THE UV PHOTOLYSIS OF CHLORINE AZIDE

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Summary

The photolysis of ClN_3 at 272 and 300 nm results in prompt emission between 600 and 900 nm from two different species which most probably are different states (either electronic or vibrational) of ClN. One state, at present still unidentified, has a radiative lifetime of 26 ± 5 μs and is quenched by Cl_2 with a rate constant of $(7.5 \pm 2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The other state, tentatively identified as the b $^1\Sigma^+$ state, has a radiative lifetime of 0.25 ± 0.05 ms and is quenched by Cl_2 with a rate constant of $(1.5 \pm 0.5) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}.

1. Introduction

The azides are a class of endoergic compounds which decompose into energy-carrying fragments [1]. Solid ionic azides release azide radicals on pyrolysis which recombine to produce electronically excited nitrogen molecules [2]. In contrast, covalent azides decompose to produce electronically excited singlet nitrene radicals (RN) and molecular nitrogen [1]. For the few azides which have been studied in any detail, HN_3 [3 - 23], NCN_3 [24 - 30] and CH_3N_3 [31 - 33], the electronically excited nitrene produced in photolysis has been observed in absorption, or inferred from chemical arguments, but has not been observed in emission to the triplet nitrene ground state. The singlet-to-triplet transitions of all the halonitrenes have been observed in emission when these species were produced by chemical methods [34 - 41]. In addition, Gleu [42] observed the NCl (b $^1\Sigma^+$–X $^3\Sigma^-$) emission at 665 nm in his spectroscopic studies on the pyrolysis of ClN_3. It seemed to us that electronically excited ClN also ought to be produced in the photolysis of ClN_3. We therefore did several experiments in our laser photolysis facility [3, 43] to test this hypothesis.

The UV absorption spectrum of ClN_3 has been measured in the gas phase by Clark and Clyne [44] and in hexane solution by Dehnicke and

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Ruschke [45]. Both groups report a continuous spectrum with a fairly strong absorption peak at about 210 nm and a weaker (about a factor of 4 smaller) secondary absorption maximum at about 250 nm. In addition, Dehnicke and Ruschke report a third very weak tertiary peak at about 380 nm.

We report two sets of experiments on the photolysis of mixtures of argon, Cl_2 and ClN_3 at wavelengths of 300 and 272 nm.

2. Experimental details

We have previously described in great detail the apparatus used in these experiments [3, 43]. The photolysis gas was contained in a stainless steel reaction cell and was photolyzed by single pulses from a doubled dye laser which entered and exited the cell through long side arms containing several sets of baffles. A photomultiplier–filter combination observed fluorescence from the photolyzed gas normal to the photolysis beam. The current from the photomultiplier flowed to ground through a load resistor which could be varied between 0.1 and 60 kΩ. An oscilloscope which was triggered by the photolysis laser monitored the voltage across the load resistor. In the first set of experiments at 300 nm, a quartz flat in the optical train of the photolysis laser deflected a small fraction of the laser energy into an energy meter and, in addition, a vacuum photodiode monitored the laser pulse at the exit of the photolysis cell and displayed the laser pulse temporal profile on a second trace of the oscilloscope. In the second series of experiments, the energy meter monitored the laser pulse energy at the exit of the photolysis cell. The laser energy was about 450 μJ at 300 nm and about 40 μJ at 272 nm.

A Corning Glass 2-62 short-wavelength cut-off filter in combination with an EMI 9659 QA photomultiplier gave an effective bandpass of 600 - 900 nm.

