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FINAL TECHNICAL REPORT

SHORT WAVELENGTH CHEMICAL LASER DEMONSTRATION BASED ON N(²D) CHEMISTRY

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EXECUTIVE SUMMARY

The overall goal of this project was to demonstrate lasing on the $\text{NCl}(b \rightarrow X)$ transition at 665 nm. Our scheme is based on chemical production of excited nitrogen atoms in the ^2D metastable state and subsequent reaction of $\text{N}(^2\text{D})$ with Cl_2 to produce $\text{NCl}(b)$. Our intermediate objectives were: (1) demonstrate chemical generation of $\text{N}(^2\text{D})$, (2) identify and measure rate constants important to the chemical scheme, and (3) demonstrate production of $\text{NCl}(b)$ from the $\text{N}(^2\text{D}) + \text{Cl}_2$ reaction. The program results and accomplishments are summarized below.

We have developed a procedure for pulsed chemical generation of $\text{N}(^2\text{D})$ based on the reaction of oxygen atoms with cyanide radicals. These reagents are produced by pulsed photolysis of C_2N_2 and N_2O with radiation from an ArF excimer laser. $\text{N}(^2\text{D})$ production was confirmed by observation of NO β -band emission produced by the reaction of $\text{N}(^2\text{D})$ with N_2O .

We have measured for the first time two important CN rate constants, $k(\text{Cl}_2)$ and $k(\text{F}_2)$; and have shown that CN follows the same pattern as halogen atoms in reaction with Cl_2 and F_2 .

We have prepared two manuscripts, one describing the procedure for pulsed chemical generation of $\text{N}(^2\text{D})$ and one presenting the results of our rate constant measurements. These manuscripts will be submitted for publication in appropriate scientific journals.

Finally, we have shown that because Cl_2 reacts at a significant rate with CN, Cl_2 is not an appropriate Cl donor molecule for producing $\text{NCl}(b)$ from reaction with $\text{N}(^2\text{D})$. The destruction of CN by Cl_2 accounts for our failure to observe production of $\text{NCl}(b)$. We do however recommend that the overall concept of using $\text{N}(^2\text{D})$ reactions to produce electronically excited molecular products should not be abandoned. $\text{N}(^2\text{D})$ reaction with any one of a number of other halogen atom donors could yield $\text{NCl}(b)$ or $\text{NF}(b)$; and oxygen atom donors could yield $\text{NO}(B)$. For this reason, we urge that this technology be pursued to the extent of experimentally investigating other $\text{N}(^2\text{D})$ co-reagents.

INTRODUCTION

This report describes research effort aimed at demonstrating a Short Wavelength Chemical Laser (SWCL). The work was performed under Contract No. 9-X2H-1467G-2 awarded to Hercules Incorporated by the Strategic Defense Initiative Organization. The periods of performance were 30 September 1987 to 11 March 1988 and 1 March 1989 to 30 October 1989.

The overall objective of this program was to chemically produce the $b^1\Sigma$ electronically excited state of NCl and demonstrate gain on the ($b^1\Sigma \rightarrow X^3\Sigma$) transition at 665 nm. Our proposed approach was to chemically produce nitrogen atoms in the 2D metastable state from the reaction of oxygen atoms with cyanogen radicals, and then produce NCl(b) from the reaction of $N(^2D)$ with Cl_2 . To avoid complications associated with reagent mixing we proposed that O and CN be produced by pulsed photolysis of N_2O and C_2N_2 ; and, that all of the reagent gases (N_2O , C_2N_2 and Cl_2) be premixed. Now, in order to drive the $N(^2D)/Cl_2$ reaction to dominance over other $N(^2D)$ quenching processes, Cl_2 should be present in excess. So a critical process in this scheme is the reaction of Cl_2 with CN; first, because CN lost by this path is unavailable for the $N(^2D)$ production process, and second, because the rate constant for this reaction was unknown.

In accordance with the foregoing assessment, our program was structured as follows. First, confirm generation of $N(^2D)$ following pulsed photolysis of C_2N_2 and N_2O . Second, measure the $CN + Cl_2$ rate constant. Third, determine whether NCl(b) is produced by our proposed scheme and, if so, determine whether the production rate is sufficient to yield gain on the NCl($b \rightarrow X$) transition.

