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R. D. Coombe

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# Photodissociation of bromine azide

R. D. Coombe

Department of Chemistry, University of Denver, Denver, Colorado 80208 (Received 11 January 1983; accepted 14 March 1983)

Bromine azide was photodissociated by using excimer laser sources at 222 and 308 nm. The primary fragments produced are  $N_2(A^{-3}\Sigma_{+}^{-})$  and  $NBr(X^{-3}\Sigma^{-})$ , with some  $N_2(B^{-3}\Pi_g)$  produced at 222 nm. In contrast to analogous experiments with ClN<sub>3</sub>, NBr( $b^{-1}\Sigma^{-}$ ) was not observed. From the formation of these products, it is concluded that the heat of formation of BrN<sub>3</sub> is greater than 122 kcal/mol. The  $N_2(A^{-3}\Sigma_{+}^{-})$  produced by photodissociation decays by a combination of pseudo-first order and second order processes. The first order process is reaction with the parent BrN<sub>3</sub>, generating  $N_2(B^{-3}\Pi_g)$  as a product. The rate constant for  $N_2(A^{-3}\Sigma_{+}^{-})$  quenching by BrN<sub>3</sub> is  $1.2 \pm 0.2 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This first order process dominates for photolysis at 222 nm. The second order process involves reaction of  $N_2(A^{-3}\Sigma_{+}^{-})$  with another photodissociation fragment, and produces intense emission in the vicinity of 292 nm. This emission has been tentatively identified as the  $D'({}^{3}\Pi_{2}_{g}) \rightarrow A'({}^{3}\Pi_{2}_{u})$  transition in Br<sub>2</sub>. The second order process is much more important in the decay of  $N_2(A^{-3}\Sigma_{+}^{+})$  produced by photolysis at 308 nm.

#### INTRODUCTION

A paper recently published in this journal described experiments in which gaseous ClN<sub>3</sub> was photodissociated by pulsed laser radiation.<sup>1</sup> The results showed that although the longest wavelength features of the absorption spectrum of this molecule are similar to those of other covalent azides and isocyanates,  $^{2,3}$  the photodissociation dynamics are very different. $^{4,5}$  In particular, ClN<sub>3</sub> is metastable with respect to the ground electronic states of NCl and  $N_2$ , and the extra energy made available allows the production of excited electronic states of both these fragments for photolysis wavelengths above the quartz limit (~200 nm). Direct production of  $N_2(A^{3}\Sigma_{\mu}^{*})$ metastables, which carry nearly 144 kcal/mol, was found for photolysis at both 193 and 249 nm. In addition, NCl( $b^{1}\Sigma^{*}\nu'$ ) was produced, and the radiative and collisional decay kinetics of this species were studied.<sup>6</sup>

These results suggest that photodissociation of halogen azides may be used for real time studies of the chemistry of nitrogen halide diatomics, as well as offering a very unique pulsed source of electronically excited molecular nitrogen. Within this context, this paper presents initial results of a study of the laser photodissociation of  $BrN_3$ . Since its original synthesis by Spencer<sup>7</sup> in 1925, bromine azide has been investigated by only a few groups. Milligan and Jacox,<sup>8</sup> using low temperature matrix isolation techniques, measured the infrared spectrum of the trapped molecule, and observed the production of NBr upon its photolysis with broadband UV radiation. Clark and Clyne<sup>9</sup> noted experiments with BrN<sub>3</sub> as part of a study of nitrogen chlorides. Dehnicke<sup>10</sup> reported UV absorption spectra for BrN<sub>3</sub> and other halogen azides dissolved in hexane and  $CCl_4$ , pointing out similarities with other covalent azides. Most recently, Frost and co-workers<sup>11</sup> prepared BrN<sub>3</sub> and measured its photoelectron spectrum.

Very little of this limited body of information on  $BrN_3$ relates to the dissociation dynamics of the molecule. The objectives of the work described in this paper were therefore to establish the energetics of  $BrN_3$  dissociation to particular fragments, and to observe the decay kinetics of excited species in the environment of the parent molecules and the dissociation fragments. Gaseous  $BrN_3$  was photolyzed at 222 and 308 nm with the output of a pulsed excimer laser. Unexpectedly, the results obtained were quite different from those found in the work on  $ClN_3$  noted above.<sup>1,6</sup> In particular,  $BrN_3$ would appear to be much more metastable than  $ClN_3$ , carrying a minimum of 51 kcal/mol of energy with respect to the ground states of NBr and N<sub>2</sub>. Apart from allowing direct production of excited triplet states of N<sub>2</sub> at photolysis wavelengths as long as 308 nm, this additional energy makes possible a number of interesting reactions among  $BrN_3$  and its dissociation fragments, analogs of which were not observed in the  $ClN_3$  case.

#### EXPERIMENTAL DETAILS

#### Generation of gaseous BrN<sub>3</sub>

Although the chemistry used for the preparation of  $BrN_3$  was taken from Spencer's original synthesis, <sup>7</sup> the apparatus and method employed in these experiments were much different, more closely resembling the technique described by Frost and co-workers.<sup>11</sup> In view of the brevity of previous descriptions of the synthesis of this compound, we will describe the method in some detail. A diagram of the BrN3 generator is shown in Fig. 1. The apparatus was assembled inside a fume hood, with the glass portions positioned behind a polycarbonate blast shield. A stream of  $N_2$  saturated in  $Br_2$ was produced by bubbling nitrogen gas through liquid bromine contained in a trap held at 273 K. Since the pressure in the trap was regulated to 800 Torr, the bromine accounted for 8% of the gas mixture. The  $Br_2/N_2$  mixture was admitted to the reactor via a small regulating valve as shown. The reactor was operated under vacuum at a total pressure of ~60 Torr. Bromine azide was produced by passage of the  $Br_2/N_2$  mixture through a U tube in which  $H_2O$ -moistened NaN<sub>3</sub> powder was suspended on glass wool. Although the exact process by which BrN<sub>3</sub> is generated is unknown, HN<sub>3</sub> would appear to be an intermediate, since its presence has

