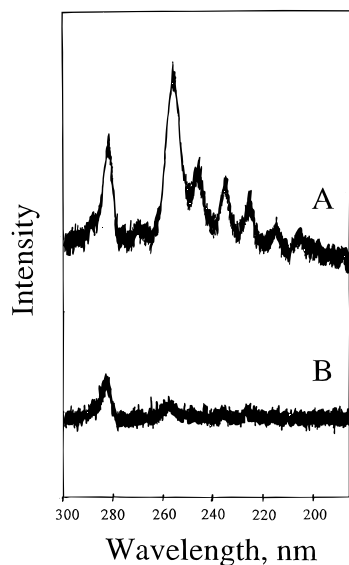
Although the quenching process in these experiments has not been identified, it is not direct quenching of the Cl<sub>2</sub> ion pair states because Cl<sub>2</sub> ion pair state lifetimes are on the order of 10 ns in the system, and the gas kinetic collision rate is 8 μs<sup>-1</sup> Torr<sup>-1</sup>. Therefore, under the conditions of these experiments a Cl<sub>2</sub> molecule in an ion pair state will see less than one collision before it emits. The quenching process must, however, involve a species that leads to the formation of Cl<sub>2</sub> in its ion pair state and could be quenching of Ar(<sup>3</sup>P<sub>0,2</sub>) atoms due to changes in the walls as the reagents are introduced into the system.

No emission from ClF was observed in these experiments. To ascertain whether this was due to an experimental problem or due to the fact that no emitting states of ClF were generated in the NFCl<sub>2</sub> plus metastable reactions, a tank of ClF was obtained (which unfortunately was contaminated with Cl<sub>2</sub>), and a bulb of ClF in argon was prepared and added to the stream of metastables. Still, no ClF emission was observed. With the idea that perhaps the ClF emission was too weak to see 4 cm (0.019 ms) downstream of the mixing zone, the rectangular viewing port described in the Experimental Section was installed, allowing the emission 1 cm below the mixing region

**Figure 3.** (A) Cl<sub>2</sub> emission intensity at 258 nm as a function of Cl<sub>2</sub> density upon the addition of a 5% mixture of Cl<sub>2</sub> in argon to the stream of Ar(<sup>3</sup>P<sub>0,2</sub>) metastables. (B) Cl<sub>2</sub> emission intensity at 258 nm as a function of NFCl<sub>2</sub> density upon the addition of a 5% sample of NFCl<sub>2</sub> in argon to the stream of Ar(<sup>3</sup>P<sub>0,2</sub>) metastables.**Figure 4.** (A) Total Cl<sub>2</sub> emission intensity at 258 nm as a function of NFCl<sub>2</sub> density from Figure 3A. (B) Cl<sub>2</sub> emission intensity at 258 nm corrected for Cl<sub>2</sub> contamination plotted as a function of NFCl<sub>2</sub> density. An upper limit on the Cl<sub>2</sub> contamination in the NFCl<sub>2</sub> sample was calculated as described in the text.

to be viewed. All of the ClF and NFCl<sub>2</sub> reactions were repeated, but no emission from ClF emission was observed in any of the experiments, and the conclusion is that ClF emission cannot be detected in this system.

The spectrum of the emission produced when N<sub>2</sub> was passed through the dc discharge with no added reagent consisted of N<sub>2</sub>(B<sup>3</sup>Π<sub>g</sub>→A<sup>1</sup>Σ<sub>u</sub><sup>+</sup>, first positive) emission in the visible, and



**Figure 5.** UV emission spectra observed upon the addition of (A) NFCl<sub>2</sub> and (B) Cl<sub>2</sub> to a stream of He(2<sup>3</sup>S, 2<sup>1</sup>S) metastables. The band at 284 nm is assigned to the He discharge since it was observed when no reagent was added to the system and looked very similar to the feature that appears in Figure 2C. The other bands are assigned to Cl<sub>2</sub> (see text).

N<sub>2</sub>(C<sup>3</sup>Π<sub>u</sub> → B<sup>3</sup>Π<sub>g</sub>, second positive) and NO(A<sup>2</sup>Σ<sup>+</sup> → X<sup>2</sup>Π, γ band) emission in the UV.<sup>22</sup> When NFCl<sub>2</sub> was added, the NF(b<sup>1</sup>Σ<sup>+</sup> → X<sup>3</sup>Σ<sup>-</sup>) emission at 528 nm appeared in the visible, and there was a general decrease in the intensity of the N<sub>2</sub> first positive and of the NO γ band emission. No UV emission from Cl<sub>2</sub> or ClF was observed, however, from the addition of either NFCl<sub>2</sub> or Cl<sub>2</sub>. Visible and UV emission were observed when NFCl<sub>2</sub> was reacted with He metastables. Two visible bands at 528 and 664 nm were assigned to the Δν = 0 sequence bands of the b<sup>1</sup>Σ<sup>+</sup> → X<sup>3</sup>Σ<sup>-</sup> transitions in NCl and NF. The UV emission spectrum is shown in Figure 5A and consists of a peak with a maximum at 258 nm assigned to Cl<sub>2</sub>(D' → A') and a series of bands at shorter wavelengths with individual band maxima at 246, 236, 226, 216, and 206 nm. These bands correlate well with the short wavelength bands observed in the 193 nm photolysis of NFCl<sub>2</sub> and are assigned to transitions originating from high lying electronic states Cl<sub>2</sub>.<sup>3,24</sup> The relative intensity and the distinct nature of these UV bands were a function of the He pressure, and to see them well required helium pressures of 15 Torr. The emission observed when Cl<sub>2</sub> was added to the flow of He metastables is shown in Figure 5B. Zhao and Setser reported NCl(b → X) emission from the reaction of NFCl<sub>2</sub> with He metastables; however, since they were only interested in the NCl emission, they did not report any other emission that they may have observed.<sup>12</sup>

