The P( ${}^{4}S_{u}$ ) + N<sub>3</sub>( ${}^{2}\Pi_{g}$ ) Reaction: Chemical Generation of a New Metastable State of PN

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The kinetics and spectroscopy of the chemiluminescent reaction between  $P({}^4S_u)$  atoms and  $N_3({}^2\Pi_g)$  radicals were studied with a discharge-flow apparatus. The chemiluminescence exhibited three band systems, which were identified as PN ( $A^{1}\Pi \rightarrow X^{1}\Sigma^{+}$ ), PF ( $B^{3}\Pi \rightarrow X^{3}\Sigma^{-}$ ), and a previously unobserved system in PN. From the spectrum of the new system, molecular constants of the excited state were found to be  $T_e = 25863 \pm 16 \text{ cm}^{-1}$ ,  $\omega_e' = 957 \pm 8 \text{ cm}^{-1}$ , and  $\omega_e X_e' = 18 \pm 2 \text{ cm}^{-1}$ . This excited state appears to be significantly Franck-Condon shifted from the ground state, with 0,3 being the most intense band of the spectrum. From comparison of this system with the analogous  $N({}^4S_u) + N_3({}^2\Pi_g)$  reaction, the new excited state of PN is expected to be a triplet metastable, either  $a^{3}\Pi$  or  $a'^{3}\Sigma^{+}$ . Analysis of the time behavior of the removal of P atoms from the system indicated a rate constant of  $(4.7 \pm 0.4) \times 10^{-11} \text{ cm}^{3} \text{ s}^{-1}$  for the P + N<sub>3</sub> reaction. The lifetime of the excited metastable state of PN is greater than 4 ms.

### Introduction

Recent experiments<sup>1-3</sup> performed in our laboratory have indicated that reactions of ground-state azide radicals,  $N_3(^2\Pi_g)$ , are strongly constrained by both spin and orbital angular momentum conservation rules to produce excited metastable nitrenes. The  $N-N_2$  bond in the radical is extremely weak, with a dissociation energy on the order of 10 kcal mol<sup>-1</sup>. Consequently, reaction with an atomic species R can populate excited states of the product nitrene (NR) lying at energies nearly as high as the dissociation limit of these molecules, such that chemiluminescence is typically observed in the UV and visible regions. Only certain product channels are allowed by the angular momentum constraints operating in these systems. The ground state of the azide radical correlates to  $N_2(X^1\Sigma_g^+)$  and an excited nitrogen atom,  $N(^2D)$ . For species R with weak spin-orbit coupling, reactions  $R + N_3$ can be envisioned as proceeding on an excited-state potential energy surface leading to states of RN which correlate to R +  $N(^{2}D)$ . These states are metastable with respect to the ground state of the nitrene which correlates to  $R + N(^{4}S)$ .

An excellent example of this behavior is seen in the N(<sup>4</sup>S) + N<sub>3</sub> reaction recently studied in our laboratory.<sup>3</sup> Spin conservation suggests that this reaction should produce excited triplet or quintet states of N<sub>2</sub>. Although a number of such states are energetically accessible, conservation of orbital angular momentum directs the reaction into particular states of N<sub>2</sub> correlating to N(<sup>4</sup>S) + N(<sup>2</sup>D). Only two such states are accessible, N<sub>2</sub>(B<sup>3</sup>\Pi<sub>g</sub>) and N<sub>2</sub>(W<sup>3</sup>Δ<sub>u</sub>). Intense N<sub>2</sub> B<sup>3</sup>Π<sub>g</sub> → A<sup>3</sup> Σ<sub>u</sub><sup>+</sup> chemiluminescence has been found to dominate the emission from N + N<sub>3</sub>, with a photon yield of 20% relative to the limiting HN<sub>3</sub> flow. This yield represents a lower limit on the intrinsic N<sub>2</sub>(B<sup>+</sup>Π<sub>g</sub>) branching fraction in the reaction.