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FIG. 1. Diagram of the apparatus used for preparation of gaseous  $BrN_3$ .

been observed downstream (see discussion below and in Ref. 1). One possible reaction scheme is as follows:

 $Br_2(g) + H_2O(1) \rightarrow HOBr(aq) + HBr(aq)$ , (1)

 $HBr(aq) + NaN_{3}(s) \rightarrow HN_{3}(aq) + NaBr(aq) , \qquad (2)$ 

$$HN_{3}(aq) + HOBr(aq) - BrN_{3}(g) + H_{2}O(1) . \qquad (3)$$

 $H_2O$  is removed from the vapor exiting the first U tube by anhydrous  $CaSO_4$  ("Drierite") contained in a second U tube.

The generator effluent was passed directly through a 10 cm long cell positioned in the optical path of a Perkin-Elmer 337 infrared spectrometer. In typical experiments, the relative amount of BrN3 present in the flow was monitored by the strength of the absorption at 2060 cm<sup>-1</sup> (see below). The pressure in the generator and IR cell was controlled by the flow rate of the  $N_2$ , and by a regulating valve downstream of the cell. The regulating valve was opened such that a pressure of 60 Torr in the generator and IR cell produced a pressure of 6 Torr in the photolysis cell. Since BrN3 detonates upon condensation, <sup>7</sup> the  $BrN_3/N_2$  flow was not trapped prior to entering the pump. Instead, the stream of gases was passed through a coil of copper tubing held at  $\sim$  350 K, in the hope of thermally decomposing the azide. The pump oil was changed after every experiment.

The nitrogen flow rate was held at ~10 sccm, as monitored by using a rotameter flowmeter (Matheson). The generator pressure was monitored with a Granville-Phillips convectron pressure gauge. For the conditions noted above, one filling of the NaN<sub>3</sub> U tube would last for 4 to 6 h of run time. At the end of each experiment, N<sub>2</sub> was passed through the reactor (bypassing the Br<sub>2</sub> saturator) at 60 Torr until the BrN<sub>3</sub> features in the IR spectrum had disappeared; this usually required about 1 h. The reactor was then pressured up to 1 atm, and N<sub>2</sub> passed through the system (which was vented into the fume hood) for 12 h. Using these methods, no explosions occurred in our experiments.

The lifetime of the  $BrN_3$  in the stainless steel IR cell was investigated by filling the cell to 60 Torr with the reactor effluent, closing off the cell, and monitoring the decay of the  $BrN_3$  absorptions. The IR beam was blocked except for short periods during which the transmission was measured. The  $BrN_3$  concentration was found to decay nearly linearly with time, reaching 10% of its initial value after 45 min.

#### Apparatus for photolysis experiments

The apparatus used for pulsed photolysis of BrN<sub>3</sub> was much like that described in Ref. 1, with some differences in instrumentation. The light source used in the experiments was a Tachisto 400XR multigas laser which produced an output at 308 nm (XeCl) of 200 mJ and 30 mJ at 222 nm (KrCl), at a repetition rate of 2 Hz. The photolysis cell was a 10 cm long stainless steel block with two perpendicular 2.5 cm diam channels for transmission of the laser beam and observation of emissions. The channel ends were sealed with four 2 mm thick  $CaF_2$  windows. The laser energy admitted to the cell was limited by an iris positioned in front of the entrance window, and the maximum fluences used were 40 mJ/cm<sup>2</sup> at 308 nm and 6 mJ/cm<sup>2</sup> at 222 nm. The laser energy was monitored by using a Scientech energy meter positioned at the output window of the cell. As noted from the UV absorption spectra presented below, these laser fluences resulted in dissociation of a maximum of 4% of the  $\text{BrN}_3$  present in the photolysis zone. The pressure in the photolysis cell (typically 6 Torr) was monitored with a Granville-Phillips convectron gauge.

Emissions produced by the photodissociation were observed at 90° to the axis of the laser beam. The emission was dispersed by a 0.25 m Jarrell-Ash scanning monochromator, which was calibrated with the output of

J. Chem. Phys., Vol. 79, No. 1, 1 July 1983



FIG. 2. Absorption spectrum of 64 Torr of a  $BrN_3/N_2$  sample from 190 to 420 nm. The weak feature peaked near 415 nm corresponds to a  $Br_2$  impurity.

a low pressure mercury lamp. Emissions at wavelengths between 200 and 900 nm were detected with a GaAs photomultiplier tube (RCA C31034), which was mounted in a thermoelectrically cooled housing to reduce dark noise. The output of the PMT was amplified by a Hewlett-Packard 465 fast amplifier before further analysis.

Two kinds of experiments were performed with this apparatus. First, spectra of the emissions were recorded by scanning the monochromator as the laser was pulsed at 2 Hz. The signal strength in a selected time interval after the laser pulse was integrated by using an Evans Associates 4130 gated integrator, which also amplified the integrated signal. The output voltage corresponding to the integrated signal was plotted vs the monochromator wavelength on a Hewlett-Packard 7100B strip chart recorder. In a second type of experiment, the temporal behavior of individual emission features was observed. In this case, the monochromator was fixed at the wavelength of the feature of interest, and the time varying output of the photomultiplier tube (amplified by the HP-465) was digitized, stored, and averaged over successive laser pulses by using a Nicolet 1270 signal processing system. The averaged data were recorded with a Hewlett-Packard 7035A X-Y plotter. The time response of this data collection system was limited by the HP-465 amplifier, which has a bandwidth of 2 MHz.