PULSED GENERATION OF $N(^2D)$

During the first experimental phase of our contract effort we developed a procedure for pulsed chemical generation of $N(^2D)$ based on the reaction of oxygen atoms with cyanide radicals,

Schmatjko and Wolfrum⁽¹⁾ report the rate constant for this reaction to be $1.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. In our scheme CN radicals and O atoms are produced simultaneously by pulsed photolysis of C_2N_2 and N_2O with radiation at 193 nm from an ArF excimer laser. Cross sections for photolytic dissociation of both C_2N_2 and N_2O are reported to be $\sim 10^{-19} \text{ cm}^2$.^(2,3) Thus, a photon flux of $10^{24} \text{ cm}^{-2} \text{ s}^{-1}$, which is easily achieved with our excimer laser, can dissociate 0.1% of each of these species. There is, however, an important factor in the photodissociation of N_2O which must be taken into consideration. Photolysis of N_2O at 193 nm produces $\text{O}(^1\text{D})$ with a quantum yield near unity,⁽⁴⁾ and $\text{O}(^1\text{D})$ reacts with N_2 at nearly gas kinetic rates to produce NO or N_2 and O_2 .⁽⁵⁾ Therefore, to achieve a significant yield of ground state O atoms we make use of the fact that $\text{O}(^1\text{D})$ is rapidly quenched to the $\text{O}(^3\text{P})$ ground state by N_2 .⁽⁶⁾ We have done kinetic modeling which predicts that approximately half of the $\text{O}(^1\text{D})$ produced by photolysis is quenched to the ground state if the gas mixture contains 2 Torr of N_2 ; and that the conversion process is nearly complete in 1 μs . So, if sufficient N_2 is added to the gas mixture, usable densities of ground state O atoms can be produced.

The presence of N_2O provides a convenient way to confirm the production of $\text{N}(^2\text{D})$ as a result of the following reaction.

The rapid radiative decay of NO(B) produces the familiar NO β -band emission. So detection of the β -bands provides evidence that $\text{N}(^2\text{D})$ is present in the mixture. Also, by observing the time profile of the emission intensity, the time evolution of $\text{N}(^2\text{D})$ density can be monitored.

Experimental

Experiments were conducted using flowing mixtures of Ar (99.999%), N_2 (99.995%), C_2N_2 (98.5%) and N_2O (99.99%). The gases were obtained from commercial sources and used without further purification. Cyanide radicals and oxygen atoms were produced by photolysis of C_2N_2 and N_2O with pulsed radiation at 193 nm from our ArF excimer laser (Lumonics Series TE-860-4).

The photolysis cell is of modular construction fabricated from 2.54 cm pyrex O-ring joints. Reagent and buffer gases were mixed upstream of the cell and were continuously flowed during each test. Fused silica side windows at the midpoint of the cell allow optical access to the photolysis region. End extensions contain co-linear baffles with 6 mm diameter holes to collimate and define the size of the excimer beam and reduce scattered light from the fused silica end windows. The end extensions were purged with a small flow (~ 15 SCCM each) of buffer gas to prevent product accumulation in these otherwise stagnant regions.

The system was pumped by a 650 l/min mechanical pump (Welch Model 1374). Pressure in the cell was measured with a capacitance manometer (MKS Type 122AA) and gas flow rates were measured with electronic mass flow meters (MKS Type 258B). Each mass flow meter was calibrated for its specific gas by measuring the rate of pressure rise into the known system volume at several different flow rates.

β -band emission at the center of the cell was viewed through one of the side windows. The light passed through a monochromator (ARC Model 502) and was detected with a photomultiplier (EMI 9558QB). Spectral data was obtained by feeding the amplified photomultiplier output to a gated integrator/boxcar averager (SRS Model SR-250) and plotting the averaged output as the monochromator was slowly scanned. β -band time profiles were obtained by setting the monochromator at one of the more intense vibrational bands and feeding the signal to a transient recorder (LeCroy Model TR8837-F).

