averaged reference peak (curve 1 in Figure 5a) has a full-width at half-maximum of 3.7 ps. Autocorrelation measurements of the DFDL pulses yield a much shorter pulsewidth of ca. 350 fs.²¹ Hence the measured shape of the reference pulse is dominated by the instrument function of our apparatus. Its width is determined by the temporal resolution of the streak camera and the uncertaincy in the determination of the center of the reference pulse in each streak.

The measured temporal profile of the fluorescence F(t) is the convolution of a molecular response function R(t) with the temporal profile of the excitation pulse P(t) and an instrument function Q(t):

$$F(t) = \int_{-\infty}^{+\infty} dt' R(t-t') S(t'-t_0)$$
(2)

$$S(t) = \int_{-\infty}^{+\infty} \mathrm{d}t' \, Q(t-t') \, P(t') \tag{3}$$

The response function for the rise and decay of the tautomer fluorescence is

$$R(t) = A(\exp(-t/\tau_{\rm D}) - \exp(-t/\tau_{\rm R})); \quad t > 0$$

= 0; $t < 0$ (4)

The temporal profile of the reference pulse is also described by 2 and 3, setting $R(t) = \delta(t)$. This suggests that we may identify S(t) with the measured pulse shape of the reference pulse. We performed several numerical simulations and a least-squares fit to the experimental temporal profile of the tautomer fluorescence using the experimentally determined S(t). Figure 5b shows a few simulated curves for various rise times $\tau_{\rm R}$. The decay time $\tau_{\rm D}$ was fixed to 540 ps, the fast decay component mentioned above. The least-squares fit to the experimental data yielded $\tau_{\rm R} = 2.7$ \pm 0.2 ps. In this fit the rise time $\tau_{\rm R}$, the amplitude A, the time origin τ_0 , and a constant background were simultaneously optimized. The decay time $\tau_{\rm D}$ was kept fixed since the decay portion of the streak is too short to allow a meaningful fit. However, variation of $\tau_{\rm D}$ in the range 540 ps to 8 ns affected the calculated $\tau_{\rm R}$ only by ±0.1 ps. The simulated curve corresponding to the best fit is superimposed as a dotted line on the experimental curve in Figure 5a. It is also shown as a dotted line in Figure 5b in comparison to other simulated fluorescence rise curves.

The value of 2.7 ps for the deconvoluted rise time is comparable to the experimental time resolution of 3.7 ps. In the preceding experiment we performed essentially the same measurement with excitation pulses of 10-ps duration. In this case the simulated fluorescence time profile with $\tau_R = 5$ ps could not be distinguished from the simulation with $\tau_R = 0.1$ ps, and both simulations could be made to coincide almost perfectly with the experimental curve through a small shift of the time origin. From this observation we conclude that deconvoluted rise times smaller than the time resolution of the experiment (i.e. the width of the function S(t)in eq 3) must be interpreted with caution. The simulated curves in Figure 5b show, however, that in the present experiment a rise time of 2.7 ps can be clearly distinguished from the case of an instantaneous rise, i.e. the instrument-limited rise (approximated by $\tau_{\rm R} = 0.1$ ps).

The data analysis presented above is valid for a streak camera which has the same transit time for all wavelength components of the fluorescence. If this is not the case, the rise time measurement of a spectrally broad emission will yield a slower apparent rise time. To estimate the contribution of this effect we repeated the experiment with the dye coumarine 6, which has a fluorescence spectrum similar to that of 3-HF. The apparent rise time of this fluorescence, which is expected to rise instantaneously, was found to be 2.5 ps. This is not significantly shorter than the apparent rise time observed for 3-HF. Hence we must conclude that the true rise time of the tautomer fluorescence of 3-HF is faster than the time resolution of our apparatus, which is approximately 1 ps. This leads to an estimate of $k_{AB} \ge 10^{12} \text{ s}^{-1}$ for the rate constant of ESIPT in 3-HF.