Emitting fragments generated in the NF<sub>2</sub>Cl or NCl<sub>3</sub> plus Ar metastable rare gas atom reactions are summarized in Table 3, with the NFCl<sub>2</sub> reactions for comparison. When NF<sub>2</sub>Cl was admitted to the stream of Ar metastables, the emission appeared to the eye as an emerald green flame. Consistent with this observation, the spectrum, shown in Figure 1A, reveals an intense single blue degraded peak at 528 nm assigned to the b → X transition in NF. The weak emission features in the 650–570 nm region are the Δν = 1, 2, and 3 sequence bands of the NCl(b → X) transition. Nitrogen first positive emission appears in the 650–700 nm region and obscures the NCl(b → X) Δν = 0 sequence band. The UV emission spectrum was virtually identical to the NFCl<sub>2</sub> + Ar(<sup>3</sup>P<sub>0,2</sub>) UV emission spectrum with Cl<sub>2</sub> features at 258 and 198 nm. Since Cl<sub>2</sub> cannot be formed in a direct reaction of NF<sub>2</sub>Cl with Ar metastables, the observed

**TABLE 3: Emission from Fragments Generated in the Reactions of Ar(<sup>3</sup>P<sub>0,2</sub>)<sup>a</sup> with NFCl<sub>2</sub>, NF<sub>2</sub>Cl, and NCl<sub>3</sub>**

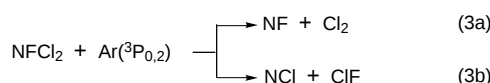
| molecule           | emission observed                                                                                                                                                                                                                                                                              |
|--------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| NFCl <sub>2</sub>  | NF(b <sup>1</sup> Σ <sup>+</sup> → X <sup>3</sup> Σ <sup>-</sup> ); Δν = 0<br>NCl(b <sup>1</sup> Σ <sup>+</sup> → X <sup>3</sup> Σ <sup>-</sup> ); Δν = -1, 0, +1, +2, +3<br>Cl <sub>2</sub> (D' → A') at 258 nm, secondary reaction<br>Cl <sub>2</sub> emission at 198 nm, secondary reaction |
| NF <sub>2</sub> Cl | NF(b <sup>1</sup> Σ <sup>+</sup> → X <sup>3</sup> Σ <sup>-</sup> ); Δν = 0<br>NCl(b <sup>1</sup> Σ <sup>+</sup> → X <sup>3</sup> Σ <sup>-</sup> ); Δν = +1, +2, +3 (weak)<br>ArF( <sup>2</sup> B → X) at low pressures of argon                                                                |
| NCl <sub>3</sub>   | NCl(b <sup>1</sup> Σ <sup>+</sup> → X <sup>3</sup> Σ <sup>-</sup> ); Δν = -1, 0, +1, +2, +3<br>Cl <sub>2</sub> (D' → A') at 258 nm, secondary reaction<br>Cl <sub>2</sub> emission at 198 nm, secondary reaction                                                                               |

UV emission must be due to residual chlorine present in the sample as a contaminant. Cl<sub>2</sub> is a product of both the synthesis and NF<sub>2</sub>Cl thermal decomposition, and it is, consequently, nearly impossible to completely eliminate Cl<sub>2</sub> from the sample. Again, as in the NFCl<sub>2</sub> experiments, no ClF emission was detected in this experiment. When the Ar pressure was reduced to 2.0 Torr, a peak at 192 nm assigned to the B → X transition in ArF appeared as a second maximum just to the blue of the 198 nm Cl<sub>2</sub> feature.<sup>26</sup>

Addition of the NCl<sub>3</sub> sample below the argon discharge generated an intense orange emission flame similar to that observed for the NFCl<sub>2</sub> + Ar(<sup>3</sup>P<sub>0,2</sub>) reaction, and the spectrum (Figure 1C) indicates the Δν = 0, +1, +2, and +3 sequence bands of the b<sup>1</sup>Σ<sup>+</sup> → X<sup>3</sup>Σ<sup>-</sup> transition in NCl. The UV emission was again essentially the same as that observed in the NFCl<sub>2</sub> and NF<sub>2</sub>Cl reactions and was similarly assigned to ion pair transitions in Cl<sub>2</sub>.

## Discussion

When molecular species react with metastable argon atoms, Penning ionization, associative ionization, neutral excitation, neutral dissociation, and neutral dissociative excitation may occur.<sup>10</sup> The last of these, neutral dissociative excitation, is assumed to be responsible for the production of excited state diatomic fragments in the Ar(<sup>3</sup>P<sub>0,2</sub>) reaction systems. On the basis of the product emissions observed in the NFCl<sub>2</sub> system, there are two pathways leading to diatomic fragments by which the reaction proceeds, as shown here.