The ClN_3 was prepared according to the method of Spencer [46] as outlined by Clark [35] and Clark and Clyne [44]. A mixture of Cl_2 in argon was flowed slowly through a column packed with sodium azide, then dried by flowing through a $CaCl_2$ column and finally stored in a 5 l glass bulb. Clark and Clyne claimed a conversion efficiency of about 50% using this technique, but our yields seemed to us to be much lower. We were unable to detect significant pressure changes from ClN_3 decomposition upon discharging small volumes of sample with a tesla coil. In the second series of experiments, we estimated a ClN_3 mole fraction of only 0.001 based on the attenuation of the laser beam through the photolysis cell and Clark and Clyne's [44] published extinction coefficient at 272 nm. The Cl_2 mole fraction in the mixture was 0.08. We did several qualitative photolysis shots at 272 nm using ClN_3 which had been synthesized according to Gleu's [42] modification to Raschig's [47] method. Relatively pure ClN_3 was generated by slowly dropping dilute H_2SO_4 into a solution of NaOCl and NaN_3. The

evolving gas was then dried over $CaCl_2$. The results of these photolyses were qualitatively similar to the experiments at 272 nm using Clark and Clyne's method of ClN_3 synthesis.

Clark and Clyne [44] have shown mass spectrometrically that the only detectable impurity generated by their method of ClN_3 synthesis is HN_3. Using IR analysis, we found that our application of Gleu's [42] procedure for ClN_3 synthesis produces no detectable HN_3, and furthermore the pressure rise from explosions of ClN_3 generated by Gleu's method showed the ClN_3 to be pure. Even though some HN_3 could have been present in the photolysis mixtures generated by Clark and Clyne's technique, our earlier studies on HN_3 photolysis [3] have shown that no prompt emission is generated in HN_3 photolysis. Indeed no emission of any kind is generated in HN_3 photolysis when the HN_3 is highly diluted in argon [48].

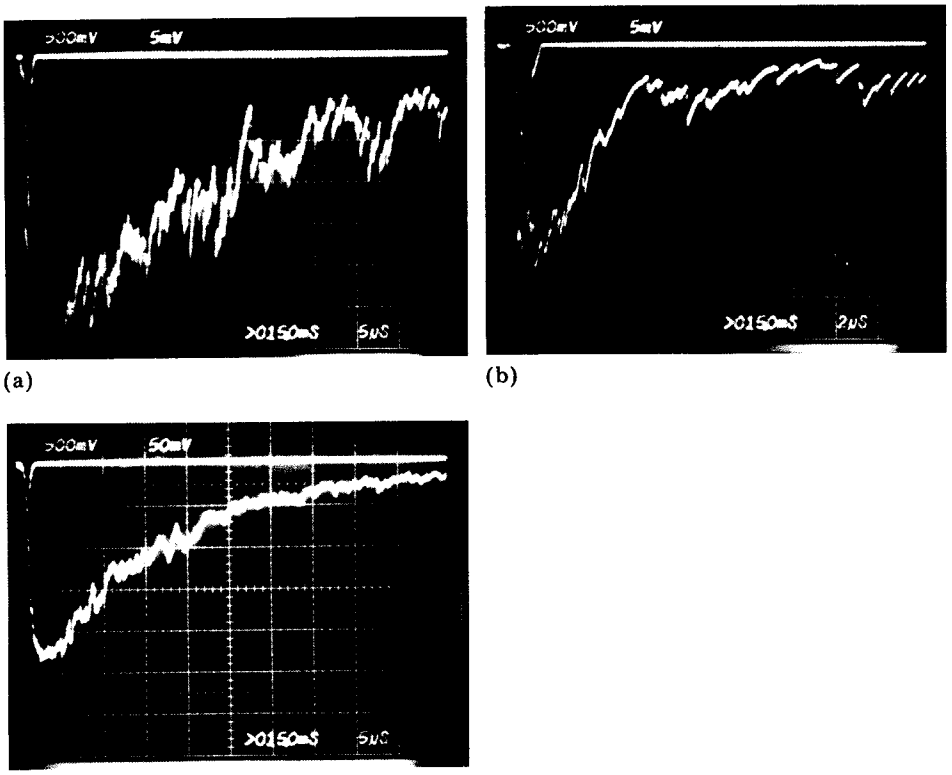
Because significant decomposition of the sample took place between laser shots, the cell was pumped out and refilled from the storage flask between shots. A pressure transducer (Validyne DP-7) which had been calibrated against oil and mercury manometers measured the total pressure in the cell.