This rise time must be compared to the rise time measured by McMorrow, Dzugan, and Aartsma (MDA) in several alkanes.¹² They find a rise time of 8 ps at room temperature which increases to ca. 40 ps at 77 K. Such an increase of the rise time with decreasing temperature would indicate an effective barrier to ESIPT and would predict even longer rise times for the low temperatures in argon matrices. We have reasons to question the results of MDA. They use a Kerr-shutter method with light pulses for excitation and gating of 33-ps duration. This corresponds to a time resolution of 46 ps when Gaussian pulse shapes are assumed. Hence, in view of our own experience with deconvolution and the similar noise level in our and their data, a deconvoluted rise time of less than 40 ps should be interpreted very cautiously.

In summary it appears that 3-HF in the condensed phase is no exception to the rule of exothermic excited-state intramolecular proton transfer: that the reaction has no intrinsic energy barrier and occurs on the time scale of vibrational relaxation in the excited state.

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Photolysis of Nitrogen Trichloride

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Spectra and time profiles of the emission resulting from pulsed irradiation of NCl_3 at 248 and 308 nm were collected and analyzed. Two distinct spectral features were observed, one a long series of bands separated by 320 ± 30 cm⁻¹, the second an unresolved emission underlying the bands. The two features exhibit different time behavior and lifetimes in the limit of zero pressure. The photochemistry is interpreted via a model which involves the interaction of three electronic states of NCl₃.

Introduction

The halogen amines are in general thermodynamically unstable with the exception of NF_3 . The explosive nature of the spontaneous decomposition is well-known and has had an inhibiting effect on the scientific research of these interesting compounds.^{1,2} NCl_3 has been studied more than most of the other members of the

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Figure 1. Diagram of the NCl₃ generator.

group. The investigations have been primarily dedicated to extracting kinetic information from the gas-phase decomposition and from reactions of NCl₃ with various atomic species.³⁻⁷ However, very little detail is available from these kinetic studies and the dissociation mechanism is not understood. Clearly, information regarding the electronic states and the dissociation channels open to these states is a prerequisite for understanding the dynamics of such molecular processes. Therefore, we have performed laser photolysis experiments on gaseous NCl₃ in helium and collected spectra and time profiles of the resulting emissions. These experiments have yielded some very unexpected and previously unreported results from which we have been able to draw conclusions concerning the spectroscopy of NCl₃. These results and conclusions are presented in this paper.

Experimental Section

NCl₃ was easily synthesized by using a variation of the method reported by Clark and Clyne.⁶ A diagram of our NCl₃ generator is shown in Figure 1. Cl_2 diluted with helium was bubbled through an aqueous solution of ammonium sulfate in 1 M sulfuric acid. The product NCl₃ was swept out of the solution with helium and was condensed with the excess Cl_2 from the gas stream in a cold trap. The trap was allowed to warm up and any trapped Cl_2 vaporized quickly and was removed by a continuous stream of helium. NCl₃ vapor was carried in helium through Teflon tubing from the trap to the photolysis system.

To verify that we were indeed synthesizing NCl₃ and not any measurable amounts of HNCl₂ or H₂NCl, a mass spectrum and an IR spectrum of the gas stream were obtained. The mass spectrum agreed with that reported by Clark and Clyne for NCl₃.⁶ The IR spectrum of the gas stream showed no evidence of N-H vibrational stretching modes which would be in evidence for the mono- and dichloroamines. The only feature in the IR spectrum was the strong NCl₃ asymmetric stretch at 640 cm⁻¹ which has been previously reported.⁸ No other infrared active vibrations of NCl₃ were observed, but at the relatively low NCl₃ concentrations which existed in the gas stream, only strong features would be observable.

Safety precautions were taken due to the explosive nature of the condensed liquid. The generator was set up in a hood behind a polycarbonate shield and the glass trap was wrapped with metal screen. The hood shield was kept lowered whenever there was liquid NCl_3 in the trap. We did not experience any explosions, possibly because the pressure above the condensed NCl_3 was never



Figure 2. Spectra of the emission obtained following photolysis of NCl_3 : (A) photolysis at 248 nm; (B) photolysis at 248 nm, spectrum of the bands only; (C) photolysis at 308 nm. (1) and (2) are second-order reflections of the laser light.