Results and Discussion

The first experiment was conducted to confirm that $N(^2D)$ was indeed being generated by photolysis of N_2O and C_2N_2 . A mixture consisting of N_2O ($2.6 \times 10^{16} \text{ cm}^{-3}$), C_2N_2 ($5.1 \times 10^{15} \text{ cm}^{-3}$), N_2 ($5.7 \times 10^{16} \text{ cm}^{-3}$) and Ar ($1.1 \times 10^{17} \text{ cm}^{-3}$) was set flowing through the photolysis cell. Pulsed radiation from the excimer laser was also directed through the cell. A spectral scan of the afterglow emission following pulsed photolysis of N_2O and C_2N_2 yielded the β -band spectrum shown in Figure 1. We interpret this

β -band emission as confirmation of $N(^2D)$ production from the photolysis products O and CN.

Figure 1. β -band spectrum obtained from pulsed photolysis of N_2O and C_2N_2 .

To verify our assessment of the dominant kinetic processes occurring in the gas mixture we compared results predicted by kinetic modeling with experimental results. The modeling calculations were done using a modified version of the Air Force Weapons Laboratory kinetics code CHEM adapted to run on an IBM personal computer. The results of these calculations are reactant and product species concentrations as functions of time. More than 30 separate rate processes were included in the calculations and extensive use was made of kinetic data from Black's work on pulsed photolysis of C_2N_2/O_2 mixtures.⁽⁷⁾ But many of these processes play only a minor role; so in the

interest of brevity only seven processes that we feel are most significant are included in the reaction scheme shown in Table I. Experimental time profiles of the β -band emission intensity were measured and plotted for three different initial concentrations of N_2O ($2.6, 3.6$ and $5.2 \times 10^{16} \text{ cm}^{-3}$). Initial concentrations of the other gases were the same as given above for the spectral measurement and not changed from experiment to experiment. Using our kinetic model we then calculated $NO(B)$ concentration as a function of time

TABLE I. Abbreviated Reaction Scheme for $N(^2D)$ Generation

Process	Rate Constant ($\text{cm}^3 \text{ s}^{-1}$)	Reference
$CN + O \rightarrow N(^2D) + CO$	1.4×10^{-11}	1
$CN + N_2O \rightarrow N_2 + NCO$	1.0×10^{-13}	Estimate
$N(^2D) + N_2O \rightarrow N_2 + NO(B)$	2.6×10^{-12}	8*
$NO(B) \rightarrow NO(x) + h\nu$	$3 \times 10^5 \text{ (s}^{-1}\text{)}$	9
$N(^2D) + C_2N_2 \rightarrow C_2N + N_2$	7.0×10^{-11}	Estimate
*This value is for the total $N(^2D)$ removal rate by N_2O . The $NO(B)$ yield is only $\sim 0.3\%$.		

for the same three sets of initial gas concentrations. Because the β -band intensity is proportional to $[NO(B)]$, normalized plots of measured intensity and calculated concentration should correspond to each other, providing the kinetic model is correct. A comparison of the normalized experimental and modeling data for one of the initial conditions which we cite as typical is shown in Figure 2. In this plot the smooth line represents the modeling results. The fact that the comparison is so obviously favorable indicates that the most important kinetic processes are accounted for in the model. Both experimental and model profiles reach peak values at nearly the same time. Both appear to decay at about the same rate, and both show an increase in decay rate as the N_2O concentration is increased.

It is interesting to pursue the decay rate dependence on N_2O density a little further. The decaying portions of the model profiles were found to fit

Figure 2. Comparison of normalized data. $[NO(B)]$ calculated from model - smooth line; experimental β -band intensity - jagged line.

a single exponential decay very well. A plot of the corresponding decay rates versus $[N_2O]$ falls on a straight line. The calculated slope of this line is $1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, precisely the value used in the model for the $CN + N_2O$ rate constant. This correspondence suggests that the decay profile in both the model and the experiment represents the CN loss rate. This is the expected result if the processes are pseudo-first-order in O atoms; but it appears to hold even though there are only slightly more O atoms ($8.7 \times 10^{12} \text{ cm}^{-3}$) than CN radicals ($7.6 \times 10^{12} \text{ cm}^{-3}$).