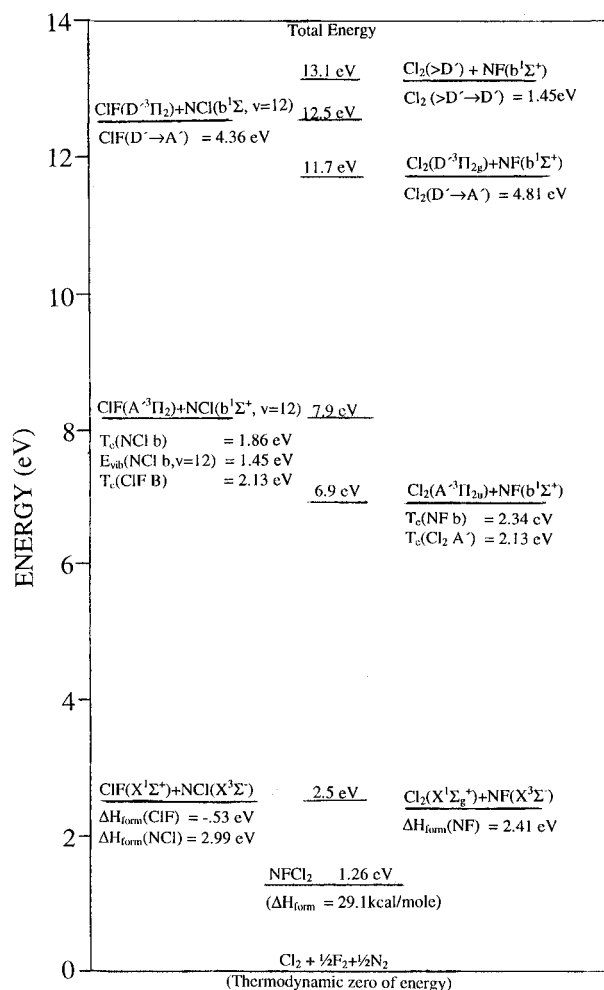
Analogous diatomic pathways can be written for the NF<sub>2</sub>Cl/Ar(<sup>3</sup>P<sub>0,2</sub>) system, and for the NCl<sub>3</sub>/Ar(<sup>3</sup>P<sub>0,2</sub>) system, a single channel leading to the formation of NCl and Cl<sub>2</sub> can be written. Two aspects of this process will be analyzed here, the energetics and the spin constraints.

To examine the energetics of the reactions requires that the ΔH<sub>form</sub> values for the products and reactants and the energies of the excited states of the products be known. For NFCl<sub>2</sub>, the only ΔH<sub>form</sub> available is the experimental lower limit of -10 kcal/mol determined from the NFCl<sub>2</sub> gas-phase photolysis experiments.<sup>3</sup> Therefore, G1, G2-MP2, and G2-MP4 methods were used with Gaussian 94 to compute the energies of NFCl<sub>2</sub>, N<sub>2</sub>, F<sub>2</sub>, and Cl<sub>2</sub>.<sup>13–17</sup> These energies were used together with the formation reaction to compute the ΔE<sub>form</sub> for NFCl<sub>2</sub>. The ΔH<sub>form</sub> was calculated from ΔE<sub>form</sub> + ΔnRT where Δn is the change in the number of moles in the formation reaction. The results of the three calculations are included in Table 4 and show about a 5% variation. To estimate the reliability of the calculated ΔH<sub>form</sub> of NFCl<sub>2</sub>, ΔH<sub>form</sub>'s were calculated for NF<sub>3</sub>, NCl<sub>3</sub>, and NF<sub>2</sub>Cl, species for which experimental values have been reported. These values are also included in Table 3. For

**TABLE 4: Theoretical and Experimental  $\Delta H_{\text{form}}$ 's in kcal mol<sup>-1</sup> for NF<sub>3</sub>, NF<sub>2</sub>Cl, NFCl<sub>2</sub>, and NCl<sub>3</sub>**

| molecule           | G1     | G2-MP2 | G2-MP4 | av theor | exptl               |
|--------------------|--------|--------|--------|----------|---------------------|
| NF <sub>3</sub>    | -35.36 | -38.38 | -38.29 | -37.55   | -31.43 <sup>a</sup> |
| NF <sub>2</sub> Cl | -3.94  | -5.90  | -6.16  | -5.33    | +5 <sup>b</sup>     |
| NFCl <sub>2</sub>  | +24.12 | +22.61 | +22.28 | +23.00   | +29.1 <sup>c</sup>  |
| NCl <sub>3</sub>   | +49.54 | +47.67 | +47.59 | +48.32   | +63 <sup>d</sup>    |

<sup>a</sup> Reference 37. <sup>b</sup> Reference 29. <sup>c</sup> Predicted experimental value assuming that the average theoretical  $\Delta H_{\text{form}}$  is 21% too low. <sup>d</sup> Reference 9.



**Figure 6.** Energy level diagram for NFCl<sub>2</sub> and the diatomic channels NF + Cl<sub>2</sub> and NCl + ClF. The energies listed under "Total Energy" were calculated from the energies of the diatomic fragments for each channel indicated.

NF<sub>3</sub> and NCl<sub>3</sub>, the average calculated  $\Delta H_{\text{form}}$ 's are 19 and 23% lower, respectively, than the experimental values. (It is noted, however, that there is significant uncertainty in the experimental  $\Delta H_{\text{form}}$  of NCl<sub>3</sub>.) Assuming that the theoretical value for NFCl<sub>2</sub> is 21% too low predicts an "experimental" value of 29.1 kcal/mol. The theoretical and experimental values of  $\Delta H_{\text{form}}$  for NF<sub>2</sub>-Cl were not used in this analysis because the validity of the experimental value is debatable.<sup>29</sup> The results of the G1, G2-MP2, and G2-MP4 methods gave very similar  $\Delta H_{\text{form}}$ 's for NF<sub>2</sub>-Cl and yield an average value of -5.33 kcal/mol.

Figure 6 is an energy level diagram for NFCl<sub>2</sub> and the diatomic dissociation channels. The right side of the diagram shows the energetics of the NF plus Cl<sub>2</sub> pathway using the known energies for NF(b<sup>1</sup>Σ<sup>+</sup>), Cl<sub>2</sub>(D'), and Cl<sub>2</sub>(A'), converted to electronvolts.<sup>24,30</sup> Using the adjusted  $\Delta H_{\text{form}}$  for NFCl<sub>2</sub>, the diagram indicates that there is sufficient energy in the reaction

with Ar <sup>3</sup>P<sub>2</sub> atoms (11.7 eV) or with Ar <sup>3</sup>P<sub>0</sub> (11.5 eV) to generate NF(b<sup>1</sup>Σ<sup>+</sup>) and Cl<sub>2</sub>(D'). To generate the Cl<sub>2</sub> state that is responsible for the emission at 198 nm, however, would require an additional 4.15 kcal/mol in the reaction involving the more energetic Ar(<sup>3</sup>P<sub>0</sub>) or 8.75 kcal/mol in the reaction with Ar(<sup>3</sup>P<sub>2</sub>).