3. Results

Photolysis of ClN_3 at 300 nm resulted in prompt emission in the red ($600 \text{ nm} \leqslant \lambda \leqslant 900 \text{ nm}$). Most of the ClN_3 decomposed with the first pulse, as subsequent pulses resulted in greatly reduced light emission (see Fig. 1). This is in spite of the fact that the total volume of the photolysis cell was of the order of 11 l, while the volume of gas illuminated by the photolysis laser was about 40 ml. The time between laser pulses was sufficiently long that diffusion of gas back into the observation region should have been complete. At higher total pressures the rapid decomposition of ClN_3 was moderated, but significant decomposition was still evident after only a few shots. Thus the photolysis pulse appears to initiate a rapid chemical decomposition of ClN_3 via a chain mechanism. These observations indicate the extreme instability of ClN_3. By contrast, HN_3 is much more stable since repeated photolysis of pure HN_3 at pressures up to 2 Torr results in no noticeable degradation in the light emission from the secondary photolysis product $NH_2(^2A_1)$ [48]. The maximum ClN_3 partial pressure studied was not more than 50 mTorr.

The rate of decay of emission following ClN_3 photolysis was monitored as a function of the pressure of the photolysis mixture. The prompt emission indicates that the emitting species is produced directly in the photolysis rather than via some secondary chemical process (see later). For the purposes of the following discussion, we shall assume that the emitting species is electronically excited NCl. In Section 4 we discuss why NCl* is the logical choice for the photolytically produced emitting species.

After the photolysis pulse shuts off, the decay of the electronically excited ClN is given by



(a) (b)

(c)

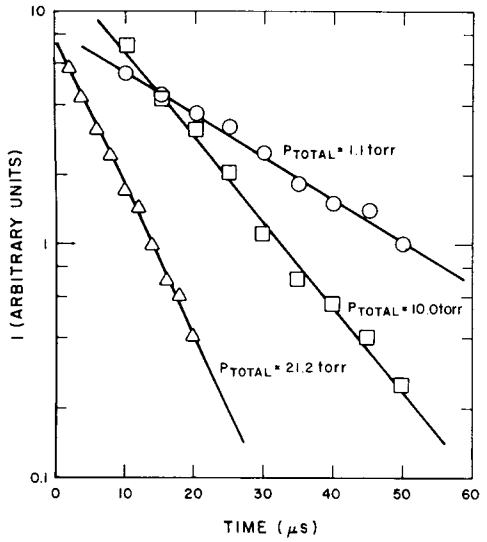
Fig. 1. NCl* fluorescence following the photolysis of ClN_3–Cl_2–Ar mixtures at 300 nm ($X_{ClN_3} \lesssim 0.003$, $X_{Cl_2} \approx 0.018$): (a) shot 1, P_{total} = 1.1 Torr, 5 mV = 4.0 photoelectrons μs^{-1}; (b) shot 2, P_{total} = 1.1 Torr, 5 mV = 4.0 photoelectrons μs^{-1}; (c) shot 1, P_{total} = 5.2 Torr, 50 mV = 43.1 photoelectrons s^{-1}.

$$\frac{d[NCl^*]}{dt} = -k_1[Q][NCl^*] - \tau_{rad}^{-1}[NCl^*] \quad (1)$$

where Q represents a quencher of the electronic excitation (Cl_2, ClN_3 or argon). Under pseudo-first-order conditions ($[Q] \gg [NCl^*]$) eqn. (1) can be solved to give

$$\ln\left(\frac{[NCl^*]}{[NCl^*]_0}\right) = -(\tau_{rad}^{-1} + k_1[Q])t \quad (2)$$