Similarly strong constraints should operate in other azide systems for which the spin-orbit coupling is small. A major objective of the present work was to test this hypothesis for the reaction of azide radicals with  $P({}^{4}S_{u})$  atoms. From the analogy with N + N<sub>3</sub>, it was anticipated that P + N<sub>3</sub> would form excited triplet or quintet states of PN correlating to  $P({}^{4}S) + N({}^{2}D)$ . Only one excited state of PN has been reported previously, however, that being the  $A({}^{1}\Pi)$  state giving rise to the  $A{}^{1}\Pi \rightarrow X{}^{1}\Sigma^{+}$  bands near 250 nm. Excited triplets are well-known for the isoelectronic species CS and for CO. The  $a{}^{3}\Pi$  state in CS has a radiative lifetime of 16 ms,<sup>4</sup> and the analogous state in CO (which gives rise to the well-known Cameron bands) has a lifetime of 90 ms.<sup>5</sup> The  $a^3\Pi$  states in CO and CS are the analogues of the  $B^3\Pi_g$  state in N<sub>2</sub>, but unlike N<sub>2</sub> lie at lower energies than the  $a'^3\Sigma^+$  state (the analogue of N<sub>2</sub>( $A^3\Sigma_u^+$ )). From the angular momentum rules, we expect P + N<sub>3</sub> to produce PN in the  $a^3\Pi$  state (correlating to P(<sup>4</sup>S) + N(<sup>2</sup>D)) such that  $a^3\Pi \rightarrow X^1\Sigma^+$  emission would be observed. In this paper, we report measurements of the rate constant of the P + N<sub>3</sub> reaction and spectrscopic observations of the chemiluminescence produced by this system. The data obtained are significant in regard to both the spectroscopy of the PN molecule and the strength of angular momentum constraints in azide reactions.

### **Experimental Section**

The discharge flow apparatus used in the experiments was much like those previously described in detail.<sup>3</sup> The reactor was fabricated from a 2.54-cm-i.d. Pyrex tube and was equipped with an axial sliding injector to provide time resolution. The reactor walls were coated with halocarbon wax to minimize losses of atoms and radicals. Atoms were produced in two side arms joined to the reactor about 30 cm upstream of a fixed observation port. One side arm was equipped with a 2450-MHz microwave discharge cavity, the other with a low-power radio-frequency (rf) discharge. Fluorine atoms were produced by passage of CF<sub>4</sub>/Ar mixtures through the microwave cavity. Phosphorus atoms were produced by passing  $PF_3$  diluted in argon (0.8%  $PF_3$ ) through the rf discharge. HN<sub>3</sub> (4% in helium) was admitted to the flow via the movable injector. The flow reactor was pumped by a 500 L min<sup>-1</sup> mechanical pump, which provided a linear velocity near 1300 cm  $s^{-1}$  for a pressure of 1.5 Torr. The pressure in the reactor was measured with a silicon oil manometer, which was calibrated with an MKS Baratron capacitance manometer. The flow rates of reagent and diluent gases were measured with mass flow meters (Tylan FM 360).

Relative densities of  $P(^4S)$  atoms present in the gas flow were monitored by vacuum UV resonance fluorescence. The fluorescence cell was constructed from an aluminum block which joined the flow tube, resonance lamp, and detection system in mutually perpendicular directions. The phosphorus lamp was a quartz flow cell equipped with an MgF<sub>2</sub> window and a microwave discharge cavity. A stable flow of P atoms in the lamp was produced by passing PCl<sub>3</sub> diluted in argon (0.8% PCl<sub>3</sub>) through the discharge zone. The PCl<sub>3</sub> was purified by fractional condensation at 77 K. The lamp produced phosphorus resonance lines at 178 (3p<sup>2</sup>4s-(<sup>4</sup>P)-3p<sup>3</sup>(<sup>4</sup>S)) and 167 nm (3s3p<sup>4</sup>(<sup>4</sup>P)-3p<sup>3</sup>(<sup>4</sup>S)).<sup>6</sup> Resonance

<sup>(1)</sup> Pritt, Jr., A. T.; Patel, D.; Coombe, R. D. Int. J. Chem. Kinet. 1984, 16, 977.

<sup>(2)</sup> Pritt, Jr., A. T.; Coombe, R. D. Int. J. Chem. Kinet. 1980, 12, 741.
(3) David, S. J.; Coombe, R. D. J. Phys. Chem. 1985, 89, 5206.

<sup>(4)</sup> Meyer, B.; Smith, J. J.; Spitzer, K. J. Chem. Phys. 1970, 53, 3616.

<sup>(5)</sup> Fournier, J.; Mohammed, H. H.; Deson, J.; Vermeil, C.; Schamps, J. J. Chem. Phys. 1980, 73, 6039.