As noted above, the spectrum of the Cl<sub>2</sub> emission observed in the NFCl<sub>2</sub> + Ar(<sup>3</sup>P<sub>0,2</sub>) experiments is virtually identical to that observed in the Cl<sub>2</sub> + Ar(<sup>3</sup>P<sub>0,2</sub>) experiments. It is very unlikely that these reactions would generate identical Cl<sub>2</sub> emission spectra in view of the energetics of the two cases, particularly since according to our calculations, there is insufficient energy to produce the 198 nm Cl<sub>2</sub> emission in the NFCl<sub>2</sub> reaction. It is, however, possible that the Cl<sub>2</sub> ion pair states are not direct products of the NFCl<sub>2</sub> + Ar(<sup>3</sup>P<sub>0,2</sub>) reaction but are formed in a secondary step as shown here.



The electronic states of the diatomic species in this mechanism can be analyzed on the basis of the observed emission and spin constraints. Since reactions between singlet ground state molecules and triplet metastable atoms usually excite the molecule to the triplet state manifold, then for our system an intermediate triplet state of NFCl<sub>2</sub> is produced in step 4a. The emission data indicate that a channel exists in which the NF fragment is produced in an excited singlet state, so spin conservation rules predict that the Cl<sub>2</sub> fragment will be a triplet. There are three low lying <sup>3</sup>Π states of Cl<sub>2</sub>, the B(0u<sup>+</sup>), the A(1u), and the A'(2u) states.<sup>30</sup> The B state generates well-known red/orange emission which was not observed in these experiments. No emission corresponding to the A and A' states was observed, although none would be expected due to their long lifetimes and the high probability of collisional quenching in the system.<sup>31</sup> A "dark" dissociation channel in which the ground state fragments NF(X<sup>3</sup>Σ<sup>-</sup>) and Cl<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) are generated also correlates with the triplet NFCl<sub>2</sub> intermediate state, and this channel is the likely source of the ground state Cl<sub>2</sub> for step 4b, since it would generate identical emission to what is observed when Cl<sub>2</sub> is added to the stream of Ar metastables.

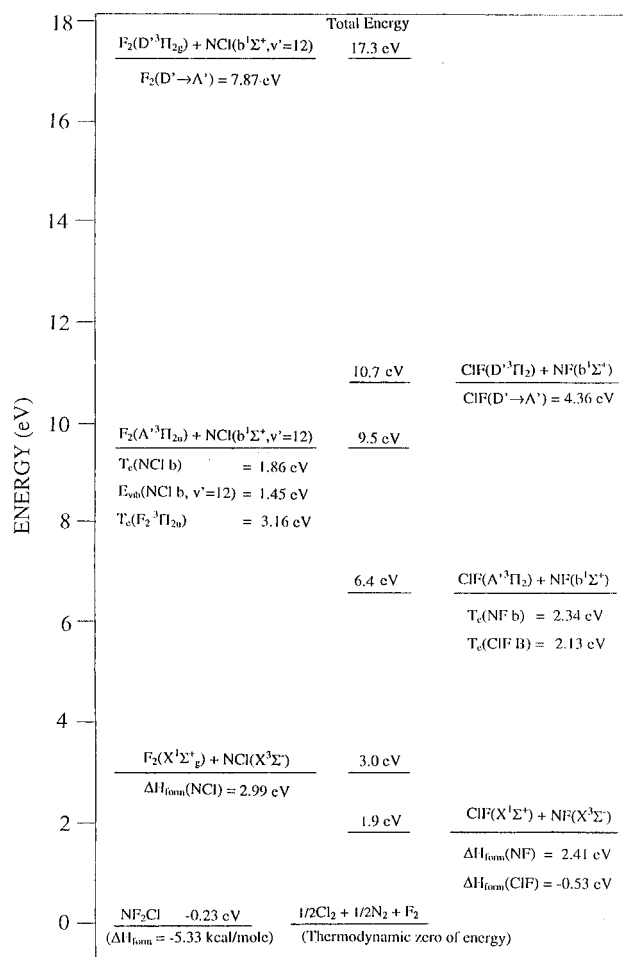
The NCl + ClF channel can also be analyzed, and the left side of the energy diagram (Figure 6) shows the energetics of this channel using the known energies in electronvolts for NCl-(b<sup>1</sup>Σ<sup>+</sup>) and ClF(D').<sup>19,20,24</sup> Since the energy of the ClF(A') state is not established, it was assumed to have the same energy as the B<sup>3</sup>Π state because the analogous states are very close in energy in Cl<sub>2</sub> and F<sub>2</sub>.<sup>30</sup> Spin constraints predict that the ClF will be generated in a triplet state with NCl(b<sup>1</sup>Σ<sup>+</sup>), similar to the NF(b<sup>1</sup>Σ<sup>+</sup>) + Cl<sub>2</sub>(triplet state) case above, and the energy diagram indicates that there is sufficient energy in the NFCl<sub>2</sub> + Ar(<sup>3</sup>P<sub>2,0</sub>) reaction for the production of ClF(D') with NCl-(b<sup>1</sup>Σ<sup>+</sup>). There is also a spin and energetically allowed "dark" dissociation channel possible leading to the formation of ground state NCl and ClF.