Figure 2 shows semilogarithmic plots of the decay of NCl* emission as a function of time at several different total pressures. The slopes of these lines represent the quantity $K_I = \tau_{rad}^{-1} + k_1[Q]$, so that k_1 is obtained by taking the slope of plots of K_I *versus* [Q] as shown in Fig. 3. The total quenching rate constant for the gas mixture is $(5.2 \pm 0.2) \times 10^3$ $Torr^{-1}$ s^{-1}, where the uncertainty given is one standard deviation in the least-squares fit to the slope. Assuming that the identity of the quenching species is Cl_2 (see later)



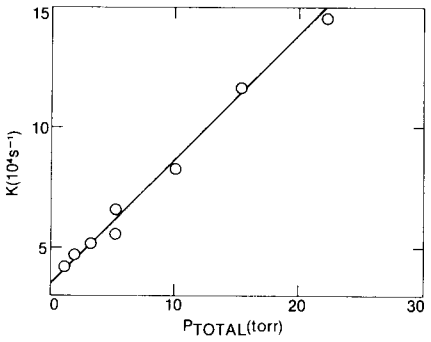


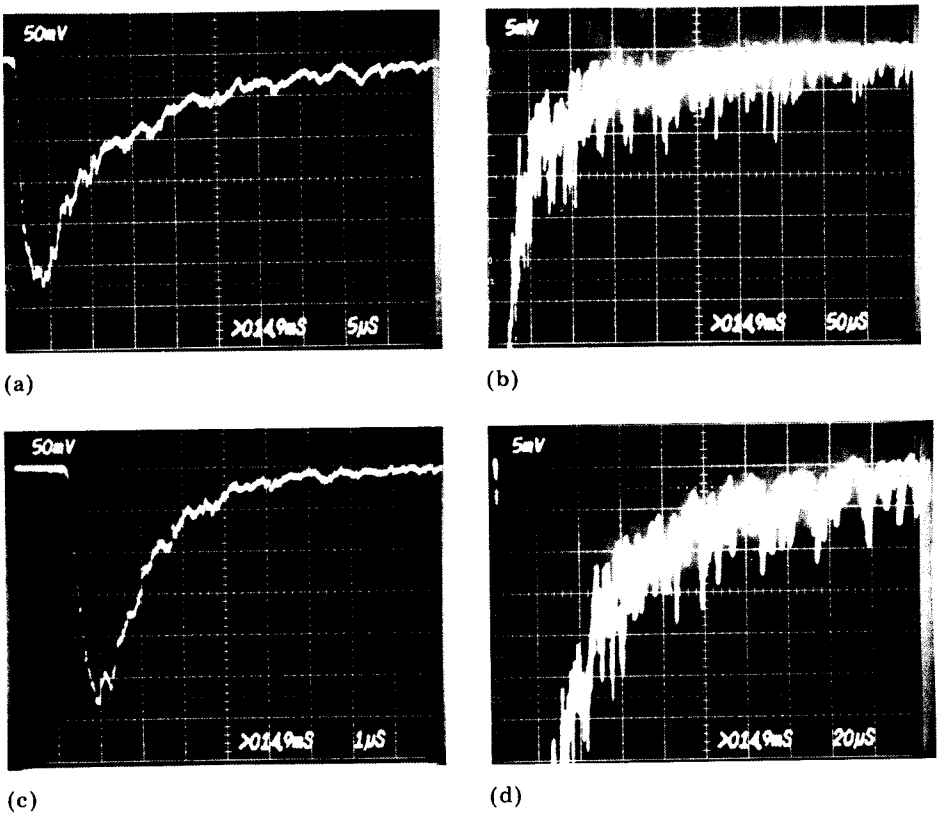
Fig. 2. NCl* fluorescence decay at several different pressures following the photolysis of ClN_3–Cl_2–Ar mixtures at 300 nm ($X_{ClN_3} \lesssim 0.003$, $X_{Cl_2} \approx 0.018$).