MEASUREMENT OF CN RATE CONSTANTS

As described in the Introduction, the laser scheme we are investigating is based on chemical production of nitrogen atoms in the 2D metastable state (from the reaction of oxygen atoms and cyanide radicals) and the subsequent reaction of $N(^2D)$ with Cl_2 to produce the excited singlet $NCl(b)$. Another attractive candidate is $NF(b)$ produced by the reaction of $N(^2D)$ with F_2 . SWCL utilization of $NF(b)$ has been proposed in an energy transfer role; whereas $NCl(b)$, with a radiative lifetime of $\sim 630 \mu\text{s}$, may lase directly. To drive the $N(^2D)$ /halogen reaction to dominance over other $N(^2D)$ quenching processes, excess halogen molecules should be premixed with the $N(^2D)$ precursor reagents O and CN. An obviously critical process in this

scheme is therefore the reaction of CN with the halogen molecule that is present. Determination of the corresponding rate constants was the objective of these experiments. As a test of our experimental setup and procedure we also measured the rate constant for reaction of O_2 with CN radicals and obtained good agreement with recent literature values.^(10,11)

Experimental

The experimental system used for the rate constant measurement was essentially the same as used for the pulsed $N(^2D)$ generation experiments previously described. The procedures used were similar to those reported by Li and co-workers.⁽¹⁰⁾ Again, cyanide radicals were produced by pulsed photolysis of C_2N_2 with the 193 nm output of an ArF excimer laser (Lumonics TE-860-4). Time resolved laser-induced fluorescence (LIF) was used to monitor the decay of the CN radicals after the photolysis pulse. LIF was excited by a dye laser (PRA LN107) tuned to the center of the P rotational branch (nominally P(6) at 388 nm) in the 0,0 band of the $CN(X^2\Sigma^+ \rightarrow B^2\Sigma^+)$ system. Excitation at this wavelength precludes pumping of the P branch of the 1,1 band which overlaps the R branch of the 0,0 band. $CN(B \rightarrow X)$ fluorescence subsequent to absorption of the dye laser radiation was monitored on the 0,1 band near 420 nm. The photolysis and probe laser beams were propagated in opposite directions down the 20 cm length of the cell.

LIF was observed at the center of the cell at 90° to the axis of the photolysis and probe beams. The light passed through an interference filter centered at 420 nm and was detected with a photomultiplier tube (Hamamatsu R928). The excimer laser was internally triggered at 20 Hz and its output observed with a photodiode. The photodiode pulse triggered a delay generator (SRS DG535) having a variable delay output. The delayed output at 20 Hz triggered a boxcar averager/gated integrator (SRS SR250) and a 2X pulse divider. The 10 Hz output from the pulse divider triggered the probe laser on alternate excimer laser pulses, such that the LIF signal was produced at 10 Hz after every other excimer laser pulse. Such pulse division provided a convenient way to subtract unwanted baseline signals. CN time profiles were obtained by monitoring the LIF signal as the photolysis to probe delay was increased in a stepwise manner. An IBM PC was used to receive LIF data from the boxcar averager, sub-

tract baseline signals received on alternate pulses, and to control the photolysis to probe delay. Data from 40 pulses were averaged for each 0.5 μ s time element probed. Typically, data were recorded over a total time duration equivalent to roughly 5 CN delay time constants.

RESULTS

Figure 3 shows a typical CN time decay, after baseline subtraction as described above. The data are well-fitted by a single exponential decay as shown in the figure.

Figure 3. CN decay data averaged and fitted to a single exponential.

The measured CN decay rate is the total CN loss rate out of the volume probed by the dye laser. Loss processes include reaction with the added reagent in question (R), reaction with other species present (R_i), and diffusion, such that the rate equation is given by

$$\frac{d[CN]}{dt} = - \left\{ k_R[R] + \sum_i k_i[R_i] + k_D[CN] \right\} \quad (3)$$

where k_R and k_i are rate constants for removal of CN by reactions with R and R_i respectively, and $k_D[CN]$ is the rate of diffusion out of the observation volume. Under pseudofirst order conditions, the time dependence of the CN density is given by

$$[\text{CN}] = [\text{CN}]_0 \exp(-Bt) \quad (4)$$

where $B = k_R[R] + \sum k_i[R_i] + k_D$. A value for k_R can therefore be obtained by measuring B over a range of different densities of R . A plot of B vs $[R]$ should be linear with slope k_R and intercept $\sum k_i[R_i] + k_D$. This procedure was used to obtain values of k_R for $R = \dot{\text{O}}_2$, Cl_2 , and F_2 .

