

# Energy Transfer from $N_2(\nu)$ to $CIN_3$ and a Kinetic Model for the Chain Decomposition of Chlorine Azide

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A number of experiments have been performed in an effort to better understand the photoinitiated chain decomposition of  $CIN_3$ . Discharge-flow methods were used to determine the rate of energy exchange between vibrationally excited  $N_2$  (a likely chain carrier) and  $CIN_3$ . The rate constant for energy transfer from  $N_2(\nu=1)$  to  $CIN_3$  was found to be  $(2.0 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  at 300 K. This process is thought to excite the  $\nu_2$  mode in  $CIN_3$  with the release of  $281 \text{ cm}^{-1}$  of excess energy. Experiments were also performed in which the decomposition of  $CIN_3$  was initiated by photolysis with a pulsed KrF laser at 249 nm, with subsequent observation of the time dependence of the densities of  $CIN_3$ , electronically excited  $NCl(a^1\Delta)$ , and vibrationally excited  $CIN_3(\nu_2)$ . A kinetic model for the  $CIN_3$  decomposition was assembled based on reactions with  $NCl(a^1\Delta)$  and  $N_2(\nu)$ .

## Introduction

Although azides ( $RN_3$ ) are well-known energetic species prone to explosive decomposition, the energy stored by these molecules has been used for many applications other than explosives. In particular, azides have recently been used as energetic precursors for the low-temperature deposition of thin films<sup>1,2</sup> and as energy storage agents for the pumping of new laser systems.<sup>3</sup> In our laboratory, chlorine azide ( $CIN_3$ ) has been used as a source of electronically excited  $NCl(a^1\Delta)$ , a metastable species which can collisionally excite iodine atoms to the  $5^2P_{1/2}$  state.<sup>4</sup> Under appropriate circumstances, a population inversion can be achieved among the  $5^2P_{1/2}$  and  $5^2P_{3/2}$  levels in this system and lasing is observed<sup>3</sup> at  $1.315 \mu\text{m}$ . The operation of the laser requires that the  $CIN_3$  initially present be removed since it is an efficient quencher of excited  $I^*(5^2P_{1/2})$ . This removal is thought to occur by chain decomposition processes.

It has been speculated<sup>5,6</sup> that the chain decomposition of azides is driven by energy transfer processes involving excited dissociation fragments, in particular vibrationally excited  $N_2$ . The vibrational frequency in  $N_2$  ( $2331 \text{ cm}^{-1}$ ) is near-resonant with the  $\nu_2$  vibration in azides, which typically is found in the range from 2000 to  $2150 \text{ cm}^{-1}$ . This vibration is an asymmetric stretch along the  $N_3$  chain and is well mapped onto the dissociation coordinate leading to the nitrene  $NR$  and  $N_2$ , such that sequential excitation by collisions with  $N_2(\nu>0)$  might well lead to dissociation. Benard and co-workers<sup>6</sup> have speculated that this mechanism is responsible for the chain decomposition of  $FN_3$  observed in high-temperature shock tube studies. Also, flowing streams of  $N_2(\nu)$  have been used to dissociate gas phase  $NCN_3$  for the deposition of  $C_3N_4$  thin films.<sup>2</sup> In the case of  $CIN_3$ , the  $\nu_2$  frequency is  $2050 \text{ cm}^{-1}$  and excitation of this vibration by collisions with  $N_2(\nu)$  is exothermic by  $281 \text{ cm}^{-1}$ . Since the binding energy of  $CIN_3(1A')$  along the coordinate leading to  $NCl(a^1\Delta) + N_2(X^1\Sigma_g^+)$  has been calculated<sup>7</sup> to be just  $5700 \text{ cm}^{-1}$ , sequential excitation of  $CIN_3$  by as few as three collisions with  $N_2(\nu)$  might dissociate the molecule. Further, since considerable energy is released when this dissociation occurs, it seems quite likely that  $N_2(\nu)$  would be regenerated to continue the chain.

Because of the weakness of the  $CIN-N_2$  bond,  $CIN_3$  can also be dissociated by collisions with species in low-energy excited electronic states. It has been shown,<sup>5</sup> for example, that  $CIN_3$  is dissociated by collisions with  $O_2(a^1\Delta_g)$  to produce  $N_2$  and  $NCl(a^1\Delta)$ . This process occurs with a room temperature rate constant near  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . Similarly, it has been suggested<sup>4,5</sup> that  $CIN_3$  can be dissociated by collisions with  $NCl(a^1\Delta)$  or with  $I^*(5^2P_{1/2})$ .  $I^*$  quenching by  $CIN_3$  has a rate constant<sup>4</sup>  $k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , and it is thought that this process also dissociates the azide to  $N_2$  and  $NCl(a^1\Delta)$ . In our previous work<sup>3</sup> on the  $CIN_3/NCl(a^1\Delta)/I^*$  laser system, a kinetic model was assembled which included  $CIN_3$  chain decomposition carried by  $N_2(\nu)$ ,  $NCl(a^1\Delta)$ , and  $I^*$ . Although the model was largely speculative (rate constants for energy exchange between  $N_2(\nu)$  and  $CIN_3$  were unknown, as was the time dependence of  $CIN_3$  in the system), it gave fair agreement with the  $NCl(a^1\Delta)$  time profile observed in the experiments and predicted laser threshold times within a factor of 2 of the observed values.

We have continued to explore these issues by using discharge-flow methods to determine the rate constant for energy transfer from  $N_2(\nu)$  to  $CIN_3$ , and by using pulsed laser photolysis methods to perform additional measurements of the decomposition of this azide. In the latter case, measurements of the time decay of  $CIN_3$  in the system were performed and vibrational excitation in the  $\nu_2$  mode of the azide was detected. Time profiles for  $CIN_3$ ,  $NCl(a^1\Delta)$ , and  $CIN_3(\nu_2)$  were measured for a variety of initial conditions. The data from both the discharge-flow and laser photolysis experiments were used to assemble a new kinetic model for the decomposition.

## Experimental Details

Gaseous  $CIN_3$  was synthesized by the passage of a stream of  $Cl_2$  diluted in He (5%  $Cl_2$ ) and saturated with  $H_2O$  over  $NaN_3$  suspended on glass wool. The azide generator was derived from a design developed by Schlie and co-workers and has been described elsewhere.<sup>8</sup> The efficiency with which  $Cl_2$  was converted to  $CIN_3$  in the reactor was greater than 90%, as determined by IR and UV spectra of the effluent. The principal impurity present is expected to be  $Cl_2$ ; in fact, no  $Cl_2$  was

detected in the UV spectra and the 90% conversion figure is a minimum determined from signal-to-noise considerations. Continuously flowing streams of  $\text{ClN}_3/\text{He}$  from this reactor were used in the several different experiments of this study.