allowed to drop below the ambient room pressure and because we produced no measurable amounts of the mono- and dichloroamines. There is some evidence that explosions are likely when NCl₃ evaporates in vacuo or when NH_2Cl and $NHCl_2$ are present.⁶

A small portion of the NCl₃/helium gas stream was admitted to a 75-cm photolysis cell through a Teflon needle valve and the remaining gas mixture was returned to the hood. The concentration of NCl₃ in the photolysis cell was calculated from measurements of the transmission of 220-nm light from a deuterium source through the cell and from the ϵ value, 2000 L mol⁻¹ cm⁻¹, reported by Clark and Clyne for this wavelength.⁶ Typical conditions in the photolysis cell were a pumping speed of 550 cm s⁻¹ at 0.2 Torr total pressure.

An excimer laser operating at 2 Hz irradiated the NCl₃/He gas mixture along the axis of the photolysis cell. The resulting emission was collected at right angles to the axis of the cell with a 0.25-m monochromator and a cooled GaAs photomultiplier tube. The spectrum of the emission was obtained by scanning the monochromator and sending the amplified signal from the photomultiplier tube to a gated integrator, gated to collect data from 1 ns to 15 μ s following the laser flash, digitizing electronics, and an IBM-PC where the integrated intensity as a function of emission wavelength was then stored. The spectral slit width of the spectrometer was about 2.0 nm. Time profiles of the emission at a single wavelength were obtained by sending the amplified photomultiplier signal to a Nicolet 1270 data aquisition and analysis system for collection of emission intensity vs. time data. The Nicolet was interfaced to an IBM-PC and the time data were transferred to the computer for disk storage and later analysis.

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TABLE I: Wavelengths (nm) of the Bands Appearing in the Spectra of Figure 2^a

			-
Figure 2C	Figure 2B	Figure 2A	
501			
509			
517			
525			
533			
542	541		
554	549		
562	561	560	
573	570	568	
585	580	581	
596	592	592	
607	604	603	
	616	615	
633	630	628	
646	644	639	
660	655	654	
675	670	668	
690	685	684	
704	701	699	
722	718	716	
	735	734	
	751	752	
		768	

^a The uncertainty in the position of the band maxima is ± 3 nm. This large error is due to the manner in which the wavelengths are determined by measuring their position with respect to the positions of second- and third-order reflections of the laser light.



Figure 3. Variation of the emission intensity collected at 520 nm with the incident laser fluence of the KrF laser. The line shown is a linear least-squares fit to the data.

Results

When the gaseous NCl₃ was irradiated with either 248-nm light (KrF) or 308-nm light (XeCl) from the excimer laser, a paleyellow glow was observed along the length of the photolysis cell. The spectra obtained of the emission are shown in Figure 2. The spectrum of the emission for the 248-nm excitation consists primarily of unresolved emission from 476 to 744 nm with a maximum at 546 nm and with distinct bands appearing on the long wavelength side, (Figure 2A). Several times, however, we obtained the spectrum shown in Figure 2B following photolysis at 248 nm in which the unresolved emission is absent leaving only the bands. The emission spectrum resulting from the 308-nm excitation also shows a band system overlying some unresolved emission (Figure 2C). The band positions and the band separation, $320 \pm 30 \text{ cm}^{-1}$, are the same in all three spectra. Table I lists the wavelengths of the band maxima observed in all three spectra. We measured the dependence of the emission intensity on the laser fluence at 520 and 654 nm. The graph in Figure 3 shows a plot of the data obtained at 520 nm. At both wavelengths a linear relationship was found to exist, which indicates that a one-photon process was responsible for the observed emission. No other emission was observed between 200 and 900 nm.

We tried unsuccessfully to control which of the two emission spectra would be obtained following the 248-nm photolysis. We know that whether we obtained the spectrum in Figure 2A or the spectrum in Figure 2B was not a function of (1) differences in the NCl₃ synthesis process, (i.e., the presence vs. the absence of an impurity does not seem to be involved); (2) different pressure



Figure 4. Time profiles of the emission following photolysis of NCl₃ at 248 nm: (A) emission collected at $\lambda = 500$ nm; (B) emission collected at $\lambda = 647$ nm. The smooth lines are the results of curve fitting routines.

conditions in the photolysis cell; (3) different electronic data collection parameters; (4) an artifact of the photomultiplier tube; or (5) emission from the walls of the photolysis cell. Wall reactions can be eliminated as a possible source of either of the spectra by considering the time constraints involved. The radial velocity was too slow to allow the species present in the cell to get to the wall in the 15 μ s following the laser pulse during which the emission was collected with the gated integrator.