The reactions of NFCl<sub>2</sub> with N<sub>2</sub> metastables (6.31 eV) and He (19.8 eV) probes dissociating triplet states at energies lower and higher than the state produced in the Ar metastable (11.7 eV) studies. For the reactions with N<sub>2</sub> metastables, neutral dissociative excitation is assumed to be responsible for the production of excited state diatomic fragments as in the Ar metastable reactions. The NF(b→X) emission at 528 nm shows that the NF channel is open; however, no emission from Cl<sub>2</sub> was observed. There are several reactive species in active N<sub>2</sub>, and these must all be considered regarding their possible

participation in the production of  $\text{NF}(\text{b}^1\Sigma^+)$  from  $\text{NFCl}_2$ . For nitrogen atoms to be involved would require that the N atom extract an F atom from the  $\text{NFCl}_2$  directly or break apart the  $\text{NFCl}_2$  molecule to produce electronically excited NF. This seems very unlikely, particularly since the density of nitrogen atoms below the discharge is quite small in typical systems. The visible and UV spectra of the active nitrogen indicate the presence of several excited electronic states of  $\text{N}_2$ ,  $\text{A}^3\Sigma_u^+$ ,  $\text{B}^3\Pi_g$ , and  $\text{C}^3\Pi_u$ .<sup>22</sup> Of these, only the A state has a sufficiently long lifetime to suffer enough collisions with  $\text{NFCl}_2$  to be an important contributor to product formation. Figure 6 shows that there is sufficient energy in the reaction with a 6.3 eV  $\text{N}_2(\text{A}^3\Sigma_u^+)$  metastable to generate  $\text{NF}(\text{b}^1\Sigma^+)$  plus  $\text{Cl}_2$  in a low-lying triplet state and  $\text{NCl}(\text{b}^1\Sigma^+)$  plus  $\text{ClF}$  in a low-lying triplet state. The details of the potential surface of the dissociating  $\text{NFCl}_2$  state must be responsible for the fact that the  $\text{NCl}(\text{b}^1\Sigma^+)$  channel is not observed, even though it is not prohibited by the energetics of the reaction. Dark channels are possible both energetically and by spin considerations as in the argon metastable reactions. The fact that no  $\text{D}' \rightarrow \text{A}'$  emission was observed when either  $\text{NFCl}_2$  or  $\text{Cl}_2$  was added is consistent with the fact that there is insufficient energy in the  $\text{N}_2$  metastable to promote ground state  $\text{Cl}_2$  to the  $\text{D}'$  state and does not preclude the dark channels.

The He metastables are the most energetic of the metastables used in this study, and are the only ones with both triplet and singlet components at 19.8 and 20.6 eV, respectively. Since the  $\Delta\nu = 0$  sequence band of the  $\text{NCl}(\text{b}^1\Sigma^+ \rightarrow \text{X}^3\Sigma^-)$  transition and emission from several high-lying electronic triplet states of  $\text{Cl}_2$  were observed, spin constraints predict that the dissociating state of  $\text{NFCl}_2$  is generated in the reaction with He metastables is a triplet. The high-lying ion pair states of  $\text{Cl}_2$  are a product of the dissociating excited triplet state of  $\text{NFCl}_2$  since only the  $\text{D}' \rightarrow \text{A}'$  emission at 258 nm was observed when the  $\text{Cl}_2/\text{Ar}$  sample was reacted with He metastables. This is in contrast to reactions of  $\text{NFCl}_2$  with Ar or  $\text{N}_2$  metastables where the  $\text{Cl}_2$  emission at 258 and 198 nm was assigned to secondary reactions with ground state  $\text{Cl}_2$ . The  $\Delta\nu = 0$  sequence band of the  $\text{NF}(\text{b} \rightarrow \text{X})$  emission was also observed in the He metastable reactions, so the  $\text{NF} + \text{ClF}$  channel is open; however, as in the other metastable reactions, no information regarding the electronic state of the product  $\text{ClF}$  is available from the data. In the  $\text{NFCl}_2 + \text{He}(^1,3\text{S})$  studies done by Zhao and Setser,<sup>12</sup> it was proposed that  $\text{NFCl}_2$  is ionized in the collision, and then  $\text{NCl}(\text{b})$  is formed following the recombination of the parent ion with an electron. It is not possible to verify whether this mechanism or direct excitation of a triplet state of  $\text{NFCl}_2$  is responsible for the excited state product formation from the data available. In either case, however, the dissociating state of  $\text{NFCl}_2$  must be a triplet state because of the spin multiplicity of the products. Furthermore, if the excited triplet state of  $\text{NFCl}_2$  is generated in a direct reaction with He, then it can be assigned to a reaction involving  $\text{He}(^3\text{S})$  atoms rather than  $\text{He}(^1\text{S})$ . This is reasonable in view of the fact that there is a much larger density of  $\text{He}(^3\text{S})$  generated in the discharge than of  $\text{He}(^1\text{S})$ .<sup>10</sup>