The chemicals used in the experiments were  $NaN_3$ (Alfa-Ventron, 99%), Br<sub>2</sub> (Mallinckrodt, Analytical grade), N<sub>2</sub> (Matheson H. P., 99.99%), and NO (Matheson C. P., 99.0%). These chemicals were used without further purification.

## RESULTS

#### Absorption spectra of BrN<sub>3</sub>

The infrared absorption spectrum of gaseous  $BrN_3$  was measured with the Perkin-Elmer 337 spectrometer noted above. The spectrum was recorded as the  $BrN_3/N_2$  mixture was passed continuously through a

10 cm absorption cell at pressures on the order of 60 Torr. Since the windows of the cell were  $CaF_2$  disks, the spectrum was recorded from 4000 to  $1000 \text{ cm}^{-1}$ . Only three absorption features were evident in the spectrum, and all of these are attributed to BrN<sub>3</sub>. A feature found at 1145  $cm^{-1}$  corresponds to the N<sub>3</sub> symmetric stretching vibration ( $\nu_4$ ), and a strong band at 2060 cm<sup>-1</sup> represents the  $N_3$  asymmetric stretch ( $\nu_2$ ). These frequencies are in good agreement with those reported by Milligan and Jacox<sup>8</sup> from low temperature matrix isolation data. In addition, we observed a weaker feature near 2290 cm<sup>-1</sup>, which was not reported from the matrix work. The intensity of this band tracked those of the other two features as the Br<sub>2</sub> flowrate in the generator was varied. Its frequency corresponds closely to that expected for the overtone  $2\nu_4$ . The analogous overtone, with similar intensity relative to  $\nu_2$ , has been observed for HN<sub>3</sub>,<sup>12</sup>

The ultraviolet spectrum of bromine azide at wavelengths above the quartz limit was recorded with a Cary 219 UV-visible spectrometer. For this purpose, a stainless steel 10 cm cell was evacuated and then filled with the  $BrN_3/N_2$  mixture. The cell was thoroughly passivated with the gas mixture prior to measurement of the spectrum, such that the lifetime of the  $BrN_3$  in the cell was on the order of 45 min as noted above. The UV spectrum recorded is shown in Fig. 2. Four absorption features are evident, three of which are attributable to BrN<sub>3</sub>. The broad, weak feature centered near 415 nm corresponds closely to the known spectrum of  $Br_2$ . The stronger features centered at 287 and 216 nm appear to be associated with  $BrN_3$ , as does the strongest feature which continues to rise below 190 nm. These features correspond closely with those found by Dehnicke<sup>10</sup> for BrN<sub>3</sub> in hexane and CCl<sub>4</sub> solutions, and resemble those found in the gas phase spectrum of  $ClN_3$ ,<sup>1</sup> but are slightly shifted to the red. The absorptions appear to be continuous in nature. The extinction coefficients associated with these features can be estimated only if an assumption is made concerning the concentration of BrN3 in the cell. From the known extinction



FIG. 3. Spectrum of visible emissions produced by photolysis of 6 Torr of a  $BrN_3: N_2 \simeq 1: 15$ sample at 222 nm. The features labeled correspond to bands of the  $N_2$  first positive transition.

coefficient of Br<sub>2</sub> at 410 nm, the absorption observed at this wavelength corresponds to a Br<sub>2</sub> partial pressure of 1.8 Torr in the cell. If all of the bromine in the cell is assumed to be present as either  $Br_2$  or  $BrN_3$ , then, from the initial bromine flowrate and the reaction mechanism noted above, the BrN<sub>3</sub> partial pressure is calculated to be 3.3 Torr. From the measured time decay of BrN3 in the cell, this result corresponds closely to decay of an initially pure sample of  $BrN_3/N_2$  to  $BrN_3/Br_2/N_2$  in the time interval between filling of the cell and measurement of the UV spectrum, suggesting that the initial yield of BrN3 is near unity. The reduction of the BrN<sub>3</sub> density in the cell was in fact verified by measurement of the IR spectrum of the sample after the UV spectrum was recorded. This treatment yields extinction coefficients of 260 and 1310 l mol<sup>-1</sup> cm<sup>-1</sup> for the absorption bands at 287 and 216 nm, respectively.

The ultraviolet absorption spectrum also indicates that  $BrN_3$  will absorb the output of excimer lasers operating on KrCl (222 nm) and XeCl (308 nm) transitions. The extinction coefficients at 222 and 308 nm are 1230 and 192  $\ell$  mol<sup>-1</sup> cm<sup>-1</sup>, respectively.

#### Photolysis at 222 nm

KrCl excimer laser photolysis of BrN<sub>3</sub>/N<sub>2</sub> mixtures, at a total pressure of 6 Torr, produced intense emissions in both the visible and ultraviolet regions of the spectrum. The visible emission recorded between 640 and 800 nm is shown in Fig. 3. All of the features observed in this region correspond to the well known first positive  $(B^{3}\Pi_{e} \rightarrow A^{3}\Sigma_{w}^{*})$  spectrum of molecular nitrogen. Emission from  $B(^{3}\Pi_{e})$  vibrational levels as high as v' = 6(and possibly higher levels in the incompletely resolved regions of the spectrum) was observed, in the  $\Delta v = 3$ , 2, and 1 sequences. In strong contrast to results obtained from the photodissociation of ClN<sub>3</sub>, <sup>1</sup> no visible emission corresponding to the  $b^{1}\Sigma^{*} \rightarrow X^{3}\Sigma^{-}$  transition of NBr was found. The  $\Delta v = 0$  sequence of this transition should appear as a very sharp feature near 674 nm. The  $\Delta v = +1$ sequence should occur near 710 nm, a region unobscurred by the N<sub>2</sub>  $B \rightarrow A$  emissions. No evidence of NBr( $b^{1}\Sigma^{*}$ ) was found in any of the numerous experiments performed. It is possible that singlet products are produced via a lower energy channel leading to NBr( $a^{1}\Delta$ )  $+ N_{2}(X^{1}\Sigma_{s}^{*})$ . Emission from NBr ( $a^{1}\Delta$ ) occurs in the vicinity of 1.1  $\mu$ m, <sup>13</sup> however, beyond the sensitivity range of our photomultiplier tube.