Time profiles of the emission collected following excitation at 248 nm were analyzed. The observed time decays of the bands were distinctly longer than the time decay observed for the unresolved emission in the emission spectrum of Figure 2A. Examples of the time profiles are shown in Figure 4. The length of the observed decay for the bands increased as the wavelength of the band increased. When profiles were collected at wavelengths between the bands, distinctly double-exponential decays were observed which consisted of a short-lived decay like that of Figure 4A and a long-lived decay like that of Figure 4B. All of the time profiles collected exhibited the same rise time which was longer than the rise due to the response of the data collection electronics. The 1/e lifetimes were obtained with curve-fitting routines provided in RS/1 on a VAX780 computer. For NCl₃ concentrations of 5×10^{14} molecules/cm³ and a total pressure of 0.2 Torr, the observed 1/e rise time was about 1.0 μ s and the observed 1/e decay times were 34 μ s at 657 nm and 2.8 μ s at 500 nm. When the decay rates were plotted vs. the total pressure at fixed $P(NCl_3)$: P(He), the extrapolated decay time at $P_{\text{total}} = 0$ was 48 μ s for data collected at 657 nm and 4 μ s for data collected at 500 nm. The rise time showed no [NCl₃] or total pressure dependence for P_{total} = 0.1 - 0.4 Torr.

The time profiles of the bands following photolysis at 308 nm exhibited a rise time that was as fast as the rise time of the electronics. In addition, the decay times were much shorter than the decay times of the bands resulting from the 248-nm photolysis.

Attempts were made to photolyze NCl_3 using other excitation energies from the excimer laser. With 193-nm light (ArF), no visible emission was observed. However, with 222-nm light (KrCl), some very weak emission was observed, but the signal to noise ratio was too low to enable us to characterize the emission. (The low emission intensity was probably in part due to the fact that the laser energy at 220 nm is about an order of magnitude lower than it is at 248 nm.)

Discussion

The spectra of the emission following photolysis at 248 nm are shown in Figure 2 A and B. Even though we were unable to characterize the conditions under which the spectrum in Figure 2B was obtained, the fact that we obtained it at all gives us

important information. This spectrum is almost certainly a single vibrational progression from a weakly bound excited state to a strongly bound and very harmonic ground state. The band separation does not decrease from the high- to the low-energy end of the approximately 6200-cm⁻¹ energy range of the spectrum. This implies that the lower state has a relatively deep potential well, with little anharmonicity observed in the region where these transitions are occurring. The same banded emission appears as one component of the Figure 2A spectrum since the bands that appear on the long wavelength side of the unresolved emission are in the same position (see Table I) and have the same separation as the bands in the Figure 2B spectrum. The short wavelength bands are apparently washed out by the unresolved emission which is the second component of and primarily characterizes the Figure 2A spectrum. When we also consider the two different time profiles obtained, both of which have the same rise time but different decay times, we conclude that photolysis at 248 nm produces two emitting species. The emitters are apparently secondary photoproducts formed from the same precursor that is directly produced by the absorption of 248-nm light. The rise time is then the lifetime of this precursor.

The emission spectrum obtained after photolysis of NCl₃ at 308 nm looks similar to the Figure 2B spectrum, but the maximum is shifted to shorter wavelengths and may have some underlying continuum. The bands overlap with bands in Figure 2B and the band separation is the same, indicating that the lower state of the transition is the same as that for the Figure 2B spectrum. But since the decay times were much shorter than those observed for the 248-nm photolysis bands, the upper state is not the same. The time profiles obtained for the 308-nm photolysis did not show obvious evidence of more than one emitter nor was there any measurable rise time for this emission in contrast with the emission following the 248-nm photolysis. Therefore, the initial state pumped by the absorption of the 308-nm light is different than the initial state pumped by the 248-nm light. We believe that the observed emission following the 308-nm photolysis is mainly from a single emitter that is produced directly in an excited state by the 308-nm laser pulse.