<sup>(6)</sup> Clyne, M. A. A.; Nip, W. S. In Reactive Intermediates in the Gas Phase; Setser, D. W., Ed.; Academic: New York, 1979.

## A New Metastable State of PN

fluorescence was observed subsequent to passage of the  $PF_3/Ar$  mixture through the rf discharge located on one of the sidearms of the flow reactor. The fluorescence was dispersed with an Acton Research VM-502 monochromator and detected with a CsI photomultiplier tube, whose response was recorded with a home-built photon counter. The data described below were obtained under conditions where the P atom density was proportional to the resonance fluorescence signal, as indicated by a curve of growth of the fluorescence intensity vs. the PF<sub>3</sub> flow rate. The curve was linear for PF<sub>3</sub> densities less than  $10^{12}$  cm<sup>-1</sup>. Absolute P atom densities were not measured. We note, however, that Clyne and Ono have reported the average yield of P atoms from a discharge through PCl<sub>3</sub> in helium (0.5% PCl<sub>3</sub>) to be near 4% for conditions similar to those of the present experiments.<sup>7</sup>

Chemiluminescence produced by the  $P + N_3$  reaction was dispersed by a 0.25-m monochromator and was detected by a cooled GaAs photomultiplier tube. The PMT response was measured by an electrometer, and the resulting spectra were recorded with a strip chart recorder. Chemiluminescence in the visible region was quite weak, and accordingly in some experiments the configuration of the detection system was changed such that the cone of sight of the monochromator extended down the axis of the flow reactor. This configuration gave much greater sensitivity than that in which the monochromator looked side-on to the flow reactor. The side-on configuration was used for measurements of time profiles of the various emissions. Higher resolution spectra of individual features were recorded with a similar apparatus assembled with a 1.0-m monochromator. Although the ultimate spectral resolution of this system was about 0.01 nm, the finite intensity of the chemiluminescence was such that wider spectral slitwidths were required, giving a resolution of 0.05 nm.

#### Results

Kinetics of the  $P + N_3$  Reaction. Measurements of rate constants were made by monitoring the rates of P atom removal by various chemical media. Relative P atom densities were determined by resonance fluorescence as described above. To check the performance of the apparatus for a known system, the rate constant of the reaction  $P + O_2 \rightarrow PO + O$  was determined at 298 K. Time profiles of the P atom density were determined for various flow rates of added  $O_2$  (present in pseudo-first-order excess), and the rate constant was obtained from the slope of a plot of decay rate vs.  $O_2$  density. The value obtained,  $(1.1 \pm 0.1) \times 10^{-13}$  cm<sup>3</sup> s<sup>-1</sup> (where the uncertainty represents  $1\sigma$ ), is in very good agreement with a value previously reported in the literature  $((9.9 \pm 0.2) \times 10^{-14}$  cm<sup>3</sup> s<sup>-1</sup>).<sup>7</sup>

For experiments with the  $P + N_3$  reaction, azide radicals were produced by the very rapid reaction of fluorine atoms with  $HN_3$ :

$$\mathbf{F} + \mathbf{H}\mathbf{N}_3 \to \mathbf{H}\mathbf{F}^{\ddagger}(v \le 5) + \mathbf{N}_3 \tag{1}$$

This reaction has a rate constant<sup>3</sup>  $k_1 = (1.6 \pm 0.4) \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>. In typical experiments, F atom densities were greater than  $1 \times 10^{13}$  cm<sup>-3</sup>, such that the time constant for formation of N<sub>3</sub> radicals was less than 1 ms. Previous measurements<sup>8,9</sup> of the rate constant for the reaction of N<sub>3</sub> with F (producing excited NF) have indicated a value  $1.8 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>, such that the time constant for loss of N<sub>3</sub> by this route in our experiments would be several tens of milliseconds. Although very recent measurements by Habdas et al.<sup>10</sup> have indicated a much larger rate constant for F + N<sub>3</sub>,  $k = (5 \pm 2) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>, the data presented below support the previously reported smaller value. Hence, N<sub>3</sub> radicals were present as a pseudo-first-order reagent (with respect to phosphorus atoms, present at an initial density less than  $10^{11}$  cm<sup>-3</sup>) for many milliseconds after mixing. The N<sub>3</sub> density was taken



Figure 1. Rate of decay of the phosphorus atom density vs. the density of N<sub>3</sub> radicals. The line is a linear least-squares fit to the data and indicates a rate constant  $k = (4.7 \pm 0.4) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>.

to be equivalent to the initial  $HN_3$  density in the system.