Ten separate measurements of the CN decay rate were made for densities of added O_2 ranging from $6 \times 10^{13} \text{ cm}^{-3}$ to $6 \times 10^{14} \text{ cm}^{-3}$. The C_2N_2 density was $3 \times 10^{15} \text{ cm}^{-3}$, from which we estimate the density of CN radicals produced by the photolysis to be $\leq 1 \times 10^{13} \text{ cm}^{-3}$. Argon was added as a buffer gas to bring the total pressure up to 3 Torr. A plot of the CN decay rate vs the O_2 density is shown in Figure 4. A least squares fit of these data yields the value $k(\text{O}_2) = (2.2 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, with the uncertainty representing 2σ from the plot. This value is in good agreement with data previously reported in the literature,^(10,11) and serves to confirm our experimental method.

Figure 4. Plot of CN decay rate vs O_2 concentration.

Figure 5 shows results from measurements of CN decays in the presence of added amounts of Cl_2 . The Cl_2 density was varied from $4 \times 10^{14} \text{ cm}^{-3}$ to $4 \times 10^{15} \text{ cm}^{-3}$, and the C_2N_2 density, Ar density, and total pressure were the same as in the O_2 experiments noted above. A least squares fit to these data yields a rate constant $k(\text{Cl}_2) = (6.0 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for CN removal by Cl_2 .

Figure 5. Plot of CN decay rate vs Cl_2 concentration.

A mixture of 10% F_2 in helium was used for measurement of the $\text{CN} + \text{F}_2$ rate constant. Helium was also used as a buffer gas in these experiments to preclude possible complications arising from different CN diffusion rates in He and Ar. Initial attempts to measure CN decay rates in the presence of F_2 were disappointing. Unlike the experiments with O_2 and Cl_2 , decays were much slower ($\sim 500\mu\text{s}$) and obviously not single exponential. Instead, the data exhibited two distinct decay components. It was found, however, that when the pressure was increased by throttling the pump, the decays became more closely fitted by single exponentials. Increasing the total pressure by throttling decreases the flow velocity. It seemed plausible, therefore, that the nonexponential decays resulted from CN depletion in the observation region due to fast flow and/or faster diffusion in helium. Accordingly, the flow and pressure conditions were changed to reduce the flow velocity from 1500 cm s^{-1} to 150 cm s^{-1} . The C_2N_2 density was $1.3 \times 10^{15} \text{ cm}^{-3}$ and the F_2 density

was varied from $2.5 \times 10^{15} \text{ cm}^{-3}$ to $2.5 \times 10^{16} \text{ cm}^{-3}$. Helium was added to bring the total pressure to 10 Torr. Under these conditions the CN decay profiles were very well fit by single exponentials, and the corresponding plot of CN decay rate vs F_2 density was found to be linear, as shown in Figure 6. The slope obtained from a least squares fit to the data indicates the rate constant for CN removal by F_2 to be $k(F_2) = (6.4 \pm 0.8) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$.

Figure 6. Plot of CN decay rate vs F_2 concentration.

Discussion

To our knowledge, rate constants for reactions of CN with molecular halogens have not been previously reported. The present data indicate that the rate for reaction of CN with Cl_2 is two orders of magnitude faster than that for reaction of CN with F_2 , even though both processes have very large exothermicities (39 and 74 kcal/mole, respectively). Considering the CN radical to be halogen-like in its behavior, this difference is consistent with reported rate constants^(12,13) for reactions of halogen atoms with Cl_2 and F_2 . Table II shows rate constants for the $Cl + F_2$ and $F + Cl_2$ reactions, along with the present data. Note that the $Cl + F_2$ reaction is nearly four orders of magnitude slower than $F + Cl_2$, even though its exothermicity is 23

kcal/mole, whereas that of $F + Cl_2$ is only 2 kcal/mole. This very great difference in rate constants must be attributable in some way to the potential energy surfaces of these reactions in the vicinity of the intermediate configurations ClF_2 and FCl_2 . ClF_2 is a stable radical which has been studied both theoretically⁽¹⁴⁾ and experimentally,⁽¹⁵⁾ the latter principally with

TABLE II. Rate Constants for Reactions with Molecular Halogens

Reagent	$k(Cl_2), cm^3 s^{-1}$	$k(F_2), cm^3 s^{-1}$
F ^a	$1.6 \pm 0.5 \times 10^{-10}$	—
Cl ^b	—	$\leq 5 \times 10^{-14}$
CN ^c	$6.0 \pm 0.3 \times 10^{-12}$	$6.4 \pm 0.8 \times 10^{-14}$
a = Reference 12 b = Reference 13 c = Present data		

matrix isolation methods. Its geometry, vibrational frequencies, and one excited electronic state are known. Conversely, FCl_2 has not been observed and presumably is unbound. Hence, the mechanisms of the $Cl + F_2$ and $F + Cl_2$ reactions may well be very different, the former getting trapped in the ClF intermediate, which might prefer dissociation to the reagents $Cl + F_2$ rather than to $ClF + F$.