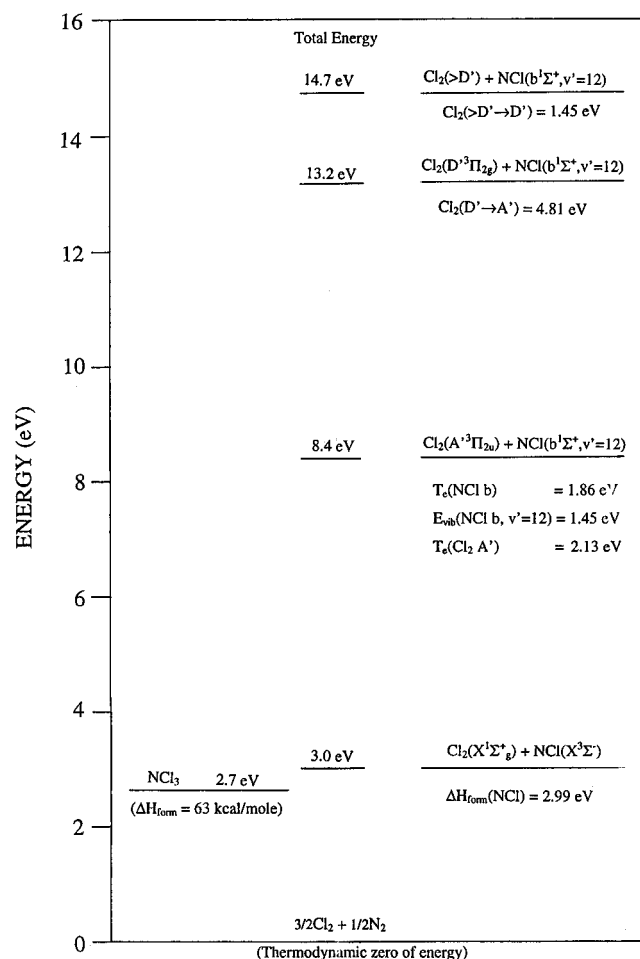
The  $\text{NF}_2\text{Cl}/\text{Ar}(^3\text{P}_{0,2})$  and  $\text{NCl}_3/\text{Ar}(^3\text{P}_{0,2})$  were carried out to compare the processes in these chemically related systems to those observed in the  $\text{NFCl}_2/\text{Ar}(^3\text{P}_{0,2})$  system. An energy diagram for the  $\text{NF}_2\text{Cl}$  system is shown in Figure 7. Since, as mentioned above, the experimental  $\Delta H_{\text{form}}$  value for  $\text{NF}_2\text{Cl}$  is not well established, the average theoretical value from Table 4 is included in the diagram. The experiment shows that the  $\text{NF}(\text{b}^1\Sigma^+)$  fragment is formed in the reaction. Thus, assuming that an excited electronic triplet state of  $\text{NF}_2\text{Cl}$  is formed in the  $\text{NF}_2\text{Cl} + \text{Ar}(^3\text{P}_{0,2})$  reaction, the spin constraints predict that the second fragment,  $\text{ClF}$ , must be produced in a triplet state. There



**Figure 7.** Energy level diagram for  $\text{NF}_2\text{Cl}$  and the diatomic channels  $\text{NF} + \text{Cl}_2$  and  $\text{NCl} + \text{ClF}$ . The energies listed under "Total Energy" were calculated from the energies of the diatomic fragments for each channel indicated.

is sufficient energy to generate  $\text{ClF}(\text{D}')$ , as shown in the energy level diagram, although no  $\text{ClF}(\text{D}' \rightarrow \text{A}')$  emission was observed. There are also other low-lying triplet states that are energetically accessible, the  $\text{B}^3\Pi_0^+$  and  $\text{A}'(^3\Pi_2)$  states. A "dark" channel leading to the production of the ground state fragments,  $\text{NF}(\text{X}^3\Sigma^-)$  and  $\text{ClF}(\text{X}^1\Sigma^+)$ , also correlates with a triplet intermediate state of  $\text{NF}_2\text{Cl}$ . The left side of the energy level diagram represents the energetics of the  $\text{NCl} + \text{F}_2$  channel. Spin rules dictate that production of  $\text{NCl}(\text{b}^1\Sigma^+)$  must be accompanied by production of the  $\text{F}_2$  fragment in a triplet state. However, generation of the  $\text{D}'$  state of  $\text{F}_2$  is not possible when the energetics of the  $\text{NCl} + \text{F}_2$  channel are examined. This channel would yield a lower limit for the  $\Delta H_{\text{form}}$  of  $\text{NF}_2\text{Cl}$  of 135 kcal/mol, an unreasonably high value and certainly out of the question compared to the  $\Delta H_{\text{form}}$ 's of Table 4. The formation of one of the low-lying triplet states of  $\text{F}_2(^3\Pi_{0u}$  or  $^3\Pi_{2u})$  plus the  $\text{b}^1\Sigma^+$  state of  $\text{NCl}$  and the "dark" channel leading to  $\text{NCl}(\text{X}^3\Sigma^+) + \text{F}_2(\text{X}^1\Sigma_g^-)$  are allowed product channels based on spin and energy considerations.

The formation of  $\text{ArF}(^2\text{B})$  was observed in the  $\text{Ar}(^3\text{P}_{0,2}) + \text{NF}_2\text{Cl}$  reaction when the argon pressure was reduced to 2 Torr. This product is allowed by the spin constraints of the system, and there are several possible mechanisms by which it could be generated. First, direct abstraction of a fluorine atom from  $\text{NF}_2\text{Cl}$  could lead to the  $\text{ArF}(^2\text{B})$  formation, leaving a doublet  $\text{NFCl}$  as the other reaction product, although  $\text{NFCl}$  was not detected in these studies. Ground state  $\text{F}_2(\text{X}^1\Sigma_g^-)$  generated in the "dark" channel is also a candidate for a secondary reaction



**Figure 8.** Energy level diagram for NCl<sub>3</sub> and the diatomic channel NCl + Cl<sub>2</sub>. The energies listed under "Total Energy" were calculated from the energies of the diatomic fragments for each channel indicated.

with Ar(<sup>3</sup>P<sub>0,2</sub>) leading to the ArF(<sup>2</sup>B) + F(<sup>2</sup>P) production. Finally, the mechanism of excimer formation via an excited molecular halogen channel has been reported for the Cl<sub>2</sub>\* + Xe(Kr), Br<sub>2</sub>\* + Xe, and IBr\* + Xe reactions.<sup>27</sup> By analogy with these reactions, it is possible that ArF(<sup>2</sup>B) could also be formed via an excited molecular fluorine channel where an excited triplet state of fluorine acts as a precursor.