Fig. 3. NCl* fluorescence decay rates as a function of the total pressure from the photolysis of ClN_3–Cl_2–Ar mixtures at 300 nm ($X_{ClN_3} \lesssim 0.003$, $X_{Cl_2} \approx 0.018$).

and that the conversion of Cl_2 to ClN_3 is small, *i.e.* $[Cl_2] \gg [ClN_3]$, we obtain a quenching rate constant of 8.7×10^{-12} cm^3 molecule^{-1} s^{-1}.

The reciprocal of the intercept from Fig. 3 gives the radiative lifetime of the electronic state of NCl observed. The value is 29 ± 2 μs, where again the uncertainty given is one standard deviation in the least-squares fit.

The experiments at 272 nm showed a very definite bi-exponential decay of fluorescence (Fig. 4), which had not been obvious in the 300 nm experiments, with very different kinetics for each of the two decay components. The two decays were so widely separated temporally that two different oscilloscope shots with sweep speeds an order of magnitude apart had to be taken at each photolysis gas pressure. Figures 5 and 6 show typical decay plots for the two components, and Fig. 7 shows the plot of decay rates *versus* total pressure for both the fast and the slow components. The lifetimes of the two states differ by an order of magnitude, and the quenching rate constant of the slower state is 1.5 orders of magnitude slower. The lifetime of the more rapidly decaying state is 24 ± 8 μs in accord with the lifetime of the state produced in the 300 nm photolysis studies. Again, if we assume that the major quenching species is Cl_2 the data for the rapidly decaying state imply a quenching rate constant of 6.3×10^{-12} cm^3 molecule^{-1} s^{-1} in fair agreement with the results at 300 nm. An average of the results for the two sets of photolysis runs gives a rate constant of $(7.5 \pm 2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for quenching the rapidly decaying state by Cl_2.



(a) (b)

(c) (d)

Fig. 4. NCl* fluorescence following the photolysis of ClN_3–Cl_2–Ar mixtures at 272 nm ($X_{ClN_3} \approx 0.001$, $X_{Cl_2} \approx 0.078$): (a) pressure, 2.53 Torr; 50 mV = 40 photoelectrons μs^{-1}; (b) pressure, 2.53 Torr, 5 mV = 4.0 photoelectrons μs^{-1}; (c) pressure, 38.9 Torr; 50 mV = 503 photoelectrons μs^{-1}; (d) pressure, 38.9 Torr; 5 mV = 4.0 photoelectrons μs^{-1}.

The slowly decaying state has a lifetime of 250 ± 40 μs and a quenching rate constant of 1.5×10^{-13} cm^3 molecule^{-1} s^{-1} if it is assumed as before that Cl_2 is the dominant quenching species.

The preceding kinetic analysis contained the assumption that ClN* was not quenched by the argon bath gas or the ClN_3. The consistency in quenching rate constants from two sets of data in which the Cl_2 mole fractions differed by a factor of 4 indicates that Cl_2 was indeed the major quenching species. Some minor quenching by the argon or by ClN_3 could be responsible for the 30% difference between the two sets of data on the quenching of the fast component.

4. Discussion

Throughout the experimental analysis we assumed that the emissions we observed were from an electronically excited state of ClN produced

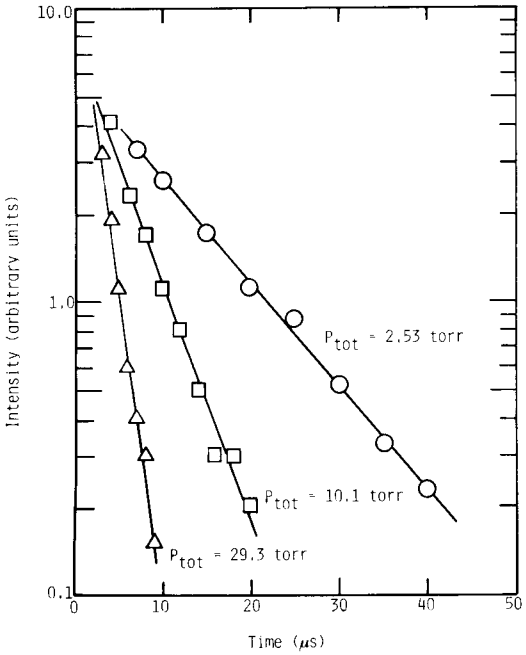


Fig. 5. Decay of the fast fluorescence component from 272 nm photolysis of ClN_3–Cl_2–Ar mixtures at several different total pressures ($X_{ClN_3} \approx 0.001$, $X_{Cl_2} \approx 0.078$).