Experiments involving measurements of the rates of energy transfer from  $\text{N}_2(\nu)$  were performed with a 1.0 m long, 3.8 cm internal diameter Pyrex discharge-flow reactor. Flows of  $\text{N}_2(\nu)$  were generated by passage of  $\text{N}_2/\text{He}$  mixtures (typically 10%  $\text{N}_2$ ) through a water-cooled 300 mA dc discharge positioned on a sidearm of the flow reactor. After exiting the discharge zone, the flow of excited gases was passed over a Ni mesh to remove atoms and electronically excited species.<sup>9</sup>  $\text{N}_2(\nu)$  was detected downstream of the discharge by admitting a small flow of  $\text{CO}_2$  to the flow via a sliding injector, such that the subsequent energy exchange produced vibrationally excited  $\text{CO}_2$  which was detected at an observation port downstream by its emission on the  $\nu_3$  band near  $4.3 \mu\text{m}$ . This emission was chopped at 343 Hz and detected with a cooled InSb detector equipped with a narrow band interference filter centered on the  $\text{CO}_2$  transition. The response of the detector was amplified by a lock-in amplifier (Stanford Research Systems) and displayed on a strip chart recorder. Flows of  $\text{ClN}_3/\text{He}$  (5%  $\text{ClN}_3$  as above) were admitted to the reactor via a second injector 10 cm downstream of the  $\text{CO}_2$  injector.

The flows of all gases admitted to the reactor were measured with calibrated mass flow meters (Tylan and MKS). The system was pumped by a  $1500 \text{ L min}^{-1}$  mechanical pump such that the flow velocity for the pressures of the experiments (typically near 0.7 Torr) was approximately  $1250 \text{ cm s}^{-1}$ . The pressure in the system was measured with a capacitance manometer.

Laser photodissociation experiments were performed by photolysis of the  $\text{ClN}_3/\text{He}$  mixtures with the output of a pulsed KrF excimer laser at 249 nm (Questek). The photolysis cell was a 2.54 cm diameter Pyrex tube equipped with quartz windows for transmission of the 249 nm laser beam and KCl windows for transmission of the IR probe beam used for detection of the  $\text{ClN}_3$  and for transmission of IR emissions from the gases in the cell. IR absorption was detected on the  $\nu_2$  band of  $\text{ClN}_3$  near  $2050 \text{ cm}^{-1}$  by using a source constructed from a heated wire and a detector comprised of a cooled InSb detector with a narrow band interference filter centered at this frequency. Calibrations of the absorption measurement were done repeatedly over the course of the experiments by comparison of IR absorptions with densities of  $\text{ClN}_3$  determined from measured UV absorptions and published UV absorption cross sections.<sup>10</sup> Emission from vibrationally excited  $\text{ClN}_3$  was observed using the same detector and filter combination, but with the IR source blocked. Emission from electronically excited  $\text{NCl}(\text{a}^1\Delta)$  at  $1.077 \mu\text{m}$  was detected by a cooled Ge detector (North Coast Optics) equipped with a narrow band filter centered at this wavelength and with a bandwidth (full width half-maximum) of 12 nm. The time profiles of emission and absorption signals were amplified and digitized with a LeCroy TR8828C signal processor.

## Results

**1. Quenching of  $\text{N}_2(\nu)$  by  $\text{ClN}_3$ .** Vibrationally excited  $\text{N}_2$  was generated using the dc discharge flow reactor described above, with detection by the admission of  $\text{CO}_2$  to the flow. The total density of  $\text{N}_2$  in the flow was typically set at  $2.3 \times 10^{15} \text{ cm}^{-3}$ . The density of the added  $\text{CO}_2$  was near  $1.0 \times 10^{14} \text{ cm}^{-3}$ . For the conditions of our experiments, the intensity of  $4.3 \mu\text{m}$  emission from vibrationally excited  $\text{CO}_2(\nu_3)$  should be proportional to the density of vibrationally excited  $\text{N}_2(\nu)$  in the system.

The energy exchange between  $\text{N}_2(\nu=1)$  and  $\text{CO}_2$  is nearly resonant (exothermic by  $18 \text{ cm}^{-1}$  for the forward process) and for sufficient densities of both species full equilibration would result. From the known values<sup>11</sup> of the rate constants for the forward and reverse reactions and the densities of  $\text{N}_2$  and  $\text{CO}_2$  in the system, the equilibrium should be established within 1.0 ms, comparable to the mixing time. The decay of the emission reflects the loss of energy from this equilibrium pool, largely by radiation from the excited  $\text{CO}_2$ . A steady-state treatment of the  $\text{CO}_2(\nu)$  density yields the following expression:

$$[\text{CO}_2(\nu)]_{\text{ss}} = k_e[\text{N}_2(\nu)][\text{CO}_2]/\{k_{-e}[\text{N}_2] + k_r\} \quad (1)$$

where  $k_e$  and  $k_{-e}$  are rate constants for the forward and reverse energy transfer reactions, respectively, and the rate of spontaneous emission ( $k_r$ ) for an isolated  $\text{CO}_2(\nu_3, \nu=1)$  molecule is  $417 \text{ s}^{-1}$  ( $\tau = 2.4 \text{ ms}$ ).<sup>12</sup> Hence  $[\text{CO}_2(\nu)]$  (and the intensity of its IR emission) should vary in proportion to  $[\text{N}_2(\nu)]$ . By using values of  $k_e$  and  $k_{-e}$  from the literature<sup>11</sup> and the densities of  $\text{N}_2$  and  $\text{CO}_2$  from the experiments, eq 1 yields the steady-state ratio  $[\text{CO}_2(\nu)]/[\text{N}_2(\nu)] = 0.039$ . Because of the relatively high density of  $\text{N}_2$  in the system, the large majority of the excitation resides in  $\text{N}_2(\nu)$ . Since only 0.039 of the vibrational excitation resides in  $\text{CO}_2$  at any time, the decay of the equilibrium pool of vibrationally excited species (observed by the  $\text{CO}_2(\nu)$  emission intensity) will reflect the  $\text{CO}_2(\nu)$  radiative rate ( $k_r$ ) multiplied by this factor. This treatment yields a decay rate of  $17 \text{ s}^{-1}$ . The decay rate observed in the present experiments was  $20 \text{ s}^{-1}$ , in good agreement with this predicted result. The small discrepancy may in fact indicate the contribution of some other loss mechanism such as wall quenching of  $\text{CO}_2(\nu)$ , for which the reported probability is 0.22 per collision for a variety of surfaces.<sup>13</sup>