In order to identify the sources of the observed emission, we must consider the species that are likely to be present in the cell following the laser pulse. These are Cl_2 , NCl, NCl₂, and NCl₃. Emission from NCl₃ systems that has been previously reported is from the gas-phase self-decomposition flame.⁷ The bright orange flame spontaneously appears when NCl₃ encounters a pressure drop under conditions which allow the reactive intermediates produced to stay in the low-pressure region long enough to sustain the chain reaction. We have produced the self-decomposition flame in our system by using a relatively slow pumping speed (50 cm s⁻¹) and collected the spectrum of the emission. This spectrum (Figure 5), which has been assigned to the $(B \rightarrow X)$ transition of Cl₂ after careful comparison of the spectrum with the Deslandres Table for Cl_2 ,⁹ is quite different from the banded spectra obtained from the photolysis of NCl₃ in the fast flow system. The average band separation is 248 ± 13 cm⁻¹¹, much smaller than the band separation observed in the photolysis emission spectra. In addition, the emission from the self-decomposition flame is shifted to longer wavelengths with respect to the photolysis emission. The lifetimes that we have obtained for the new band systems are also quite different from the values obtained by Clyne et al. of $83 \pm$ 5 μ s for vibrational levels 7 $\leq v' \leq$ 12 and 305 \pm 15 μ s for vibrational levels 5 = v' of the Cl₂ B(${}^{3}\tilde{\Pi}O_{u}^{+}$) state.^{10,11} Therefore, the banded emission that we observe is not from the $(B \rightarrow X)$ transition of Cl₂. NCl can also be eliminated as the source of the emission since its visible emission spectrum is known and does not resemble these spectra.¹²



Figure 5. Spectrum of the self-decomposition flame of NCl₃.

The remaining candidates are NCl₂ and NCl₃. Almost nothing is known about either of these molecules. Therefore, we examined photolysis and spectral information available for NH₃, a structurally related system. The photolysis of NH₃ at 193 nm produces NH_2 in the A state.¹³ Many ν_2 vibrational levels of the NH_2 A state are populated following the photolysis of NH₃ and, consequently, the emission spectrum consists of several overlapping vibrational progressions. The energy required to break the first NCl bond in NCl₃ is estimated to be very close to zero, so it is likely that some NCl₂ was produced after the absorption of the UV laser light. The unresolved nature of the short-lived emission is consistent with what would be observed following the population of many different vibrational levels in an excited state of NCl₂. The subsequent emission would be expected to be somewhat congested with overlapping lines which we may not be able to resolve with the 2.0-nm spectral slit width of our monochromator. In addition, the envelope of the nonresolved emission we observed is very similar to that of NH₂ collected with fairly low resolution (0.8 nm) by Xuan et. al. following the photolysis of NH_3 with the whole output of a hydrogen lamp.¹⁴ We believe that this evidence suggests that the nonresolved emission could be NCl₂ emission. On the other hand, the banded emission that we have observed following photolysis of NCl₃ at 248 and 308 nm consists of a single vibrational progression and so is inconsistent with what would be expected from NCl_2 .

The $(A \leftarrow X)$ absorption spectrum of NH₃ shows a vibrational progression in the ν_2' out-of-plane symmetric bending mode.¹⁵ The fact that this mode is active in the $(A \leftarrow X)$ transition is consistent with the large change in H-N-H angle between the X and the A states. (The ground state of NH_3 is pyramidal and the excited electronic states are planar.) No $(A \rightarrow X)$ emission has been observed for NH3 but the corresponding transition has been observed in ND₃.¹⁶ This weak emission also consists of a progression in the out-of-plane bending mode (superimposed on either 0, 1, or 2 quanta of ν_1'' , the in-plane symmetric stretch). The corresponding $\nu_2^{\prime\prime}$ vibrational mode frequency in NCl₃ is 347 cm⁻¹ (in CCl_4 solution).⁸ The band separation that we observe, 320 ± 30

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Figure 6. A model of the photochemistry of NCl_3 following photolysis at 248 and at 308 nm.

cm⁻¹, agrees with this value within our error limits. A strongly harmonic potential also exists along the ν_2 coordinate in NH₃. On the basis of these arguments, we assign the banded spectra to transitions from excited states of NCl₃ to the ground state with long progressions in ν_2'' .