An energy level diagram constructed for the NCl<sub>3</sub> + Ar(<sup>3</sup>P<sub>0,2</sub>) reaction system is given in Figure 8. As can be seen from the diagram, a sufficient amount of energy is present in the reaction with either 11.7 or 11.5 eV Ar metastables to generate Cl<sub>2</sub> emission at 258 nm. To generate the 198 nm emission, however, an additional 6.92 or 11.5 kcal/mol is needed in a reaction with a Ar(<sup>3</sup>P<sub>0</sub>) or Ar(<sup>3</sup>P<sub>2</sub>) metastable, respectively. Therefore, analogous to the NFCl<sub>2</sub> case, a two-step mechanism is proposed to account for the generation of chlorine emission. The dissociating state of NCl<sub>3</sub> formed as an intermediate in the NCl<sub>3</sub>(<sup>1</sup>X) + Ar(<sup>3</sup>P<sub>0,2</sub>) reaction correlates with two pathways both leading to the production of diatomic fragments. The NCl(b<sup>1</sup>Σ<sup>+</sup>) and Cl<sub>2</sub>(low-lying triplet state) fragments are generated in channel one. Presumably, the ground states NCl(X<sup>3</sup>Σ<sup>-</sup>) and Cl<sub>2</sub>(X<sup>1</sup>Σ<sup>+</sup><sub>g</sub>) are formed in the second, "dark", dissociation channel. The ion-pair states of chlorine are assumed to be formed via a secondary reaction between the ground state of Cl<sub>2</sub> formed in the "dark" channel and argon metastables.

The vibrational excitation of the nitrene products is a reflection of the geometry of the dissociating halogen amine, assuming no vibrational or electronic quenching of the b<sup>1</sup>Σ<sup>+</sup> states of NF and NCl. To check this assumption, the visible

spectra were run at different amine densities. Since the vibrational distributions were observed to not depend on the amine densities, this assumption is valid. For the NFCl<sub>2</sub>/Ar(<sup>3</sup>P<sub>0,2</sub>) and the NF<sub>2</sub>Cl/Ar(<sup>3</sup>P<sub>0</sub>) systems, only the Δν = 0 sequence band is observed in the NF(b → X) emission spectrum, implying that the majority of the NF fragments are emitting from the ν = 0 level of the b<sup>1</sup>Σ<sup>+</sup> state. Quenching of NF-(b<sup>1</sup>Σ<sup>+</sup>) is generally inefficient,<sup>32</sup> and quenching of ν' > 0 levels would require a polyatomic or diatomic species with a near-resonant vibrational mode. Potential collision partners in the flow system are argon atoms, the diatomic species NF, NCl, ClF, or Cl<sub>2</sub>, and parent molecules. Of these, only argon is present at high enough densities for a sufficient number of collisions, but it would not be an efficient vibrational quencher of NF(b<sup>1</sup>Σ<sup>+</sup>, ν' > 0). It is concluded, therefore, that the dissociating states of NFCl<sub>2</sub> and NF<sub>2</sub>Cl produce NF(b<sup>1</sup>Σ<sup>+</sup>, ν' = 0) directly and that the NF bond of the dissociating state is approximately the same length as r<sub>e</sub> of NF(b<sup>1</sup>Σ<sup>-</sup>), 1.2998 Å.<sup>30</sup> The length of the NF bond in the ground electronic state of both NFCl<sub>2</sub> and NF<sub>2</sub>Cl is reported to be 1.382 Å, so the dissociating state has a shorter NF bond than does the ground state in both amines.<sup>33,34</sup> Vibrational excitation up to ν' = 12 was observed in the NCl-(b → X) emission spectra observed in all three amine systems (NF<sub>2</sub>Cl, NFCl<sub>2</sub>, and NCl<sub>3</sub>). Therefore, using the same reasoning, the NCl bond of the dissociating parent amine must be longer than the bond length of the b state of NCl (r<sub>e</sub> = 1.5714 Å).<sup>30</sup> For comparison, the NCl bond length of the ground state of both NF<sub>2</sub>Cl and NFCl<sub>2</sub> is 1.730 Å and of the ground state of NCl<sub>3</sub> is 1.759 Å.<sup>33,34</sup> Applying this analysis to the NFCl<sub>2</sub> + N<sub>2</sub>(<sup>3</sup>Σ<sup>+</sup>) reaction, the fact that only Δν = 0 sequence bands were observed in the b → X emission of both NF and NCl indicates that the N-F and N-Cl bonds in the dissociating state are very similar to the r<sub>e</sub> values of the b states of NF and NCl.

For the metastable reactions of NFCl<sub>2</sub> in which both NF and NCl b → X emission was observed, the [NCl(b)]/[NF(b)] ratio was evaluated with the following expression.