Phosphorus atoms were produced by a radio frequency discharge through a PF<sub>3</sub>/Ar mixture as described above. PF<sub>3</sub> was chosen over PCl<sub>3</sub>, the source used in previous studies described in the literature, for two reasons. First, dissociation of PF<sub>3</sub> produces fluorine atoms which are useful for the production of N<sub>3</sub> as in reaction 1. Second, dissociation of PCl<sub>3</sub> produces chlorine atoms which can react rapidly with N<sub>3</sub> to produce excited NCl. The rate constant for Cl + N<sub>3</sub> has been reported<sup>11</sup> to be  $1 \times 10^{-11}$ cm<sup>3</sup> s<sup>-1</sup>. The flow rates of PF<sub>3</sub> were chosen such that the resonance fluorescence detection of P atoms was definitely in the linear region, i.e., the initial densities of PF<sub>3</sub> were much less than  $10^{12}$  cm<sup>-3</sup>.

In the experiments performed, a stream of F atoms (from a discharge through  $CF_4$ ) present at an initial density greater than  $10^{13}$  cm<sup>-3</sup> were mixed with a stream of P atoms (from a discharge through PF<sub>3</sub>) present at an initial density less than  $10^{11}$  cm<sup>-3</sup>. HN<sub>3</sub> was added through the movable injector such that reaction 1 above occurred very rapidly, generating N<sub>3</sub> radicals at a density equivalent to the initial HN<sub>3</sub> density ( $10^{12}$  to  $10^{13}$  cm<sup>-3</sup>). The N<sub>3</sub> radicals then reacted with the P atoms to produce PN:

$$P({}^{4}S_{u}) + N_{3}({}^{2}\Pi_{g}) \rightarrow PN + N_{2}(X^{1}\Sigma_{g}^{+})$$
(2)

The rate constant for reaction 2 was determined from the time decay of the phosphorus atom density in this environment. Variation of the F atom density (determined by titration<sup>12</sup> with  $Cl_2$ ) over a range from  $3 \times 10^{13}$  to  $1.3 \times 10^{14}$  cm<sup>-3</sup> resulted in no change in the P atom decay rate. The decay rate was found to vary inversely with the HN<sub>3</sub> density, however. The decays were exponential in every case, indiciating that N<sub>3</sub> radicals were indeed present in pseudo-first-order excess. Figure 1 shows the measured decay rates vs. the N<sub>3</sub> density from a number of experiments. The slope of the plot yields a rate constant  $k = (4.7 \pm 0.4) \times 10^{-11}$  cm<sup>-3</sup> s<sup>-1</sup> for reaction 2, where the uncertainty represents  $2\sigma$ .

The data shown in Figure 1 were obtained with a fluorine atom density near  $3 \times 10^{13}$  cm<sup>-3</sup>, determined by titration with Cl<sub>2</sub>. If the rate constant reported by Habdas et al.<sup>10</sup> for the F + N<sub>3</sub> reaction were to hold for the conditions of our experiments, then the N<sub>3</sub> radicals present in the system would be removed by excess F in less than 1 ms. The fact that considerably longer P atom decays were found, and that the decay times varied inversely with the HN<sub>3</sub> (i.e., N<sub>3</sub>) density, argues against the validity of the rate constant reported by these authors.

Chemiluminescence from the  $P + N_3$  Reaction. Spectra recorded of the chemiluminescence from the  $P + N_3$  reaction exhibited three distinct band systems. The intensities of bands in each of the three systems varied in proportion to the flow rates of both PF<sub>3</sub> and HN<sub>3</sub>, indicating their dependence on both P atoms

<sup>(7)</sup> Clyne, M. A. A.; Ono, Y. J. Chem. Soc., Faraday Trans. 2 1982, 78, 1149.

 <sup>(8)</sup> Coombe, R. D.; Pritt, Jr., A. T. Chem. Phys. Lett. 1978, 58, 606.
 (9) David, S. J.; Coombe, R. D. J. Phys. Chem. 1986, 90, 3260.

<sup>(10)</sup> Habdas, J.; Wategaonkar, S.; Setser, D. W. J. Phys. Chem. 1987, 91, 451.