The variation of the  $N_2 B - A$  emission intensity with incident laser energy was investigated by measuring the total intensity produced near 770 nm, within a 100  $\mu$ s time gate after the laser pulse (see discussion of the time decay of the emission below). For these experiments, the monochromator slits were set at 2.5 mm, corresponding to a spectral width of 10 nm. The data obtained are shown as a plot of integrated intensity vs incident laser energy in Fig. 4(a). As shown, the emission varies linearly with the laser energy, indicating that the  $N_2(B^3\Pi_g)$  state is produced by a process involving only one photon; i.e., as a direct dissociation product or by reaction of a direct product with one of the species initially in the flow. A log-log plot of the intensity vs laser energy produced a line with a slope of 1.2, in support of this inference. The slight deviation from a slope of 1.0, a reproducible effect, indicates a small contribution from a higher order process to the formation of  $N_2(B^3\Pi_r)$ .

The temporal behavior of the  $N_2(B - A)$  emission exhibited a large initial "spike" followed by an exponential decay over several tens of microseconds, as is shown in Fig. 5 for the 3, 1 band near 760 nm. The decay time observed is many times longer than the known radiative lifetime of the  $N_2(B^3\Pi_x, v'=3)$  state, which is about



FIG. 4. Dependence of the integrated intensity of the N<sub>2</sub> first positive emission ( $\lambda = 770$  nm) on incident laser energy, for photolysis at 222 (A) and 308 nm (B).

6  $\mu$ s,<sup>14</sup> and suggests a collisional formation process. In fact, the  $N_2(B - A)$  decay time was found to increase with decreasing BrN<sub>3</sub> flow, and a number of experiments were performed to quantify this effect. For this purpose, a substantial flow of  $BrN_3/N_2$  was established in the generator. The Br<sub>2</sub> flow was then stopped and replaced by a flow of pure nitrogen. Under these circumstances, the proportion of  $BrN_3$  in the generator output (at a fixed total pressure) gradually fell over a period of 30 to 60 min, such that the  $N_2(B - A)$  decay rate could be measured at a number of different BrN3 concentrations. These relative concentrations were monitored by observing the intensity of the IR absorption at 2060 cm<sup>-1</sup>. The time decay of the N<sub>2</sub>  $B \rightarrow A$  emission was found to be exponential, with the exception of experiments at the largest BrN<sub>3</sub> densities. In this case, a very slight curvature was observed in the plots of ln (intensity) vs time, suggesting the contribution of a higher order process to the formation rate. Several experiments were performed to amass the data shown in Fig. 6, a plot of the decay times vs the relative concentrations of BrN<sub>3</sub>. The decay times were determined from the slopes of ln (intensity) vs time plots. The relative concentrations are indicated as  $\ln(I_0/I)$ , where

 $I_0/I$  is the inverse of the IR transmission at 2060 cm<sup>-1</sup>. The linearity of the plot and the near zero intercept strongly suggest that the time decay of the  $N_2(B - A)$ emission corresponds to a pseudo-first order formation reaction involving a direct photolysis product and the parent BrN<sub>3</sub>. The rate constant for this formation process can be obtained from the slope of the plot in Fig. 6 if it assumed, as discussed above, that the  $Br_2$  entering the generator is completely converted to BrN<sub>3</sub>. In this case, the BrN<sub>3</sub> flow rate at the initial (maximum) concentration corresponds to the Br<sub>2</sub> flow rate entering the generator. Making this assumption, the data indicate a pseudo-first order rate constant given by k = 1.2 $\times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Given the assumption concerning the BrN<sub>3</sub> concentration, this result should have an uncertainty of about 20% (i.e.,  $\pm 0.2 \times 10^{-12}$ ).

Upon closer observation of the initial spike, it was found that its duration also varied with the BrN<sub>3</sub> concentration. For the largest BrN<sub>3</sub> densities used (1.5  $\times 10^{16}$  cm<sup>-3</sup>), the width of the feature was about 2  $\mu$ s, increasing to 6  $\mu$ s for a very small BrN<sub>3</sub> flowrate. The latter value agrees well with the known radiative lifetime of N<sub>2</sub>(B<sup>3</sup>Π<sub>e</sub>, v' = 3).<sup>14</sup> In view of the incorporation of laser noise in the feature, and the finite time response (~ 1  $\mu$ s) of the data collection system, a more quantitative analysis of this effect was not possible. These results do suggest, however, that some N<sub>2</sub>(B<sup>3</sup>Π<sub>e</sub>) is produced directly by the 222 nm photolysis, and that the N<sub>2</sub>(B) state is collisionally quenched by BrN<sub>3</sub>.

As noted above, the long decay time of the N<sub>2</sub> first positive emission and its dependence on BrN<sub>3</sub> suggest production of this excited state by reaction between BrN<sub>3</sub> and a precursor which is a direct dissociation fragment. In view of the results obtained for the photodissociation of ClN<sub>3</sub>, <sup>1</sup> a likely candidate for this precursor would seem to be N<sub>2</sub>( $A^{3}\Sigma_{w}^{*}$ ), the lowest lying excited electronic state of N<sub>2</sub>. A test for the presence of this species after the laser pulse was made by adding a small flow of NO to the BrN<sub>3</sub>/N<sub>2</sub> stream, since it is well known that N<sub>2</sub>( $A^{3}\Sigma_{w}^{*}$ ) rapidly transfers its energy to NO,



FIG. 5. Temporal profile of the  $N_2$  first positive emission ( $\lambda = 760$  nm) produced by photolysis of 6 Torr of a  $BrN_3 : N_2 \simeq 1$ : 16 sample at 222 nm.