Quenching experiments were performed by addition of  $\text{ClN}_3$  to the  $\text{N}_2(\nu)$  stream at a point 10 cm (8 ms) downstream of the  $\text{CO}_2$  injector. The  $\text{ClN}_3$  inlet was positioned 22.5 cm (18 ms) upstream of the observation port. The presence of  $\text{ClN}_3$  at densities up to  $2.5 \times 10^{14} \text{ cm}^{-3}$  (the maximum from our azide generator) resulted in substantial reductions in the intensity of the  $\text{CO}_2$  emission, indicating quenching of the  $\text{N}_2(\nu)$  since the large majority of the excitation is resident in this species. Considering only the vibrational energy exchange between  $\text{ClN}_3$  and  $\text{N}_2(\nu)$ , the rate equation for  $\text{N}_2(\nu)$  is given by

$$d[\text{N}_2(\nu)]/dt = -k_9[\text{N}_2(\nu)][\text{ClN}_3] + k_{-9}[\text{N}_2][\text{ClN}_3(\nu)] \quad (2)$$

where  $k_9$  and  $k_{-9}$  are rate constants for the forward and reverse energy transfer processes. In this case the forward process is exothermic by  $281 \text{ cm}^{-1}$ . A steady-state treatment of the  $\text{ClN}_3(\nu)$  density yields an expression analogous to eq 1 above:

$$[\text{ClN}_3(\nu)]_{\text{ss}} = k_9[\text{N}_2(\nu)][\text{ClN}_3]/(k_{-9}[\text{N}_2] + k_q) \quad (3)$$

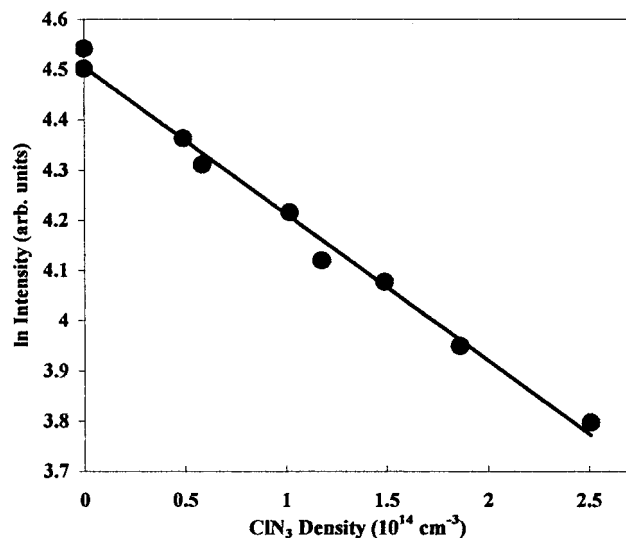
where  $k_q$  represents the rate of first-order losses of  $\text{ClN}_3(\nu)$  by radiation and collisional quenching. Substitution of eq 3 in eq 2 yields

$$d[\text{N}_2(\nu)]/dt = \alpha[\text{N}_2(\nu)][\text{ClN}_3] \quad (4)$$

where

$$\alpha = -k_9\{1 - k_9k_{-9}[\text{N}_2]/(k_{-9}[\text{N}_2] + k_q)\} \quad (5)$$

Hence the density of  $\text{N}_2(\nu)$  should decay as  $\exp(\alpha[\text{ClN}_3]t)$ , and a plot of  $\ln[\text{N}_2(\nu)]$  (i.e.,  $\ln(\text{intensity})$ ) vs  $[\text{ClN}_3]$  for a fixed time  $t$  should be linear with slope  $\alpha t$ .

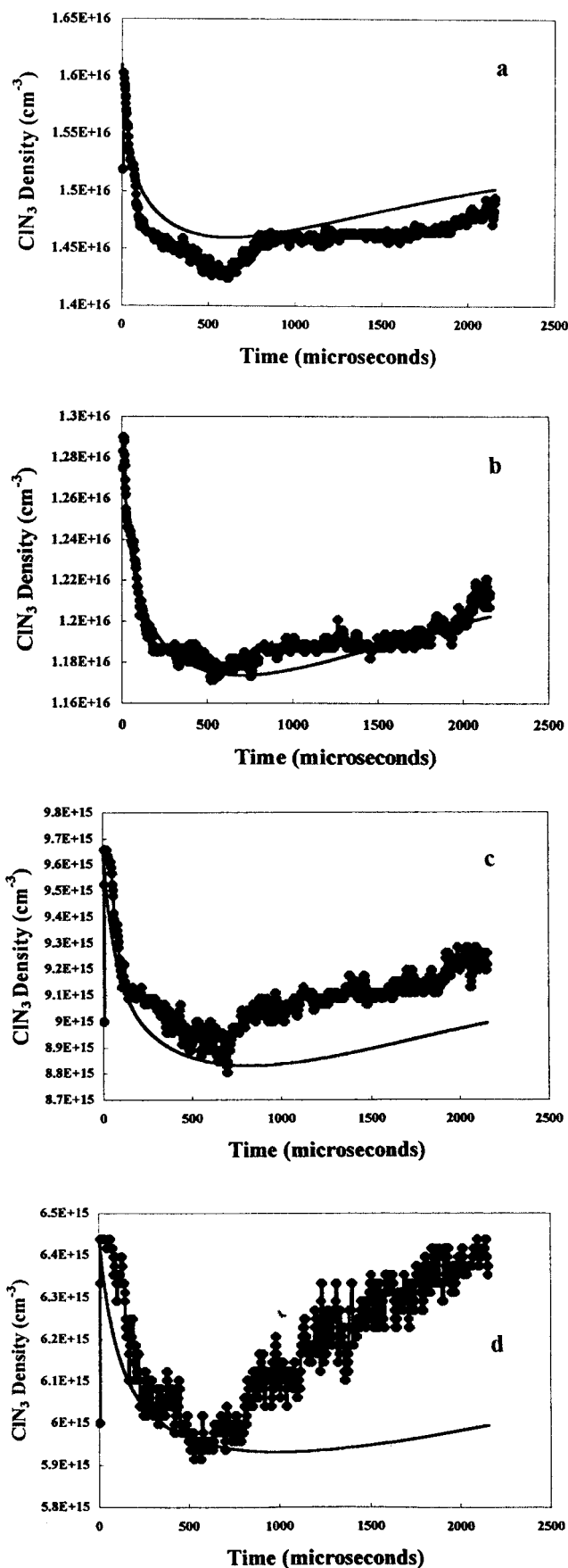


**Figure 1.** A plot of the natural log of the intensity of emission from  $CO_2(\nu_3)$  vs the density of  $CIN_3$ , measured at  $t = 0.018$  s after admission of  $CIN_3$  to the flow.