<sup>(11)</sup> Jourdain, J. L.; LeBras, G.; Poulet, G.; Combourieu, J. Combust. Flame 1979, 34, 13.

<sup>(12)</sup> Ganguli, P. S.; Kaufman, M. Chem. Phys. Lett. 1974, 25, 221.



Figure 2. Spectrum of ultraviolet emission from the P + N<sub>3</sub> chemiluminescent system. Known transitions in PN, PF, NH, and CN are labeled.



**Figure 3.** Vibrational population distribution in PN(A<sup>1</sup>II) produced by the P + N<sub>3</sub> system, plotted as f(v) (fractional population) vs. vibrational energy.

and  $N_3$  radicals. The most intense bands of the spectrum were associated with the PN  $A^1\Pi \rightarrow X^1\Sigma^+$  transition, shown in Figure 2. Bands from vibrational levels of the  $A(^1\Pi)$  state up to v' =5 were found. From the bond dissociation energy of PN ( $D_o =$ 613.6 kJ mol<sup>-1</sup>)<sup>13</sup> and the heat of formation of  $N_3$  reported by Clark and Clyne<sup>14</sup> (414 kJ mol<sup>-1</sup>), the exothermicity of reaction 2 is calculated to be 555.2 kJ mol<sup>-1</sup>. This value is in good agreement with the energy required to excite PN to v' = 5 of its  $a^1\Pi$  state, 557.6 kJ mol<sup>-1</sup>. In the recent work noted above by Habdas et al.<sup>10</sup> a different value for the heat of formation of  $N_3$ was reported, 428.5 kJ mol<sup>-1</sup>. From this value, the exothermicity of reaction 2 is determined to be 616.1 kJ mol<sup>-1</sup>, much in excess of the excitation limit observed in PN(A<sup>1</sup>\Pi).

The radiative lifetime of PN(A) has been reported<sup>15</sup> to be 230 ns. For the pressures typical of our experiments ( $\sim 1.5$  Torr), an excited PN(A) molecule would suffer at most three collisions during this time period with the argon diluent. Hence, the intensity distribution from spectra such as that in Figure 2 should accurately reflect the initial vibrational distribution in PN(A). Since Franck-Condon factors have been reported<sup>16</sup> only for transitions from v' = 0, 1, and 2 of PN(A), the vibrational distribution was calculated from the integrated intensities of the bands in spectra such as that shown in Figure 2. This distribution is plotted as f(v), the fractional population of vibrational level v, vs. energy in Figure 3. Fractional populations calculated from the Franck-Condon factors for transitions from v' = 0, 1, and 2 were in good agreement with the values found from relative intensity measurements. From the plot it is apparent that the high-energy limit of the distribution is in good agreement with the exothermicity of reaction 2 calculate from the Clark and Clyne value<sup>14</sup> for  $\Delta H_{f}(N_{3})$ . The data indicate that about 25% of the exess energy available to PN(A) is channeled into vibration. If the exothermicity of reaction 2 is calculated from the more recent value<sup>10</sup> for  $\Delta H_f(N_3)$ , the portion of the excess energy channeled into vibration is 15%.

The spectrum exhibited a second system of bands in the 300–400-nm range. These bands were quite weak, but were well resolved, particularly at longer wavelengths. Analysis of the frequencies of these bands gave results consistent with their assignment as PF B<sup>3</sup>II  $\rightarrow X^{3}\Sigma^{-}$ . The triplet splitting for PF B<sup>3</sup>II<sub>0,1,2</sub> produces three subbands<sup>17</sup> spaced by roughly 140 cm<sup>-1</sup>. These splittings were readily apparent in the longer wavelength bands of the system.

The third system found was recorded in the visible from 400-600 nm and is shown in Figure 4. The large peak near 529 nm corresponds to the NF  $b^1\Sigma^+ \rightarrow X^3\Sigma^-$  transition, a well-known feature in the chemiluminescence from the F + HN<sub>3</sub> reaction. A Deslandres table was constructed from the frequencies of the other bands shown in Figure 4, and the results are given in Table I. Molecular constants for the upper and lower states of the transition were calculated from a multiple regression analysis of the frequencies. The results of this calculation are shown in Table II, along with known values for the ground state of PN. It is clear from the data in the table that the lower state of the transition is PN(X<sup>1</sup>\Sigma<sup>+</sup>). The constants for the upper state are not at all similar to those for PN(A<sup>1</sup>\Pi), previously the only known excited electronic state of PN.