FIG. 6. Stern-Volmer plot of the decay rate of the N2 first positive emission vs the relative BrN3 concentration. The relative concentration is plotted as  $\ln (I_0/I)$ , the log of the measured infrared absorption at 2060 cm<sup>-1</sup>. Conversion to actual BrN<sub>3</sub> densities as described in the text yields a pseudo-first order rate constant  $k = 1.2 \pm 0.2 \times 10^{-12} \text{ cm}^3 \text{ mole}$ cule<sup>-1</sup> s<sup>-1</sup> for the quenching of  $N_2(A^{3}\Sigma_{u}^{*})$ by BrN<sub>3</sub>.

producing the NO( $A^{2}\Sigma^{*}$ ) state.<sup>15</sup> Evidence of this transfer would be given by observation of the well known  $A^{2}\Sigma^{*} \rightarrow X^{2}\Pi \gamma$  bands of NO. Addition of NO to the BrN<sub>3</sub> system produced very strong NO  $\gamma$  band emission, with 13 bands of the  $A^2 \Sigma^* - X^2 \Pi$  system being well resolved between 200 and 290 nm. No bands of the NO  $\beta$  system  $(B^2\Pi \rightarrow X^2\Pi)$  were found, as is characteristic of transfer from N<sub>2</sub>( $A^{3}\Sigma_{\mu}^{*}$ ).<sup>15</sup> The temporal profile of the NO emission showed an unresolved rise, reflecting the 180 ns lifetime of the NO( $A^{2}\Sigma^{*}$ ) state, <sup>16</sup> followed by a decay over 5 to 10  $\mu$ s. The decay times observed agreed well with the measured NO flow rate and the known rate constant for quenching of  $N_2(A^3\Sigma_u^*)$  by NO.<sup>17</sup> Further, the temporal profile of the NO emission indicates that the  $N_2(A^{3}\Sigma'_{u})$  is not made simply by radiation from  $N_2(B^{3}\Pi_{e})$ , since in this case the NO emission would track the decay of the N<sub>2</sub> first positive emission. Hence, these data would suggest that the 222 nm photolysis produces  $N_2(A^3\Sigma_{\mu}^*)$  as a direct fragment. This fragment then reacts with the parent  $BrN_3$  to produce  $N_2(B^2\Pi_r)$ . This mechanism is in accord with linear variation of the N<sub>2</sub> first positive intensity with the incident laser energy.

As noted above, photolysis of BrN3 at 222 nm also produced very strong emission in the ultraviolet region. This emission, the spectrum of which is shown in Fig. 7, was in fact several times more intense than the  $N_2$ first positive emission. The spectrum is characterized by a very intense feature at 292 nm, with a tail extending to below 240 nm. Apart from a shoulder near 274 nm, no structure was observed within the resolution of the 0.25 m monochromator, which was operated with 500  $\mu$ m slits (spectral resolution 2.0 nm). Three much less intense features were found to the long wavelength side of the 292 nm emission, at 312, 335, and 359 nm. This

emission was observed only when BrN3 was present in the cell. As shown in Fig. 7, a sharp spike found in the 335 nm band near 336 nm can be attributed to NH( $A^{3}\Pi$  $-X^{3}\Sigma^{-}$ ) emission. As discussed by Stedman and Setser,<sup>18</sup> the NH( $A^{3}\Pi$ ) state is produced by collisions between  $N_2(A^3\Sigma_u^*)$  metastables and HN<sub>3</sub>. Observation of this feature corroborates evidence for the presence of  $N_2(A^3\Sigma_{*}^{*})$ in the system, and suggests an HN<sub>3</sub> impurity evolved in the BrN<sub>3</sub> generator. The strong UV emission shown in Fig. 7 does not correlate with any known spectra of NBr or  $N_2$ . By using the method described above, the emission at 292 nm was found to vary quadratically with the incident laser energy. A log-log plot of integrated intensity vs laser energy was found to have a slope of 2.0. This result implies that the emitter is produced either by a nonlinear two photon absorption process, by sequential absorption of two 222 nm photons via a real intermediate state, or by collisions between two fragments of the BrN<sub>3</sub> dissociation. The latter interpretation is supported by the time dependence of the emission, shown in Fig. 8. The temporal profile exhibits a short rise after the laser pulse (over about 5  $\mu$ s), followed by a long exponential decay over several tens of microseconds. This decay time was also found to be a function of the BrN<sub>3</sub> flow rate, increasing with decreasing flow of the BrN<sub>3</sub>. As in the case of the N<sub>2</sub> B - A emission, the ln(intensity) vs time plots showed slight curvature for the largest BrN<sub>3</sub> flow rates. An analysis similar to that discussed above was performed, and the results are shown as the triangles in Fig. 6. As is evident from the figure, the decay of the UV emission tracks the decay of the  $N_2$  first positive emission, suggesting that the UV emitter is also produced by a reaction involving  $N_2(A^3\Sigma_u^*)$  metastables. Further evidence to this effect was obtained by addition of NO to the system. The



FIG. 7. Spectrum of the ultraviolet emissions produced by photolysis of 6 Torr of a  $BrN_3: N_2 \simeq 1: 15$  sample at 222 nm.

presence of only small concentrations of NO effectively quenched the UV emission.