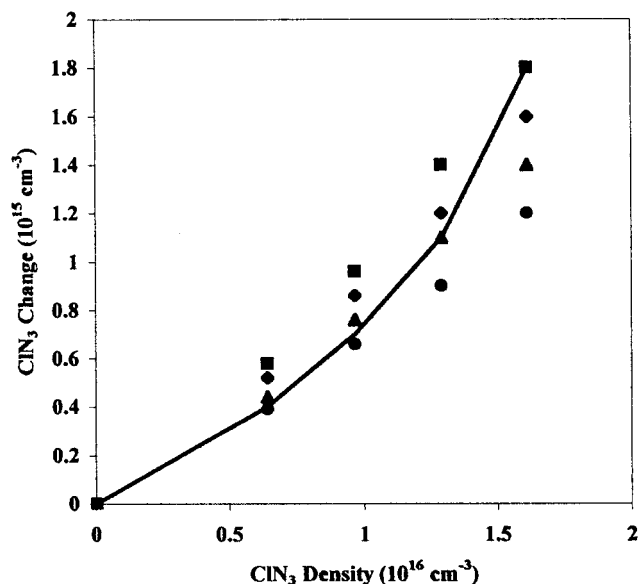
Figure 1 shows the results of experiments in which the emission intensity was measured at  $t = 0.018$  s for various densities of  $CIN_3$ . The plot is in fact linear and the slope ( $\alpha t$ ) yields a value  $\alpha = -1.63 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ . The value of the energy transfer rate constant  $k_9$  can be determined from  $\alpha$  if the first-order  $CIN_3(\nu)$  quenching rate  $k_q$  is known. Careful comparison of the frequency-integrated infrared absorption strengths of the  $\nu_2$  and  $\nu_3$  bands of  $CIN_3$  and  $CO_2$  indicates that the transition in  $CIN_3$  is 4.8 times stronger than that in  $CO_2$ , suggesting that the radiative rate of excited  $CIN_3(\nu_2, \nu=1)$  is greater than that of  $CO_2(\nu_3, \nu=1)$  by this same factor, i.e.,  $k_q \approx 2000 \text{ s}^{-1}$ . Using this result and the relationship between  $k_9$  and  $k_{-9}$  ( $k_{-9} = k_9 \exp(-281 \text{ cm}^{-1}/kT)$ ), a value  $k_9 = 1.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  is obtained. This result is in fact reasonably insensitive to the value of  $k_q$ ; for  $k_q = 500 \text{ s}^{-1}$ ,  $k_9 = 2.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ . Considering all of the uncertainties in the experiments and the treatment of the results,  $k_9 = (2.0 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .

**2. Laser Photodissociation Experiments.** Photodissociation of  $CIN_3$  using excimer laser sources at 193 or 249 nm has been performed a number of times in the past,<sup>5,10</sup> and it is known that the principal photofragments are  $NCl(a^1\Delta)$  and  $N_2(X^1\Sigma^+_g)$ . Coombe and co-workers<sup>10</sup> reported some dissociation to triplet fragments  $NCl(X^3\Sigma^-) + N_2(A^3\Sigma^+_u)$ , but this channel is believed to be minor<sup>14</sup> and the density of  $N_2(A)$  metastables very small relative to  $NCl(a^1\Delta)$ . More recently, Ray and Coombe<sup>5</sup> investigated the chain decomposition of  $CIN_3$  after photolysis at 193 and 249 nm, and found the latter wavelength to be more efficient at initiation of the chain. In the present experiments, 249 nm photolysis was used once again for the photodissociation of samples of  $CIN_3/He$  (5%  $CIN_3$ ) at densities of the azide up to  $1.61 \times 10^{16} \text{ cm}^{-3}$  and incident laser fluences up to a maximum of  $13.5 \text{ mJ/cm}^2$ . These conditions correspond to photodissociation of a maximum of 2.7% of the  $CIN_3$  initially present.<sup>10</sup> Time profiles were recorded of the density of the  $CIN_3$  parent using the IR absorption method described above, in addition to time profiles of IR emissions from  $NCl(a^1\Delta)$  and vibrationally excited  $CIN_3(\nu_2)$  for many different combinations of initial  $CIN_3$  densities and incident laser fluences. Typical data are presented in Figures 2, 4, and 6.

Figure 2 shows time profiles of the change in the  $CIN_3$  density recorded by IR absorption, for initial densities ranging from  $6.44 \times 10^{15}$  to  $1.61 \times 10^{16} \text{ cm}^{-3}$  at a fixed fluence of  $13.5 \text{ mJ/cm}^2$ . The  $CIN_3$  density declines over a period of  $500 \mu\text{s}$  after



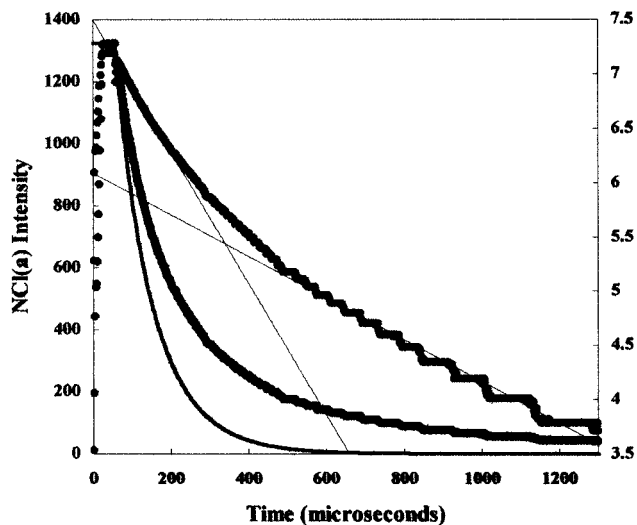
**Figure 2.** Time profiles of the densities of  $CIN_3(\nu=0)$  for four initial  $CIN_3$  densities photolyzed at 249 nm: (a)  $[CIN_3]_0 = 1.61 \times 10^{16}$ , (b)  $[CIN_3]_0 = 1.29 \times 10^{16}$ , (c)  $[CIN_3]_0 = 9.66 \times 10^{15}$ , (d)  $[CIN_3]_0 = 6.44 \times 10^{15} \text{ cm}^{-3}$ . Corresponding time profiles computed from the kinetic model are shown as solid lines.