Based on the emission spectra obtained and the corresponding time profiles of the emission, we propose the model shown diagramatically in Figure 6. Following the 248-nm laser pulse, the NCl₃ is initially excited to a state (labeled C in Figure 6) which has a lifetime that is equal to the rise time of the emission time profiles (Figure 4) of about 1 μ s. From state C, two exit channels exist. One channel is to a lower excited state (state A), followed by emission to the ground state of NCl₃, producing the banded spectrum. State A, then, has a lifetime given by the decay time of the banded emission. (However, the fact that the lifetime of the bands appeared to increase as the wavelength of the band increased is not explained by this model.) The other channel is dissociation to NCl₂, some of which is produced in different vibrational levels of an excited state. Emission from this state of NCl₂, which has a lifetime of a few microseconds, produces the unresolved emission spectrum. When NCl₃ is irradiated with

308-nm laser light, there is apparently insufficient energy to populate state C since the subsequent emission demonstrates no detectable rise time. The decay time is also different from that observed for the banded emission following the 248-nm photolysis, indicating the emitting state (state B) is not the same. State B must be at a higher energy than state A since the banded emission is shifted to shorter wavelengths compared to the banded emission originating from state A. However, since the band separation observed is the same for both photolysis energies, the banded emission for both must be ending in the same lower state.

The proposed $(C \rightarrow A)$ transition following photolysis at 248 nm is likely to be radiative in view of the observed 1- μ s lifetime of state C and the pressures at which we carried out these experiments. During 1 μ s, at a total pressure of 0.2 Torr, there would be 1-2 collisions. In our system, the collisions must not have been effective in quenching state C because we saw no pressure dependence on the rise times of the emission observed from state A. The fact that we did not observe any emission that could be assigned to the $(C \rightarrow A)$ transition, even though the energy difference appears to lie in the visible region of the spectrum, is probably because more than a single step is involved in going from state C to state A. This would place the emission in the infrared.

The coupling of the C state of NCl_3 with the excited state of the other emitter was also not induced by collisions, since again, the rise time of the NCl_2 emission showed no pressure dependence. However, this interaction could take place without collisions or radiation if a dissociative state of NCl_3 exists at about the same energy as state C.

In the future we hope to obtain excitation spectra of NCl_3 using a pulsed tunable UV source. This will enable us to study the excited states of NCl_3 and the photolysis channels open to them in more detail. If there is a large amount of ground-state NCl_2 produced in our experiments, we should be able to detect it through optical means. Finally, visible laser-induced fluorescence studies of NCl_3 will allow us to probe the low-lying excited states which we believe are the sources of the banded emission spectra that we have observed.

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Triplet-Triplet Energy Transfer in a Copper(II) Porphyrin-Free-Base Porphyrin Dimer

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Energy transfer from the excited triplet (trip-doublet and trip-quartet) state of copper porphyrin to the lowest excited triplet state of its free-base partner was detected by measurements of T-T transient absorption of a $-(CH_2)_3$ - covalently linked porphyrin dimer. The excited dimer with free base in the excited singlet is partly quenched by the copper counterpart. On the other hand, the excited dimer with copper porphyrin in the trip-multiplet state is dissipated not only by the fast electronic relaxation within the copper porphyrin but also by the intramolecular energy transfer to the free-base partner.

Introduction

Currently several groups are studying the energy transfers between two different porphyrin moieties which are covalently linked with a $-(CH_2)_n$ - chain.¹⁻⁶ In the zinc and free-base hybrid

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dimers, an energy transfer from the lowest excited singlet (S_1) state of zinc porphyrin to that of the free-base counterpart has been observed.^{2,3} A free-base dimer forms a hybrid dimer of free base and diacid in benzene containing an appropriate concentration

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