#### Photolysis at 308 nm

Experiments using a XeCl laser (308 nm) as the photolysis source were performed in a manner identical to that described above for 222 nm photolysis. Emission subsequent to the laser pulse was again observed in both the visible and ultraviolet regions of the spectrum. Analysis of the visible emission showed it to be due enitrely to N<sub>2</sub> first positive transitions. The emission intensity was many times weaker than was found for photolysis at 222 nm, however, and could be recorded only at very low resolution (spectral slitwidth 10 nm). No evidence of visible emission from NBr ( $b^{1}\Sigma^{*} - X^{3}\Sigma^{-}$ ) transitions was observed. The dependence of the N<sub>2</sub> first positive emission intensity on the laser energy was measured in the manner noted above, and the results are shown in Fig. 4(b). The intensity again varies linearly with the laser energy, a log-log plot of the data shown having a slope of 1. 1.



FIG. 8. Temporal profile of the 292 nm emission feature produced by photolysis of 6 Torr of a  $BrN_3 : N_2 \approx 1: 26$  sample at 222 nm.

#### J. Chem. Phys., Vol. 79, No. 1, 1 July 1983

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FIG. 9. Temporal profile of the 292 emission feature produced by photolysis of 6 Torr of a  $BrN_3: N_2 \simeq 1: 15$  sample at 308 nm. Also shown is a plot of (intensity)<sup>-1</sup> vs time for these data.

Measurements of the time decay of the N<sub>2</sub> first positive emission indicated a substantial difference from the results found for 222 nm photolysis, however. There was no initial "spike" suggestive of direct production of  $N_2(B^3\Pi_s)$ . Moreover, the decay time of the emission (again measured in the  $\Delta v = 2$  sequence) was much shorter for photolysis at 308 nm. The temporal profiles recorded were very noisy, even with signal averaging over many pulses and subtraction of baseline effects. Nonetheless, pseudo-first order decay times could be estimated from plots of ln(intensity) vs time, and in every case the value of  $\tau$  obtained from the slope was significantly shorter than that found for photolysis of a comparable concentration of BrN<sub>3</sub> at 222 nm. Addition of NO to the system again produced a spectrum of the NO  $\gamma$  bands, indicating the presence of N<sub>2</sub>( $A^{3}\Sigma_{u}^{*}$ ). The NO emission exhibited an unresolved rise followed by decay over 5 to 10  $\mu$ s.

The ultraviolet emission produced by photolysis at 308 nm was similar to that found for photolysis at 222 nm, the most intense feature occurring at 292 nm. The only difference apparent was that the 292 nm feature was better resolved from the shoulder at 274 nm. No structure apart from the broad features evident in Fig. 7 was found. The overall intensity of the UV emission was smaller than that found for 222 nm photolysis, although this effect was by no means as dramatic as for the visible emission. Addition of NO to the flow quenched the ultraviolet emission.

The time dependence of the 292 nm feature was observed for large flows of  $BrN_3$ . The results indicated the decay to be strongly nonexponential, in contrast to the data obtained for 222 nm photolysis. Figure 9 shows a typical temporal profile, which again exhibits the short rise after the laser pulse. The decay of the data shown is very nearly second order in the intensity, as is indicated by a plot of  $(intensity)^{-1}$  vs time shown in the figure.

## DISCUSSION

The photochemistry of small covalently bound azides is generally thought of in terms of singlet-singlet transitions involving orbitals localized on the nitrogen chain.<sup>2,3</sup> The excited singlet states produced by photolysis have been found to dissociate primarily to nitrene and molecular nitrogen fragments.<sup>2,4,5</sup> Since the dissociative state of the azide is a singlet, the fragments may be either both singlets or both triplets. For most small azides, the energy required to produce the lowest lying triplet state of N<sub>2</sub>, the N<sub>2</sub>( $A^{3}\Sigma_{\mu}^{*}$ ) state lying about 144 kcal/mol above the ground state, precludes dissociation to triplet fragments for photolysis above 200 nm. Numerous experiments on the photodissociation of HN<sub>3</sub>,<sup>4</sup>  $\mathrm{CH}_3\mathrm{N}_3$ , <sup>19</sup> NCN<sub>3</sub>, <sup>20</sup> and similar molecules have shown  $\mathrm{N}_2(X\,^1\Sigma_g^*)$  and the excited  $a\,^1\Delta$  state of the nitrene to be the dominant products for photolysis in this region. In the photolysis of ClN<sub>3</sub>, however, the 31 kcal/mol of energy born by the molecule with respect to the ground electronic states of NCl and  $N_2$  allows the direct production of  $N_2(A^3\Sigma_{\mu}^{*})$  at wavelengths as long as 249 nm, and photolysis of this molecule at 193 nm was found to produce  $N_2(A^3\Sigma_u^*)$  and  $NCl(b^1\Sigma^*)$  with equal probability.<sup>1</sup> In the present experiments with BrN<sub>3</sub>, the energy carried by the molecule allows production of  $N_2(A^3\Sigma_{\mu}^*)$  at wavelengths as long as 308 nm, and, in addition, controls the subsequent chemistry of this excited species in the system.

The observation of  $N_2(A^{3}\Sigma_{\nu}^{*})$  fragments from photolysis at 308 nm sets a lower limit on the energy carried by BrN<sub>3</sub> with respect to the ground states of NBr and N<sub>2</sub>:

$$BrN_{3}(X^{1}A') \stackrel{h\nu}{\underset{308}{\longrightarrow}} NBr(X^{3}\Sigma^{*}) + N_{2}(A^{3}\Sigma^{*}_{u}) .$$
 (4)