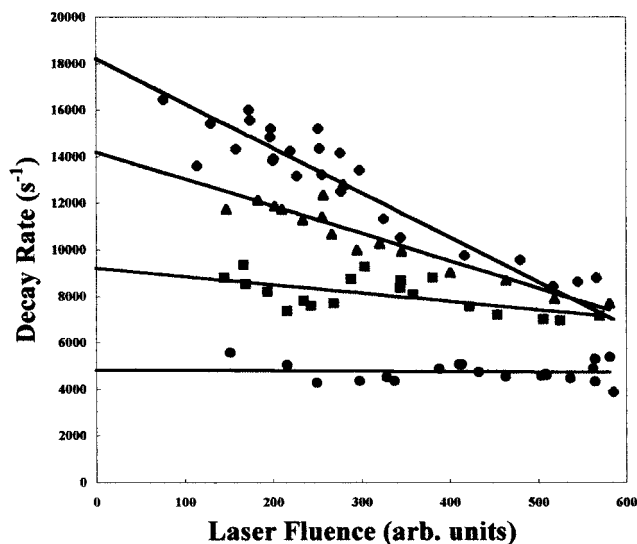
**Figure 3.** Plots of the change in the density of  $\text{CIN}_3$  at  $500 \mu\text{s}$  after the laser pulse (i.e.,  $[\text{CIN}_3]_0 - [\text{CIN}_3]_{500 \mu\text{s}}$ ) vs the initial density of  $\text{CIN}_3$ , for photolysis at 249 nm and 2.7% initial dissociation. Experimental data are shown by the solid line. (■), (◆), (▲), (●) correspond to values computed from the kinetic model for  $k_7 = 3.0 \times 10^{-12}$ ,  $2.5 \times 10^{-12}$ ,  $2.0 \times 10^{-12}$ , and  $1.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , respectively.

the photolysis pulse and the overall loss of the azide reaches more than four times that from the initial photodissociation (2.7%), suggesting the operation of a chain. The removal of the  $\text{CIN}_3$  from the system is incomplete, with the IR absorbance reaching a minimum and then increasing again beyond 1 ms in each case. The proportion of the  $\text{CIN}_3$  removed by the chain was observed to increase with the initial density of the azide (hence the initial density of photofragments). Figure 3 shows a plot of the change in the density of  $\text{CIN}_3$  at a fixed time after the laser pulse ( $500 \mu\text{s}$ ) vs the initial density of  $\text{CIN}_3$ , for a fluence of  $13.5 \text{ mJ/cm}^2$ . For the data shown, the proportion of  $\text{CIN}_3$  removed varies from 6.2% for the lowest initial density to 11.2% for the highest initial density.

Figure 4 shows a typical time profile of the density of  $\text{NCl}(a^1\Delta)$  observed via its emission at  $1.08 \mu\text{m}$ . Such data were obtained for a range of initial  $\text{CIN}_3$  densities and laser fluences. The data shown are for an initial  $\text{CIN}_3$  density of  $6.44 \times 10^{15} \text{ cm}^{-3}$  and a fluence of  $13.5 \text{ mJ/cm}^2$ . The time profile exhibits a very rapid decline over  $200 \mu\text{s}$  followed by a much more slowly decaying, lower intensity "tail" extending beyond 2 ms. The rise time of the initial intense peak corresponds to the time constant of the Ge detector used in the experiments,  $13 \mu\text{s}$ . All of the  $\text{NCl}(a^1\Delta)$  time profiles observed in the experiments were well fitted by a sum of two exponential decays (intensity =  $A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t)$ ). Figure 4 also shows a plot of  $\ln(\text{intensity})$  vs time, with lines indicating the two distinct linear components. Plots of the exponential decay rate of the initial intense component vs laser fluence for four different initial  $\text{CIN}_3$  densities are shown in Figure 5. Note that for the higher density data, the decays become slower with increasing fluence. For the conditions of the experiments, increasing fluence corresponds to increasing initial densities of the photofragments  $\text{NCl}(a^1\Delta)$  and  $\text{N}_2(v)$  with a nearly constant density of  $\text{CIN}_3$ . This result suggests that the initial  $\text{NCl}(a^1\Delta)$  decay is not dominated by second-order processes among the photofragments (for which the rate would increase with increasing fluence), but rather by pseudo-first-order interactions with  $\text{CIN}_3$ , and that interactions between the photofragments and  $\text{CIN}_3$  mitigate this decay by



**Figure 4.** Time profile of emission from  $\text{NCl}(a^1\Delta)$  from 249 nm photolysis of  $\text{CIN}_3$ , for an initial  $\text{CIN}_3$  density of  $6.44 \times 10^{15} \text{ cm}^{-3}$ . Also shown is a plot of the natural log of the emission intensity vs time, with thin lines indicating the slopes at short and long times after the laser pulse (units of the logarithmic scale are shown on the right axis). The time profile computed from the model is shown as a thick solid line.



**Figure 5.** Plots of the experimental decay rate of the fast component of the  $\text{NCl}(a^1\Delta)$  time decay vs the fluence of the photolysis laser, for four different initial densities of  $\text{CIN}_3$ : (◆)  $[\text{CIN}_3]_0 = 1.29 \times 10^{16} \text{ cm}^{-3}$ ; (▲)  $[\text{CIN}_3]_0 = 9.66 \times 10^{15} \text{ cm}^{-3}$ ; (■)  $[\text{CIN}_3]_0 = 6.44 \times 10^{15} \text{ cm}^{-3}$ ; (●)  $[\text{CIN}_3]_0 = 3.22 \times 10^{15} \text{ cm}^{-3}$ . The lines shown are least-squares fits to the data.

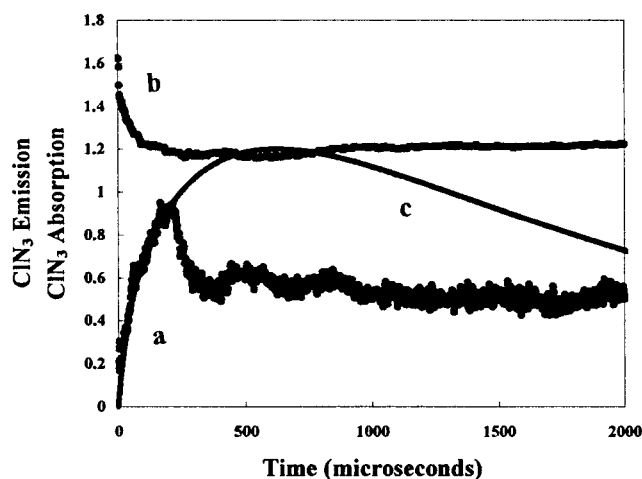
some regeneration of  $\text{NCl}(a^1\Delta)$  at higher fluences. For the lower initial  $\text{CIN}_3$  densities, the  $\text{NCl}(a^1\Delta)$  decay exhibits virtually no dependence on laser fluence, suggesting that under these circumstances processes which regenerate  $\text{NCl}(a^1\Delta)$  simply do not compete with pseudo-first-order quenching.