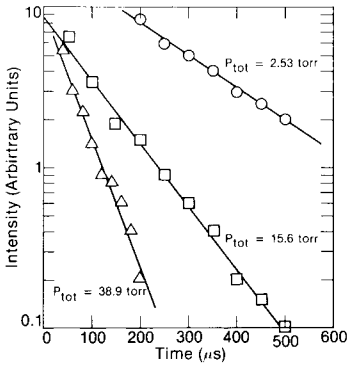


Fig. 6. Decay of the slow fluorescence component from 272 nm photolysis of ClN_3–Cl_2–Ar mixtures at several different total pressures ($X_{ClN_3} \approx 0.001$, $X_{Cl_2} \approx 0.078$).

directly in the photolysis. However, since we did not positively identify the observed emission as being that of ClN* we should consider possible alternative sources of emission. After showing that the logical candidate for the observed emission is ClN*, we speculate on the emitting state of ClN.

4.1. Sources of electronic excitation in ClN_3 photolysis

We can think of four possible alternatives to explain the observed emission in addition to direct formation of ClN* in the photolysis. It is possible that the emission is from ClN* but that ClN* is formed chemically through one of two alternative pathways:

$$ClN_3 + h\nu \rightarrow Cl + N_3 \quad (3)$$

$$Cl_2 + h\nu \rightarrow 2Cl \quad (4)$$

$$Cl + N_3 \rightarrow ClN^* + N_2 \quad (5)$$

or

$$Cl_2 + h\nu \rightarrow 2Cl \quad (4)$$

$$Cl + ClN_3 \rightarrow Cl_2 + N_3 \quad (6)$$

$$Cl + N_3 \rightarrow NCl^* + N_2 \quad (5)$$

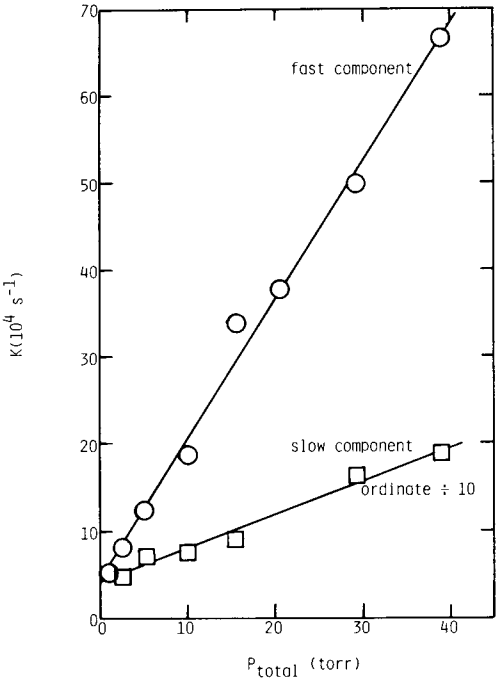


Fig. 7. Decay rates of fast and slow fluorescence components from 272 nm photolysis of ClN_3–Cl_2–Ar mixtures as a function of the total pressure ($X_{ClN_3} \approx 0.001$, $X_{Cl_2} \approx 0.078$).

In each case, if the removal of ClN* by radiation and quenching is rapid with respect to chlorine atom removal, chlorine atom removal rates will govern the characteristic decay time constant of the system. If ClN* removal is slower than chlorine atom removal, then the temporal behavior of the system will be characteristic of ClN*. The major removal process for chlorine atoms is reaction (6) which has a known rate constant of 3.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1} [49]. Given that the ClN_3 number densities are of the order of 10^{14} molecules cm^{-3} or less, the minimum time constant of the system will be of the order of milliseconds if reaction (5) determines the formation of NCl*. However, the observed system time constants are much shorter, being of the order of 10 - 200 μs, thus indicating that reactions (3) - (5) or (4) - (6) are unlikely pathways for ClN* production.