A number of experiments were performed in an effort to record higher resolution spectra of the 0,3 and 0,4 bands of the transition. These experiments made use of a 1.0-m monochromator as described above. Figure 5 shows the 0,4 band near 488 nm, recorded with a spectral slitwidth near 0.10 nm. It is evident that the band exhibits a single sharp head and is strongly red degraded. Similar results were found for 0,3 and other bands.

Figure 6 shows a typical time profile for the new PN band system. Data such as those shown in the figure were fitted to a sum of rising and falling exponential terms as follows:

$$I(t) = A(e^{-\lambda_{d}t} - e^{-\lambda_{r}t})$$
(3)

where  $\lambda_r$  and  $\lambda_d$  are the rise and decay rates, respectively. The rise rate  $\lambda_r$  was found to be approximately 4 ms. The decay rate varied inversely with the N<sub>3</sub> density (the initial HN<sub>3</sub> density), and was found to be equal to the P + N<sub>3</sub> reaction rate, as measured from the resonance fluorescence experiments described above. Time profiles of the PN A  $\rightarrow$  X emission were measured in a similar manner. These profiles indicated a mixing limited rise (corresponding to the short radiative lifetime of the excited state) followed by a decay which corresponded to the P + N<sub>3</sub> rate. PN A  $\rightarrow$  X time profiles were measured for a number of N<sub>3</sub> densities, and good agreement with the P+N<sub>3</sub> rate constant (determined as above) was found, except for very high HN<sub>3</sub> flow rates where

<sup>(13)</sup> Huber, K. P.; Herzberg, G. Constants of Diatomic Molecules; Van Nostrand: New York, 1979.

 <sup>(14)</sup> Clark, T. C.; Clyne, M. A. A. Trans. Faraday Soc. 1970, 66, 877.
 (15) Moeller, M. B.; McKeever, M. R.; Silvers, S. J. Chem. Phys. Lett. 1975, 31, 398.

<sup>(16)</sup> Moeller, M. B.; Silvers, S. J. Chem. Phys. Lett. 1973, 19, 78.

<sup>(17)</sup> Douglas, A. E.; Frankowiak, M. Can. J. Phys. 1962, 40, 832.

#### TABLE II: Molecular Constants for the Visible System in PN

	-
upper state	$T_{\rm e} = 25839 \pm 16 \ {\rm cm}^{-1}$
	$\omega_{e}' = 957 \pm 8 \text{ cm}^{-1}$
	$\omega_{e}' x_{e}' = 18 \pm 2 \text{ cm}^{-1}$
lower state	$\omega_{e}'' = 1321 \pm 5 \text{ cm}^{-1}$
	$\omega_{e}'' x_{e}'' = 6 \pm 1 \text{ cm}^{-1}$
ground state <sup>a</sup> $(X^1\Sigma^+)$	$\omega_{\rm e}'' = 1337.24 \ {\rm cm}^{-1}$
	$\omega_{e}''x_{e}'' = 6.983 \text{ cm}^{-1}$
	• •

<sup>a</sup>Reference 13.

the system was limited by the fluorine atom flow.

#### Discussion

To our knowledge, the spectrum shown in Figure 4 and the bands in Table I represent the first observation of a new excited electronic state of PN. A number of characteristics of this excited state are apparent from the data. First, the state is clearly Franck-Condon shifted from the ground state (i.e.,  $r_e' > r_e''$ ), with the 0,3 transition having the greatest intensity. Further, the bands are red degraded, again indicating that  $r_e' > r_e''$  and that  $B_e' < B_{e''}$ . The smaller vibrational frequency in the upper state implies that the potential curve of this state is broader and shallower than that of the ground state. As noted above, the molecular constants of the lower state agree well with known values for PN(X<sup>1</sup>Σ<sup>+</sup>), indicating that the transition terminates on the ground state of the molecule. From the value of  $T_e$  shown in Table II, the new excited state is placed between the ground state and PN(A<sup>1</sup>\Pi).