Figure 6 shows the time profile of emission from vibrationally excited  $\text{CIN}_3(v_2)$ , observed via its IR emission near  $4.7 \mu\text{m}$ , for a  $\text{CIN}_3$  density of  $1.61 \times 10^{16} \text{ cm}^{-3}$  and a fluence of  $13.5 \text{ mJ/cm}^2$ . Also shown is absorption data indicating loss of ground state  $\text{CIN}_3$  for these same conditions. The two time profiles are clearly related, the initial growth in  $\text{CIN}_3(v_2)$  tracking the decay in  $\text{CIN}_3$ . The  $\text{CIN}_3(v_2)$  emission was observed to extend well beyond 2 ms after the photolysis pulse. It exhibits oscillatory behavior after an initial rise over about  $200 \mu\text{s}$ , and indeed the oscillations appear to be evident in the ground-state  $\text{CIN}_3$



TABLE 1: Kinetic Model for the ClN<sub>3</sub> Chain

initiation	
ClN <sub>3</sub> + <i>hν</i> → NCl(a <sup>1</sup> Δ) + N <sub>2</sub> ( <i>v</i> )	
propagation	
NCl(a <sup>1</sup> Δ) + ClN <sub>3</sub> → NCl(X <sup>3</sup> Σ <sup>-</sup> ) + NCl(a <sup>1</sup> Δ) + N <sub>2</sub> ( <i>v</i> )	$k_7 = 2.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
→ NCl(X <sup>3</sup> Σ <sup>-</sup> ) + ClN <sub>3</sub> ( <i>v</i> =1)	$k_8 = 1.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
N <sub>2</sub> ( <i>v</i> ) + ClN <sub>3</sub> → ClN <sub>3</sub> ( <i>v</i> =1) + N <sub>2</sub>	$k_9 = 2.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
N <sub>2</sub> ( <i>v</i> ) + ClN <sub>3</sub> ( <i>v</i> =1) → ClN <sub>3</sub> ( <i>v</i> =2) + N <sub>2</sub>	$k_{10} = 2.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
N <sub>2</sub> ( <i>v</i> ) + ClN <sub>3</sub> ( <i>v</i> =2) → NCl(a <sup>1</sup> Δ) + N <sub>2</sub> ( <i>v</i> ) + N <sub>2</sub>	$k_{11} = 2.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$
termination	
NCl(a <sup>1</sup> Δ) + NCl(a <sup>1</sup> Δ) → N <sub>2</sub> ( <i>v</i> ) + 2Cl	$k_{12} = 8.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
NCl(a <sup>1</sup> Δ) → NCl(X <sup>3</sup> Σ <sup>-</sup> )	$k_{13} = 500 \text{ s}^{-1}$
ClN <sub>3</sub> ( <i>v</i> =1) → ClN <sub>3</sub> ( <i>v</i> =0)	$k_{14} = 500 \text{ s}^{-1}$
ClN <sub>3</sub> ( <i>v</i> =2) → ClN <sub>3</sub> ( <i>v</i> =1)	$k_{15} = 2000 \text{ s}^{-1}$



**Figure 6.** (a) Time profile of IR emission from vibrationally excited ClN<sub>3</sub>(*v*<sub>2</sub>) for 249 nm photolysis of [ClN<sub>3</sub>]<sub>0</sub> = 1.61 × 10<sup>16</sup> cm<sup>-3</sup>. (b) The corresponding time profile of the density of ClN<sub>3</sub>(*v* = 0) from IR absorbance. (c) Time profile of ClN<sub>3</sub>(*v*<sub>2</sub>,*v*=1) computed from the kinetic model. Units on the vertical axis are arbitrary.

absorption as well (Figure 2). This remarkable phenomenon was reproducible under a variety of density and fluence conditions.

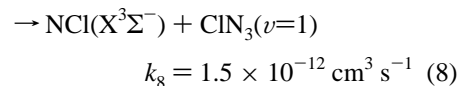
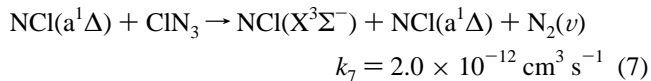
**3. Kinetic Model.** Our objective was to assemble the simplest possible kinetic model consistent with the major features of the data, based on known rate constants and reasonable assumptions about processes for which rate constants are unknown. A summary of the model is presented in Table 1. We assume that initiation of the chain begins with photolysis of ClN<sub>3</sub> to produce both NCl(a<sup>1</sup>Δ) and vibrationally excited N<sub>2</sub>:



The generation of N<sub>2</sub>(*v*) in this process seems reasonable in light of the large amount of energy released beyond that required for the production of NCl(a<sup>1</sup>Δ) and the difference in bond lengths between N<sub>2</sub> and the terminal N–N bond in the azide.<sup>15</sup>

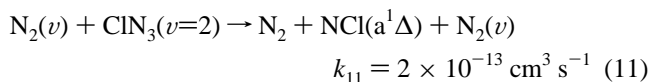
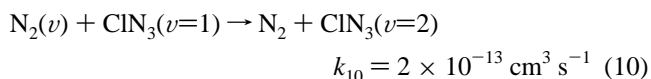
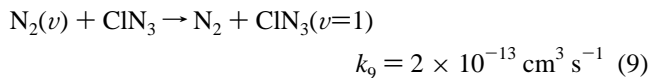
The chain can be propagated by either of the two photofragments. By analogy with the reactions<sup>5</sup> of ClN<sub>3</sub> with O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>) and I\*(5<sup>2</sup>P<sub>1/2</sub>), reaction of the azide with NCl(a<sup>1</sup>Δ) is expected to be much faster than vibrational energy exchange between ClN<sub>3</sub> and N<sub>2</sub>(*v*). Indeed, the initial decline of the ClN<sub>3</sub> absorbance (Figure 2) tracks the initial decay of the NCl(a<sup>1</sup>Δ) emission signal (Figures 4 and 5), supporting the idea that the NCl(a<sup>1</sup>Δ)/ClN<sub>3</sub> interaction dominates the chemistry of the system immediately after the photolysis pulse. We note also that the initial rise of the ClN<sub>3</sub>(*v*=1) emission signal (Figure 6) tracks the initial decays of NCl(a<sup>1</sup>Δ) and ClN<sub>3</sub>(*v*=0), suggesting that its production involves an electronic-to-vibrational energy transfer process among these two species. Hence, we postulate

that the following reactions occur:



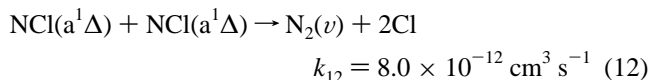
Process 7 is analogous to the reaction between ClN<sub>3</sub> and O<sub>2</sub>(a<sup>1</sup>Δ<sub>g</sub>), and process 8 is *E*–*V* energy exchange. The values of *k*<sub>7</sub> and *k*<sub>8</sub> were determined from the present data as described below.

Chain propagation by N<sub>2</sub>(*v*) would involve vibrational excitation of the ClN<sub>3</sub> in sequential collisions with this species, with the third such collision resulting in dissociation:

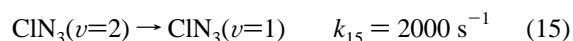
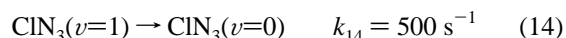
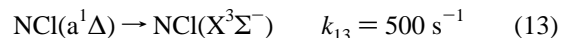


Here we assume the barrier height reported by Benard and co-workers.<sup>7</sup> The rate constants assigned to processes 9, 10, and 11 are given by the value obtained from the present data as described above. Since the density of ground-state N<sub>2</sub> in the system is very much smaller than that of ClN<sub>3</sub>, we have neglected the endothermic reverse of reaction 9.