261

Since the  $N_2(A^{3}\Sigma_{\psi}^{*})$  state lies at 143.5 kcal/mol, and the photon energy is 92.8 kcal/mol, bromine azide must contain a minimum of 50.7 kcal/mol. This result can be used to estimate the heat of formation of the molecule, since it represents a lower limit on the heat of dissociation to the ground states of NBr and N<sub>2</sub>. Since the heat of formation of NBr( $X^{3}\Sigma^{-}$ ) has been estimated to be 71.5 kcal/mol from spectroscopic data,<sup>21</sup> the heat of formation of BrN<sub>3</sub> must be greater than 122 kcal/mol. Using this value, the energy required to dissociate the molecule into Br + N<sub>3</sub> (i.e., the thermodynamic strength of the Br-N bond) can be estimated from the heat of formation of N<sub>3</sub>. Clark and Clyne reported that  $\Delta H_{f,300}$  for N<sub>3</sub> has a value of 99±2 kcal/mol.<sup>21</sup> Hence, the enthalpy change for the process

$$BrN_{3}(X^{1}A') - Br(^{2}P_{3/2}) + N_{3}(^{2}\Pi_{g})$$
(5)

can be determined as  $\Delta H = \Delta H_f(Br) + \Delta H_f(N_3)$ -  $\Delta H_f(BrN_3) \leq 0$  kcal/mol. This result would suggest that the bromine atom in BrN<sub>3</sub> should be extremely labile. Bromine azide would appear to be a truly metastable molecule, bound only by barriers in the dissociative channels leading to either NBr + N<sub>2</sub> or Br + N<sub>3</sub>.

The data presented above suggest that the metastability of BrN<sub>3</sub> makes possible the production of  $N_2(B^3\Pi_g)$  in this system via the following "upconversion" process:

$$BrN_{3}(X^{1}A') \xrightarrow{h\nu} NBr(X^{3}\Sigma^{-}) + N_{2}(A^{3}\Sigma_{u}^{*}) ,$$

$$N_{2}(A^{3}\Sigma_{u}^{*}) + BrN_{3}(X^{1}A') \rightarrow N_{2}(X^{1}\Sigma_{g}^{*}) + BrN_{3}(triplet) , \quad (6)$$

$$BrN_{3}(triplet) \rightarrow NBr(X^{3}\Sigma^{-}) + N_{2}(B^{3}\Pi_{g}) . \quad (7)$$

In reaction (6),  $BrN_3$  is excited to a high lying triplet state (presumably repulsive) by spin-allowed energy transfer from  $N_2(A^3 \Sigma_u^*)$ . The excited triplet then dissociates to ground state NBr and  $N_2(B^3\Pi_g)$ . This mechanism is in accord with the linear dependence of the  $N_2(B \rightarrow A)$  emission on the incident laser energy. The observation of emission from vibrational levels in  $N_2(B^3\Pi_r)$  as high as v' = 6 suggests that  $BrN_3$  carries a minimum of 57.4 kcal/mol, in rough agreement with the generation of  $N_2(A^3\Sigma_u^*)$  by photolysis at 308 nm. In fact, the intensities observed in our experiment are not likely to reflect the nascent vibrational distribution, since relaxation involving near resonant levels of the nearby  $W({}^{3}\Delta_{\mu})$  state is known to be rapid.<sup>22</sup> From the data presented above, the pseudo-first order rate constant for quenching of  $N_2(A^{3}\Sigma_{u}^{*})$  by BrN<sub>3</sub> is  $k = 1.2 \pm 0.2$  $\times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This value corresponds to quenching in approximately 300 collisions, where the hard spheres collision rate was estimated using 0.37 and 0.50 nm as the collision diameters of  $N_2$  and  $BrN_3$ , respectively.

Visible emission from N<sub>2</sub> first positive transitions was not observed in the photodissociation of ClN<sub>3</sub>.<sup>1</sup> In this case, the energy carried by the azide (31.4 kcal/ mol) is sufficient for generation of only the v' = 0 or v' = 1 levels in the  $B({}^{3}\Pi_{e})$  state by processes analogous to reactions (6) and (7) above, unless the N<sub>2</sub>( $A {}^{3}\Sigma_{u}^{*}$ ) is itself vibrationally excited. These lower vibrational levels of the  $B({}^{3}\Pi_{e})$  state would radiate in the near infrared.<sup>23</sup> We note also that upconversion in ClN<sub>3</sub> would require that virtually all the energy carried by the azide appear in the  $N_2$  fragment in a reaction analogous to Eq. (7). Such a process, though possible, would seem much less probable than in the present experiments with BrN<sub>3</sub>.

The present data suggest that the  $N_2(A^3 \Sigma_u^*)$  metastables produced by photolysis of BrN<sub>3</sub> decay via a combination of pseudo-first order and second order processes. For photolysis at 222 nm, the first order process (reaction with  $BrN_3$  as discussed above) dominates, as indicated by the linear dependence of the first positive emission intensity on the laser energy and by the exponential decay of this emission. The contribution of a second process to the  $N_2(A^3\Sigma_{\mu}^{\bullet})$  decay is evident in the slight curvature of plots of the log of the first positive intensity vs time for large BrN3 flows, and in the observation of the ultraviolet emission. The fact that the temporal profile of the UV emission tracks the exponential decay of the first positive emission indicates, however, that collisions with BrN3 dominate the relaxation of the  $N_2(A^{3}\Sigma_{u}^{*})$  metastables in this case. The second order process producing the UV emitter is apparently a minor route, becoming evident in the temporal profiles only at large densities of BrN<sub>3</sub>.

A different situation seems to hold for photolysis of  $BrN_3$  at 308 nm. First, we note that although the  $BrN_3$ extinction coefficient at 308 nm is much smaller than that at 222 nm, the incident laser energy was much larger at 308 nm, such that the degree of dissociation was roughly the same in both cases. At the peak laser energy, a maximum of 4% of the BrN<sub>3</sub> in the photolysis zone was dissociated for both wavelengths. The fact that the decay of the N<sub>2</sub> first positive emission was faster for 308 nm photolysis, and the nonexponential decay of the UV emission in this case, suggest that the contribution of the second order process to the overall removal of N<sub>2</sub>( $A^{3}\Sigma_{*}^{*}$ ) is greater. Hence, 308 nm photolysis must produce a greater amount of the second fragment participating in the formation of the UV emitter. Since the maximum concentration of this fragment is only 4% of that of the parent  $BrN_3$ , the second order process must require only about ten collisions if it is to make a significant contribution to the decay of  $N_2(A^3\Sigma_w^*)$ , as would appear to be the case for 308 nm photolysis of large BrN3 flows. Although this mechanism would give rise to a deviation from the linear dependence of the  $N_2(B \rightarrow A)$  emission on the laser energy, this effect might well be hidden by the scatter in Fig. 4(b). We note also that the increase in the  $N_2(A^3\Sigma_u^*)$  decay rate at 308 nm cannot account for the dramatic decrease (by a factor of about 50) in the  $N_2$ first positive intensity. The initial yield of  $N_2(A^3\Sigma_{\mu}^*)$ must also be smaller than at 222 nm.