Clearly, the $CN + F_2$ and $CN + Cl_2$ reactions follow this same pattern, with $CN + Cl_2$ being two orders of magnitude faster although both processes are very exothermic. $CN + F_2$ is nearly as slow as $Cl + F_2$, but $CN + Cl_2$ is not as fast as $F + Cl_2$. Hence CN behaves in this case like a pseudo-halogen atom, with character in between F and Cl.

It is interesting to speculate whether the difference in rates between $CN + F_2$ and $CN + Cl_2$ arises from factors similar to those at work in the $Cl + F_2$ and $F + Cl_2$ systems, i.e., whether CNF_2 is a stable radical. If so, it might be observable by using matrix methods such as those used successfully

to study ClF_2 .

NCl(b) PRODUCTION

The third part of our program was to determine whether NCl(b) is produced by our proposed photolysis/chemical scheme and, if so, determine whether the production rate is sufficient to yield gain on the $\text{NCl(b} \rightarrow \text{X)}$ transition. The results of our efforts to do this are summarized by stating that all attempts to detect $\text{NCl(b} \rightarrow \text{X)}$ emission when Cl_2 was added to the gas mixture failed. A possible reason for this negative result is the relatively fast rate at which CN reacts with Cl_2 compared to the slow rate at which CN reacts with O (because of its low concentration) to form the $\text{N}(^2\text{D})$. Suppose we add Cl_2 until the $\text{N}(^2\text{D}) + \text{Cl}_2$ reaction rate ($k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) just equals the $\text{N}(^2\text{D}) + \text{N}_2\text{O}$ reaction rate ($k = 2.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$). The Cl_2 density would need to be $2.6/12 \approx 0.2$ times the N_2O density, or typically $5 \times 10^{15} \text{ cm}^{-3}$. But with this much Cl_2 , the CN loss rate due to reaction with Cl_2 is $k(\text{Cl}_2)[\text{Cl}_2] = 6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \times 5 \times 10^{15} \text{ cm}^{-3} = 3 \times 10^4 \text{ s}^{-1}$. On the other hand, for a typical O atom density of 10^{14} cm^{-3} , the rate at which CN is used to produce $\text{N}(^2\text{D})$ is only $1.4 \times 10^3 \text{ s}^{-1}$. So in this situation, only about one in twenty CN radicals would contribute to $\text{N}(^2\text{D})$ production. We feel that this inefficiency in CN radical utilization is very likely the reason for our failure to observe NCl(b) production.

SUMMARY AND CONCLUSIONS

Our performance of this research program has resulted in the following significant accomplishments.

- We have developed a method for pulsed chemical generation of $\text{N}(^2\text{D})$ based on simultaneous photolysis of C_2N_2 and N_2O . This method appears to have considerable utility in experimental investigations of $\text{N}(^2\text{D})$ kinetics.
- We have measured for the first time two important CN rate constants, $k(\text{Cl}_2)$ and $k(\text{F}_2)$; and have shown that CN follows the same pattern as haloogen atoms in reaction with Cl_2 and F_2 .

- We have also shown that because Cl_2 reacts at a significant rate with CN, Cl_2 is not an appropriate Cl donor molecule for the $\text{N}(^2\text{D})$ /halogen reaction.

In conclusion, we recommend that even though we failed to generate a detectable concentration of $\text{NCl}(b)$, the overall concept of using $\text{N}(^2\text{D})$ reactions to produce electronically excited molecular products should not be abandoned. $\text{N}(^2\text{D})$ reaction with any one of a number of other halogen atom donors could yield $\text{NCl}(b)$ or $\text{NF}(b)$; and oxygen atom donors could yield $\text{NO}(B)$. For this reason we urge that this technology be pursued to the extent of experimentally investigating other $\text{N}(^2\text{D})$ co-reagents.

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