$$\frac{[\text{NCl}(b)]}{[\text{NF}(b)]} = \frac{\left[ \sum_{\lambda} (S_{\text{NCl}(b \rightarrow X)} q_{\text{NCl}}) \right] A_{\text{NF}}}{\left[ \sum_{\lambda} (S_{\text{NF}(b \rightarrow X)} q_{\text{NF}}) \right] A_{\text{NCl}}}$$

where the sum is over the wavelength range of the NCl or NF emission, S is the signal intensity of the NCl or NF b → X emission at wavelength λ, q is the system response at each wavelength, and A is the Einstein A coefficient. A halogen quartz lamp with known output was used to measure the system response as a function of wavelength. Two values for the lifetime of the NCl(b<sup>1</sup>Σ<sup>+</sup>) have been reported, 0.63 and 2.0 ms, which yield Einstein A values of 1.59 × 10<sup>3</sup> and 5.0 × 10<sup>2</sup> s<sup>-1</sup>, respectively,<sup>21,35</sup> and the Einstein A coefficient for NF(b<sup>1</sup>Σ<sup>+</sup>) is 44.3 s<sup>-1</sup>.<sup>36</sup> In the NFCl<sub>2</sub> plus Ar metastable reactions, the [NCl(b)]/[NF(b)] ratio is 5/4 using 630 ms for the NCl(b) lifetime (or 4/1 using 2 ms for the NCl(b) lifetime). For the NFCl<sub>2</sub> + He metastable reaction, the choice of the NCl(b<sup>1</sup>Σ<sup>+</sup>) lifetime changes the [NCl(b)]/[NF(b)] ratio from unity for the shorter τ to 3/1 for the longer τ, but for either lifetime, the NF(b) channel is not the preferred pathway. Comparison of the visible emission spectrum observed in the NF<sub>2</sub>Cl/Ar(<sup>3</sup>P<sub>0,2</sub>) system (Figure 6A) with that observed in the NFCl<sub>2</sub>/Ar(<sup>3</sup>P<sub>0,2</sub>) system (Figure 1) indicates that, in the NF<sub>2</sub>Cl case, the NCl to NF ratio is lower. Although the ratio was not calculated because of the difficulty in resolving the NCl(b → X) emission in the NF<sub>2</sub>Cl experiment, it appears that there is a preference for NF(b) over NCl(b) production. Statistically, one would expect this to be

the case, and apparently the potential curves do not select against the statistical expectation.

## Conclusion

The studies reported here have yielded new information on excited electronic states of  $\text{NFCl}_2$ ,  $\text{NF}_2\text{Cl}$ , and  $\text{NCl}_3$  via reactions of these amines with excited triplet metastable species. Excited singlet states of these amines had been probed via photolysis experiments carried out previously, and information on excited triplet states is now available from the data presented here. For  $\text{NFCl}_2$ , two excited singlet states had been observed in the 249 nm (4.98 eV) and 193 nm (6.42 eV) photolysis experiments, and evidence for three excited triplet states was observed following the reaction of  $\text{NFCl}_2$  with triplet metastables of energy 6.3, 11.7, and 19.8 eV. All five of these excited electronic states have dissociation pathways leading to the formation of diatomic fragments which can be understood on the basis of conservation of spin angular momentum. Only in the 249 nm photolysis was a nondiatom dissociation pathway producing  $\text{NFCl}$  observed. The direct production of ion pair states of the diatomic halogens appears to be possible only in the reactions of  $\text{NFCl}_2$  with He metastables; otherwise, low-lying triplet states of the halogens are generated.

The singlet and triplet electronic states of  $\text{NFCl}_2$  observed to date can be classified according to the preferred diatomic dissociation channel. The  $\text{NF} + \text{Cl}_2$  channel is the favored dissociation pathway for both the lowest excited singlet state pumped at 4.98 eV and the triplet state accessed at 6.3 eV. Dissociation of the second excited singlet state pumped at 6.42 eV and of the triplet states observed at 11.7 and 19.8 eV generally favor the  $\text{NCl} + \text{ClF}$  over the  $\text{NF} + \text{Cl}_2$  channel.

The results of the  $\text{NF}_2\text{Cl}/\text{Ar}(^3\text{P}_{0,2})$  and the  $\text{NCl}_3/\text{Ar}(^3\text{P}_{0,2})$  reaction systems are similar to those of the  $\text{NF}_2\text{Cl}/\text{Ar}(^3\text{P}_{0,2})$  system, which is not surprising since these molecules are closely related to each other. There are again diatomic dissociation channels which are easily understood on the basis of spin constraints and energetics. The variations observed in the NX species generated are also not unexpected for the series  $\text{NF}_2\text{Cl}$ ,  $\text{NFCl}_2$ , and  $\text{NCl}_3$ . In the  $\text{NF}_2\text{Cl}$  system, both  $\text{NF}(b)$  and  $\text{NCl}(b)$  are generated with an apparent preference for  $\text{NF}(b)$ . In the  $\text{NFCl}_2$  system, again, both  $\text{NF}(b)$  and  $\text{NCl}(b)$  are generated, but with a preference for  $\text{NCl}(b)$ . Of course, only  $\text{NCl}(b)$  is observed in the  $\text{NCl}_3$  system. As a part of this work, the  $\Delta H_{\text{form}}$ 's for  $\text{NF}_3$ ,  $\text{NF}_2\text{Cl}$ ,  $\text{NFCl}_2$ , and  $\text{NCl}_3$  were computed. The experimental value for  $\text{NF}_3$  is fairly well established, and the calculated value was 19% lower. For  $\text{NCl}_3$ , an experimental value had been reported, and the calculated value was similarly too low (by 21%). This suggests that the experimental  $\Delta H_{\text{form}}$  for  $\text{NFCl}_2$  is  $\sim 20\%$  higher than the computed value. The trend observed in the calculated  $\Delta H_{\text{form}}$ 's for the series  $\text{NF}_3$ ,  $\text{NF}_2\text{Cl}$ ,  $\text{NFCl}_2$ , and  $\text{NCl}_3$  ( $-31.4$ ,  $-5.3$ ,  $23.0$ , and  $48.3$  kcal/mol, respectively) conforms to expectations regarding the stability of these compounds. As the F atoms are replaced by Cl atoms, the stability decreases.

Computations of the electronic states are planned and, with the information obtained from the metastable studies presented here and the previously reported photolysis studies, will improve

our understanding of the excited electronic states of these intriguing molecules.

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