Another possible explanation for the emission is simply the formation of chlorine atoms in the photolysis, and then emission from Cl_2* formed in the recombination of chlorine atoms:

$$Cl + Cl + M \rightarrow Cl_2^* + M \qquad (7)$$

However, the removal of chlorine atoms by recombination will be much slower than their removal by ClN_3, so that here again time constants of the order of milliseconds would be expected. As additional confirmation that the emission arose from sources other than Cl_2 photolysis, some photolysis

experiments were done on mixtures of Cl_2 in argon which had not been passed through the NaN_3 column. These experiments showed much less emission intensity than the ClN_3 photolysis experiments (*i.e.* more than an order of magnitude less at low pressures) even under conditions of similar Cl_2 number densities and total pressures. In addition the observed temporal behavior was different.

The last possible source of emission comes from the sequence

$$ClN_3 + h\nu \rightarrow NCl^* + N_2 \quad (8)$$

$$NCl^* + Cl_2 \rightarrow Cl_2^* + NCl \quad (9)$$

$$Cl_2^* \rightarrow Cl_2 + h\nu' \quad (10)$$

This sequence of reactions will give an emission intensity whose temporal behavior will be determined by the difference between two exponential decay rates [3], one characteristic of the decay of ClN* and the other characteristic of the decay of Cl_2*. The observed fluorescence will in principle show a rise to some peak value with a subsequent decay which at long times will have a decay time equal to the decay time of the slower of the two exponentials. Our kinetic observations show essentially prompt emission with an emission peak coincident with the shutting off of the photolysis laser. This is consistent with prompt emission from an excited state formed directly in the photolysis. In order to see behavior from a kinetic scheme such as that given in reactions (8) - (10), the faster exponential, which determines the time the fluorescence waveform takes to reach peak intensity, would have to have a time constant of about 200 ns. The most short-lived state of Cl_2 which is accessible to excitation by known levels of ClN* is the $B\,^3\Pi_{0_u^+}$ state which has a radiative lifetime of about 300 μs [50]. The rather strongly forbidden nature of the known transitions in ClN* also precludes the possibility of a state with such a short lifetime. However, for the fast time constant to be determined by electronic quenching by Cl_2 the quenching rate constant must be 10 times the gas kinetic rate constant given that Cl_2 number densities are of the order of 10^{15} molecules cm^{-3}.

As additional confirmation that the emission was not dependent on the presence of molecular chlorine in the gas mixture, several photolyses were done at 272 nm in essentially pure ClN_3 which had been prepared by a method which precluded the presence of Cl_2 in the gas mixture. It was not possible to extract quantitative data from these runs, but the qualitative trends of the time-resolved fluorescence mirrored the observations of the ClN_3–Cl_2–Ar photolyses at the same wavelength, *i.e.* a bi-exponential decay with widely separated decay rates.

The photolytic dissociation of ClN_3 to produce ground state ClN and electronically excited N_2 was not possible energetically in the present experiments.