From application of the rules of spin conservation to reaction 2, the product PN is expected to be formed in excited triplet or quintet states. Since quintet states are not likely to be bound to the extent required to give rise to the observed spectrum, we infer that the new state is an excited triplet. This inference is borne out by the time profile of the emission as discussed above. Since the time decay of the emission is identified as the  $P + N_3$  reaction rate, the rise should correspond to the lifetime of the excited emitter. Hence, the measured rise time (4 ms) should represent a lower limit on the radiative lifetime of the state, indicating that it is metastable.

As discussed above, orbital angular momentum correlations suggest that  $P + N_3$  should produce PN in the excited  $a^3\Pi$  state which correlates to  $P(^4S) + N(^2D)$ . If PN is structurally similar to N<sub>2</sub>, this state will lie above the  $a'^{3}\Sigma^{+}$  state (the analogue of  $N_2(A^3\Sigma_u^+)$ . In this case, a visible or infrared  $a^3\Pi \rightarrow a'^3\Sigma^+$ transition (analogous to the first positive emission in N<sub>2</sub>) might be expected, followed by  $a'^{3}\Sigma^{+} \rightarrow X^{1}\Sigma^{+}$  emission. No bands attributable to  $a \rightarrow a'$  emission were found in our experiments, up to the long wavelength cutoff of the PMT ( $\sim$ 890 nm). If PN is structurally similar to CO or CS, the  $a^3\Pi$  state will lie below the  $a^{\prime 3}\Sigma^+$  state and the observed bands would correspond to the  $a^3\Pi \rightarrow X^1\Sigma^+$  transition. The identity of the upper state of the emitter as  $a^{3}\Pi$  or  $a^{\prime 3}\Sigma^{+}$  can be ascertained from a higher resolution study of the bands. For example, the Cameron bands of CO are distinctly double headed because of the spin splitting in the  ${}^{3}\Pi$ state. As is evident in Figure 5, no such splitting is observed in the new PN bands, within the 0.10-nm  $(4 \text{ cm}^{-1})$  resolution of the data. The splitting<sup>18</sup> between the double heads in bands of the  $a^{3}\Pi \rightarrow X^{1}\Sigma^{+}$  transition in the isoelectronic molecule CS is 17 cm<sup>-1</sup>. If it is assumed that a similar splitting should occur for the  $a^3\Pi$  $\rightarrow X^1 \Sigma^+$  transition in PN, then the present data would strongly favor an assignment of the upper state of the new bands as  $a^{3}\Sigma^{+}$ .

The time profiles of the PN A  $\rightarrow$  X emission and the emission from the PN metastables suggest that both excited states are produced by the P + N<sub>3</sub> reaction. PN A  $\rightarrow$  X emission has been observed,<sup>19</sup> however, from excitation of PN in collisions with N<sub>2</sub>(A) metastables. Since some weak N<sub>2</sub> first positive emission was found in our experiments, we tested the role of N<sub>2</sub>(A) metastables by adding NO (an efficient N<sub>2</sub>(A) quencher) to the flow. Although NO  $\gamma$  band emission was produced, neither the PN A  $\rightarrow$  X nor

	= 10	6570
	"a	8) 1
	6 =a	16111 (847) 16958 16958 (820) 17778 (120
	<i>v</i> ″ = 8	1/332 (1221) (863) 18195 (1237)
	v'' = T	16722 (921) 17643 (903) (803) (879) 19425 (1230)
	v'' = 6	17973 (1250) 19772 (1226) (906) 20678 (1253)
	v'' = 5	19204 (1231) (925) 20129 (915) 21044 (1272) (882) 21926 (1248)
	v'' = 4	20458 (1271) (928) 21386 (1257) (900) 22286 (1242) (914) 23200 (1274)
es Table for the Visible Bands of PN	v'' = 3	21743 (1286) (931) 22674 (1288) (889) 233563 (1277)
	v'' = 2	23042 (1299) (927) 23969 (1295) (906) 24876 (1313)
	<i>u</i> " = 1	24349 (1307)
LE I: Deslandry	v'' = 0	25674 (1325)
TABI	'n,	<b>4</b> 3 7 1 0

<sup>(18)</sup> Taylor, G. W.; Setser, D. W.; Coxon, J. A. J. Mol. Spectrosc. 1972, 44, 108.

<sup>(19)</sup> Hood, W. H.; Niemczyk, T. M. Anal. Chem. 1986, 58, 210.



Figure 4. Spectrum of visible emission from the  $P + N_3$  chemiluminescent system. Progressions of a new transition in PN are labeled. A Deslandres table for this system is shown in Table I.