Chain termination steps include those processes that remove NCl(a<sup>1</sup>Δ), N<sub>2</sub>(*v*), ClN<sub>3</sub>(*v*=1) or ClN<sub>3</sub>(*v*=2) from the system. The best known such process is the NCl(a<sup>1</sup>Δ) “self-annihilation” reaction:



where the rate constant is that reported by Benard and co-workers.<sup>7</sup> We have also included in the model first-order processes that remove the chain carriers, as follows:



These processes are intended to reflect losses by radiation, wall

quenching, and pseudo-first-order quenching by collisions with species present in the reaction mixture. The values of  $k_{14}$  and  $k_{15}$  reflect IR radiation from excited  $\text{ClN}_3$ . At the densities of the pulsed experiments, considerable radiation trapping is expected for the  $\nu = 1 \rightarrow \nu = 0$  transition in this molecule. This phenomenon is well-known for  $\text{CO}_2$ , and  $k_{14}$  was determined by multiplying the reported<sup>16</sup> radiation-trapped rate for  $\text{CO}_2$  by the factor of 4.8 noted above. The flow reactor experiments described above indicate that  $\text{N}_2(\nu)$  quenching is very slow, even on Pyrex walls. Hence, mechanisms for loss of  $\text{N}_2(\nu)$  have not been included in the model. The value of  $k_{13}$  is an estimate reflecting slow loss of  $\text{NCl}(a^1\Delta)$  by collisions with walls or impurities present.

The rate constants indicated above for reactions 7 and 8 are key to the model and were determined from the present data. Because reaction of  $\text{NCl}(a^1\Delta)$  with  $\text{ClN}_3$  is much faster than vibrational energy transfer between  $\text{N}_2(\nu)$  and  $\text{ClN}_3$ , the chain mechanisms carried by these two species are separated in time from one another. The initial loss of  $\text{ClN}_3$  in the system evident in Figure 2 is dominated by the relatively fast processes involving  $\text{NCl}(a^1\Delta)$ . Since reaction 7 does not result in loss of  $\text{NCl}(a^1\Delta)$  from the system, the initial losses of both  $\text{NCl}(a^1\Delta)$  and  $\text{ClN}_3$  must correspond to reaction 8. The rate constant  $k_8$  can thus be inferred from the observed exponential decay rates of the rapid decay component of the  $\text{NCl}(a^1\Delta)$  emission for different initial  $\text{ClN}_3$  densities in the limit of zero laser fluence (i.e., in the limit where no secondary reactions occur), Figure 5. The zero fluence intercepts of the four data sets shown all indicate rate constants between  $1.42 \times 10^{-12}$  and  $1.49 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . In the model, we have set  $k_8 = 1.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ .

The total loss of  $\text{ClN}_3$  from the system in the first few hundred microseconds after the laser pulse is determined by both processes 7 and 8. With the value of  $k_8$  set, the magnitude of  $k_7$  can be determined by fitting the kinetic model to the data shown in Figure 2 (the overall loss of  $\text{ClN}_3$ ). The coupled differential rate equations corresponding to reactions 7–15 were numerically integrated using a Runge–Kutta routine with adaptive step size control. The densities of  $\text{ClN}_3$ ,  $\text{NCl}(a^1\Delta)$ ,  $\text{N}_2(\nu)$ ,  $\text{ClN}_3(\nu=1)$ ,  $\text{ClN}_3(\nu=2)$ ,  $\text{Cl}$ , and  $\text{NCl}(X^3\Sigma^-)$  were computed at a minimum of 500 intervals over a total time of 3 ms. Initial conditions (the densities of  $\text{ClN}_3$ ,  $\text{NCl}(a^1\Delta)$ , and  $\text{N}_2(\nu)$ ) were chosen according to actual  $\text{ClN}_3$  densities and incident laser fluences employed in the experiments. Since the laser output irradiated the full volume of the reaction vessel in the experiments, the initial densities were assumed to be spatially uniform. Figure 3 (the plot of the density of  $\text{ClN}_3$  lost during the first 500  $\mu\text{s}$  vs the initial azide density) also indicates the modeled results. The best fit to the experimental data is obtained for  $k_7 = 2.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . Modeled results are also shown for  $k_7 = 1.5 \times 10^{-12}$ ,  $2.5 \times 10^{-12}$ , and  $3.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  to indicate the sensitivity of this result.

The results of calculations with the complete model are shown with the corresponding experimental data in Figures 2, 4, and 6. The agreement between the data and the results of the model is reasonable. The magnitude of the overall reduction of the  $\text{ClN}_3$  density (Figure 2) is reproduced well by the model, as is the time dependence of the  $\text{ClN}_3$  density at short times after the laser pulse ( $t < 750 \mu\text{s}$ ). Significant disagreement is evident at longer times, though, particularly for the lowest  $\text{ClN}_3$  densities. It is apparent that the chain carried by  $\text{NCl}(a^1\Delta)$  removes an amount of  $\text{ClN}_3$  several times that removed by the initial photodissociation, and it would seem that the increase in the  $\text{ClN}_3$  absorbance observed at longer times ( $> 1.0 \text{ ms}$ ) corresponds to repopulation of  $\text{ClN}_3(\nu=0)$  by radiation from

higher vibrational levels. The model reproduces the fast initial decay of the  $\text{NCl}(a^1\Delta)$  density (Figure 4), but it clearly does not reproduce the intensity of the slow component of the decay. The model predicts a significant  $\text{ClN}_3(\nu=1)$  density (Figure 6) with a time profile that agrees very well with the initial rise of the emission signal observed in the experiments. The experimental signal exhibits the onset of oscillations with an abrupt decay beginning at about 200  $\mu\text{s}$ , though, and this behavior is not reproduced by the model.

## Discussion

The data described above show that the rate constant for quenching of  $\text{N}_2(\nu)$  by  $\text{ClN}_3$  has a magnitude  $k_9 = (2 \pm 1) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  at 300 K. This value, together with the observation of emission from vibrationally excited  $\text{ClN}_3(\nu_2)$ , strongly suggests that the quenching process involves near-resonant vibration-to-vibration energy transfer. Sharma and Brau<sup>17</sup> have described such energy transfer processes in terms of the coupling of transitions in the colliding species by long-range intermolecular forces. For nearly resonant energy exchange ( $\Delta\epsilon < 20 \text{ cm}^{-1}$ ), the energy transfer rate constants are predicted to vary with the magnitudes of the transition dipole moments in the colliding molecules. For greater energy gaps, experiments have shown the rate constants to vary as  $\exp(-\Delta\epsilon/kT)$ . Since the energy gap for reaction 9 is  $281 \text{ cm}^{-1}$ , and that for  $\text{CO}_2(\nu)$  energy transfer to  $\text{N}_2$  is just  $18 \text{ cm}^{-1}$ , the rate constants for the two processes might be expected to be related by a factor  $\exp(-281 \text{ cm}^{-1}/kT) = 0.26$  at room temperature. In fact,  $k_9/k_{-e} = 0.34$ , in reasonable agreement with this result. The difference suggests some contribution to  $k_9$  from the greater transition moment in  $\text{ClN}_3$  relative to  $\text{CO}_2$ .