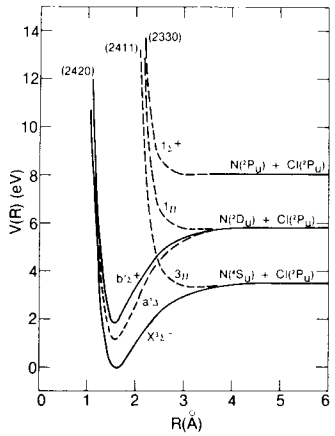


Fig. 8. Potential curves for ClN. Morse potentials with D_e values of 3.46 and 3.98 eV, r_e values of 1.61 and 1.56 Å and ω_e values of 827 and 935.6 cm^{-1} are drawn for the $X\ ^3\Sigma^-$ and $b\ ^1\Sigma^+$ states respectively. The estimated Morse parameters for the $a\ ^1\Delta$ state are D_e = 4.69 eV, r_e = 1.58 Å and ω_e = 1000 cm^{-1}. The remaining three potential curves are Lennard-Jones potentials with $C_6 = 2.21 \times 10^{-58}$ erg cm^6 as calculated from the Slater–Kirkwood formula using the method of Slater orbitals [51] to calculate the polarizability of nitrogen and chlorine, and with σ = 2.9 Å as calculated according to the rule of thumb given by Bernstein and Muckerman [52].

4.2. Electronic states of ClN

Figure 8 shows schematically the states of the ClN molecule. The only known states are the $X\ ^3\Sigma^-$, $a\ ^1\Delta$ and $b\ ^1\Sigma^+$. Since ClN is isoelectronic with O_2 it might be possible that the $^1\Sigma^+$ state which has the 2330 molecular orbital configuration ($\sigma\pi\pi^*\sigma^*$) [53] might also be bound, although probably weakly, and also probably strongly predissociated by the $^3\Pi$ and $^1\Pi$ states, which, because of their 2411 molecular orbital configuration, are expected to be repulsive like the similar states in O_2 [54]. Because the ground state of ClN_3 is a singlet, the only spin-allowed products from the photolysis at these wavelengths will be singlet states of NCl and singlet ground state nitrogen. The singlet NCl states are the $a\ ^1\Delta$, $b\ ^1\Sigma^+$ and perhaps the higher $^1\Sigma^+$ state, but only if that state is bound by at least 1.3 eV. The $^1\Delta$ state has been observed only recently in emission at 1080 nm [55] while the $b\ ^1\Sigma^+$ state has been observed in the laboratory for many years in emission on the $b\ ^1\Sigma^+ – X\ ^3\Sigma^-$ transition centered around 665 nm [34, 36, 39, 41, 42].

Had we seen emission from only one state, we would have been confident in assigning the emission as coming from the $b\ ^1\Sigma^+$ state. That we see emission from two states with substantially different characteristics means that we can only speculate on the identity of the two states. The $b\ ^1\Sigma^+$ states of NH [56] and of NF [57] have lifetimes of the order of 10 ms, and we had anticipated that ClN would have a similar radiative lifetime. However, Miller and Andrews [41] have observed time-resolved fluorescence from the BrN $A\ ^1\Sigma^+$ state in a low temperature inert matrix and have obtained a radiative lifetime for that state of 20 - 40 μs. It is not clear by how much, if

at all, the presence of the matrix shortened the observed lifetime of BrN*. Their data further indicated that the lifetime of ClN b $^1\Sigma^+$ was most probably somewhat longer than that of BrN A $^1\Sigma^+$. The radiative lifetime of ClN b $^1\Sigma^+$ should be bounded by the lifetimes of the $^1\Sigma^+$ states of NBr and NF because of the increased strength of spin–orbit coupling as the halogen atom gets heavier. Thus, we tentatively assign the state with the 250 μs lifetime to be the $^1\Sigma^+$ state of ClN.

5. Summarizing remarks

We have shown that the photolysis of ClN_3 in the UV produces two electronically excited fragments which are probably two states of electronically excited NCl. These two states have radiative lifetimes and rate constants for removal by Cl_2 which differ by an order of magnitude. We have tentatively assigned the longer-lived less easily quenched state as NCl (b $^1\Sigma^+$). The more rapidly decaying state could be higher vibrational levels of ClN (b $^1\Sigma^+$) which have a shortened lifetime due to predissociation caused by the $^3\Pi$ state or perhaps a higher-lying $^1\Sigma^+$ state. The more rapid relaxation of this state could be collision-induced predissociation or upward vibrational transfer into a predissociating level as well as electronic quenching. These speculations can only be confirmed or disproved by making spectrally resolved observations.

Acknowledgment

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