Figure 5. Detail of the 0,4 band of the visible system of PN, recorded with a spectral slitwidth of 0.10 nm ( $\sim 4 \text{ cm}^{-1}$ ).



Figure 6. Time dependence of the intensity of the 0,3 band of the visible system of PN. The line drawn through the data is a least-squares fit to a sum of rising and falling exponential terms.

the new band system in PN was quenched. Hence, we believe that both states are indeed produced by  $P + N_3$ . The observation of strong PN A  $\rightarrow$  X emission from the reaction does not imply, however, that the angular momentum constraints on the reaction are weak. At the steady-state (the maxima in the time profiles of the emissions), the densities of the emitters are given by the ratio of their rates of formation and their rates of decay in the system:  $[A] = \lambda_f^A / \lambda_d^A$  and  $[M] = \lambda_f^M / \lambda_d^M$ , where [A] and [M] are the densities of PN(A) and the PN metastable, respectively, and the  $\lambda$ 's are rates. The observed intensities are given by  $I_{A \rightarrow X}$ =  $[A]\lambda_r^A$  and  $I_{M \rightarrow X} = [M]\lambda_r^M$ , where the  $\lambda_r$  are radiative rates. Hence

$$\frac{\lambda_{\rm f}^{\rm M}}{\lambda_{\rm f}^{\rm A}} = \frac{[{\rm M}]\lambda_{\rm d}^{\rm M}}{[{\rm A}]\lambda_{\rm d}^{\rm A}} = \left(\frac{I_{{\rm M}\to{\rm X}}}{I_{{\rm A}\to{\rm X}}}\right) \left(\frac{\lambda_{\rm d}^{\rm M}/\lambda_{\rm r}^{\rm M}}{\lambda_{\rm d}^{\rm A}/\lambda_{\rm r}^{\rm A}}\right)$$

In view of the short radiative lifetime^{15} of PN(A),  $\lambda_d^A\approx\lambda_r^A,$  and hence

$$\frac{\lambda_{\rm r}^{\rm M}}{\lambda_{\rm f}^{\rm A}} = \left(\frac{I_{\rm M\to X}}{I_{\rm A\to X}}\right) \left(\frac{\lambda_{\rm d}^{\rm M}}{\lambda_{\rm r}^{\rm M}}\right)$$

As noted above,  $I_{M\to X}/I_{A\to X} \approx 0.1$ . This value must be divided by the fraction of the PN metastables that actually radiate to obtain the relative rates of formation  $\lambda_f^M/\lambda_f^A$ . This fraction is likely to be very small, since the large majority of the PN metastables may well be quenched by collisions with other species present or the reactor walls prior to radiation. We note in this regard that  $N_2(A^3\Sigma_u^+)$  metastables are thought to be quenched with near unit efficiency by a variety of surfaces.<sup>20</sup>

The rate constant measured for  $P + N_3$  is roughly a factor of three smaller than that recently determined<sup>9</sup> for  $N + N_3$ . This difference may indicate the presence of a small barrier along the reaction coordinate of the  $P + N_3$  system. We note in this regard that  $P_4$  is a strongly bound molecule, and calculations have suggested that the analogous  $N_4$  species may be bound. In view of the fact that these species have tetrahedral symmetry, however, it seems unlikely that a similar PN<sub>3</sub> species would play a role in the  $P + N_3$  reaction.

## Summary and Conclusions

The strong angular momentum constraints on  $N_3$  reactions have been specifically used for the generation of a new metastable excited electronic state of PN from the P +  $N_3$  reaction. It is expected that this new state, which is significantly Franck-Condon shifted from the ground state, is either  $a^3\Pi$  or  $a'^3\Pi^+$ . The single-headed nature of the bands favors assignment of the excited state as  $a'^3\Sigma^+$ . Its radiative lifetime would appear to be greater than 4 ms. The P +  $N_3$  reaction also produces PN(A<sup>1</sup>\Pi), although the branching fraction for production of this state may be very low, as expected from the angular momentum correlations.

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Registry No. P, 7723-14-0; N<sub>3</sub>, 12596-60-0; PN, 17739-47-8.

<sup>(20)</sup> Meyer, J. A.; Klosterboer, D. H.; Setser, D. W. J. Chem. Phys. 1971, 55, 2084.