From the data and the kinetic model, the overall rate constant for the reaction of  $\text{NCl}(a^1\Delta)$  with  $\text{ClN}_3$  is found to be  $3.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , with the channel that actually results in loss of  $\text{NCl}(a^1\Delta)$  (reaction 8) having a branching fraction of  $(43 \pm 10)\%$ . Schlie and co-workers<sup>8</sup> have reported a rate constant  $k = 5.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  for the removal of  $\text{NCl}(a^1\Delta)$  in collisions with  $\text{ClN}_3$ , based on the results of experiments in which the  $\text{NCl}(a^1\Delta)$  decay was measured after 193 nm photolysis of  $\text{ClN}_3$ . Similar results have been reported by Heaven et al.,<sup>18</sup> and by Coombe and van Benthem.<sup>19</sup> From Figure 5, though, it is apparent that the observed decays can vary substantially with laser fluence, with the decays becoming longer at higher fluences. Indeed, from the data in Figure 5, the apparent value of  $k_8$  for  $[\text{ClN}_3] = 1.6 \times 10^{16}$  and the highest laser fluence used in the present experiments is  $5.6 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , very near that reported by Schlie and co-workers.<sup>8</sup> For greater fluences, the apparent rate constant may be still smaller; Coombe and Van Benthem<sup>19</sup> report a rate constant of  $1.25 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  from experiments in which 14% of the  $\text{ClN}_3$  initially present was photodissociated at 193 nm. Extrapolation to zero fluence is needed to remove the effect of regeneration of  $\text{NCl}(a^1\Delta)$  by the chain.

In the model, we have indicated that quenching of  $\text{NCl}(a^1\Delta)$  by collisions with  $\text{ClN}_3$  proceeds by an  $E-V$  energy exchange in which the azide is vibrationally excited. We note also, though, that flow reactor studies performed by Clyne and MacRobert<sup>20</sup> have shown that  $\text{NCl}$  reacts with  $\text{Cl}_2$  to produce  $\text{NCl}_2$ , with a similar rate constant. An analogous reaction between  $\text{NCl}$  and  $\text{ClN}_3$  would produce  $\text{NCl}_2$  and  $\text{N}_3$ . We have indicated the products of the  $\text{NCl}(a^1\Delta)$  self-annihilation (reaction 12) to be molecular nitrogen and  $\text{Cl}$  atoms. While the rate constant for this process is known,<sup>7</sup> its products are not. If  $\text{Cl}$  atoms are in fact produced, they can react with  $\text{ClN}_3$  to generate  $\text{Cl}_2$  and  $\text{N}_3$ .

This reaction has been studied with discharge-flow mass spectrometry methods,<sup>21</sup> and its rate constant is reported to be  $3.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at 300 K.  $N_3$  radicals generated by this process (or by  $NCl(a^1\Delta) + CIN_3$ ) can react<sup>22</sup> with Cl atoms to produce additional  $NCl(a^1\Delta)$ , enhancing the rate of the chain carried by the nitrene. Also, the  $N_3$  radicals would themselves be removed by a self-annihilation process which would likely generate  $N_2(v)$ ; the rate constant of this process is known<sup>23</sup> to be  $2.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . These second-order processes are expected to have a minimal effect on the rate of loss of  $CIN_3$  for low initial densities of chain carriers, as in the present experiments. Although they may well be important at higher fluences, we have chosen not to include them in the current mechanism since the density of Cl atoms actually present in the system is unknown, and may be small.

Heaven and co-workers<sup>18</sup> have recently reported experiments in which both  $NCl(a^1\Delta)$  and  $NCl(X^3\Sigma^-)$  were observed after 249 nm photolysis of  $CIN_3$ . These authors indicate that the  $NCl(a^1\Delta)$  emission signals observed in their experiments suffer from interference from nearby features of the  $N_2$  first positive ( $B^3\Pi_g \rightarrow A^3\Sigma_u^+$ ) system, particularly the 0,0 band of this transition at  $1.04 \mu\text{m}$ , in the first few hundred microseconds after the laser pulse. The filter used in observations of  $NCl(a^1\Delta)$  in the present experiments (12 nm fwhm) should effectively block this  $N_2$  emission. We note also that excited  $N_2$  metastables are present in the system<sup>10</sup> at densities likely to be several orders of magnitude less than that of  $NCl(a^1\Delta)$  and should not play a significant role in the loss of  $CIN_3$  evident in Figure 2 above. The agreement between the  $CIN_3$  and  $NCl(a^1\Delta)$  time profiles observed in the present experiments lends support to the notion that the latter are not significantly contaminated by emission from excited  $N_2$ .

Both the data and the kinetic model indicate that the chain has a very limited impact on the system for low densities of chain carriers, as in the present experiments. Nonetheless, features like the long, slowly decaying tail of the  $NCl(a^1\Delta)$  emission in Figure 4 and the slight increase in the apparent value of  $k_7$  with increasing  $CIN_3$  density evident in Figure 5, neither of which is reproduced by the model, suggest the onset of additional processes which contribute to the production of chain carriers. Further, the kinetic model does not agree well with  $NCl(a^1\Delta)$  time profiles reported from a number of experiments performed at higher densities,<sup>4,5,19</sup> some of which exhibit secondary maxima. It may well be that under such circumstances the rates of chain propagation processes are accelerated by temperature increases, or that chain branching reactions play a greater role. We note also that the rate constants for vibrational energy exchange between  $N_2(v)$  and  $CIN_3$  might be greater for higher vibrational levels of  $N_2$  where the energy gap is more resonant with the  $CIN_3 \nu_2$  frequency. For very small energy defects, the rate constant  $k_9$  might approach the value for  $k_{-e}$ , i.e.,  $5.8 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .

## Conclusions

The rate constant for quenching of  $N_2(v)$  by  $CIN_3$  is  $k_9 = (2 \pm 1) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  at 300 K. This value is in keeping with a vibration-to-vibration energy transfer process, and indeed emission from vibrationally excited  $CIN_3(\nu_2)$  is observed. A relatively simple model for the chain decomposition of  $CIN_3$  carried by photofragments  $NCl(a^1\Delta)$  and  $N_2(v)$  produces computed  $NCl(a^1\Delta)$  and  $CIN_3$  time profiles in reasonable agreement with experiment. The model appears to underestimate the rate of the chain in the regime of higher densities of chain carriers.

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