The ultraviolet emission produced by photodissociation of  $BrN_3$  does not correspond to known transitions in either  $N_2$  or NBr. It does agree closely, however, with spectra of the  $D' \ {}^3\Pi 2_g \rightarrow A' \ {}^3\Pi 2_u$  transition in  $Br_2$ . Emission on this transition has been observed from electron beam pumping<sup>24</sup> or electric discharge excitation<sup>25</sup> of  $Ar-Br_2$  mixtures, and lasers operating on this transition have been demonstrated using these methods. Kolts and Setser<sup>26</sup> have observed  $Br_2 \ D' \rightarrow A'$  emission upon addition of  $Br_2$  to a stream containing  $Ar({}^3P_{0,2})$  metastable atoms. These authors suggest the excited bromine to be produced by reaction of excited bromine atoms (Br\*,  $5s \, {}^4P_J$ ,  ${}^2P_J$ ) with Br<sub>2</sub>. The excited bromine atoms were produced by energy transfer from the argon metastables. The spectrum of spontaneous emission from this system agrees very closely with the spectrum obtained in our experiment (Fig. 7), with the exception of the anomalously large itensity of the 292 nm feature in our spectrum.

The data presented above suggest that the excited  $Br_2$ is produced by energy transfer from  $N_2(A^{3}\Sigma_{w}^{*})$ . Since the intensity of the emission varies as the square of the laser energy, the  $Br_2$  is not simply present as an impurity in the flow, but must be generated by reaction of a photolysis product. One mechanism which is consistent with these results is as follows:

$$BrN_{3}(^{1}A') \xrightarrow{h\nu} N_{2}(A^{3}\Sigma_{u}^{*}) + NBr(X^{3}\Sigma^{-})$$
$$\xrightarrow{h\nu} Br(4^{2}P_{3/2}) + N_{3}(X^{2}\Pi_{z}) ,$$
$$Br + BrN_{3} \rightarrow Br_{2} + N_{3} , \qquad (8)$$

 $N_2(A^{3}\Sigma_{u}^{*}) + Br_2 - N_2(X^{1}\Sigma_{g}^{*}) + Br_2(D^{'3}\Pi 2_{g}) .$ (9)

A number of authors<sup>27-29</sup> have observed the excitation of I<sub>2</sub> by collisions with N<sub>2</sub>( $A^{3}\Sigma_{u}^{*}$ ) in a process analogous to reaction (9). In this case, the I<sub>2</sub>  $D' \rightarrow A'$  emission peaked near 342 nm is observed. This energy transfer process is only moderately fast, however, with a rate constant  $k = 6.9 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>29</sup> As noted above, quenching of N<sub>2</sub>( $A^{3}\Sigma_{u}^{*}$ ) to produce the 292 nm emitter (presumable excited Br<sub>2</sub>) must require only a few collisions. Spectroscopic studies<sup>30</sup> of the Br<sub>2</sub>  $D' \rightarrow A'$  transition have suggested the energy of the upper state to be near 49 000 cm<sup>-1</sup>. Since the 0, 0 transition of the N<sub>2</sub>  $A \rightarrow X$  transition lies at 49 756 cm<sup>-1</sup>, the energy transfer process between N<sub>2</sub>( $A^{3}\Sigma_{u}^{*}$ ) and Br<sub>2</sub> could be near resonant. Experiments directed toward determing the rate of this process are currently underway in our laboratory.

#### SUMMARY AND CONCLUSIONS

Bromine azide is metastable with respect to dissociation to either NBr( $X^{3}\Sigma^{-}$ ) + N<sub>2</sub>( $X^{1}\Sigma_{g}^{*}$ ) or Br( ${}^{2}P_{3/2}$ ) + N<sub>3</sub>( $X^{2}\Pi_{g}$ ). From the nature of excited species produced by photolysis of this molecule, its heat of formation was determined to be greater than 122 kcal/mol. This fact dominates not only the nature of the initial photofragments, but also the subsequent chemistry of the system. The primary fragments produced by photodissociation at 222 and 308 nm are N<sub>2</sub>( $A^{3}\Sigma_{u}^{*}$ ) and NBr( $X^{3}\Sigma^{-}$ ), with some N<sub>2</sub>( $B^{3}\Pi_{g}$ ) being produced at 222 nm. No evidence for formation of the singlet products N<sub>2</sub>( $X^{1}\Sigma_{g}^{*}$ ) + NBr( $b^{1}\Sigma^{*}$ ) was found. A lower energy singlet channel leading to N<sub>2</sub>( $X^{1}\Sigma_{g}^{*}$ ) + NBr( $a^{1}\Delta$ ) may be operative, but observation of the near infrared emission from NBr( $a^{1}\Delta$ ) was not possible with the present apparatus.

 $N_2(A^3\Sigma_u^*)$  metastable molecules produced by the photolysis decay by both pseudo-first order reaction with the parent molecules and by a second order process involving another photofragment. The pseudo-first order process produces  $N_2(B^3\Pi_g)$ . From the decay of the  $N_2B-A$  emission, the rate constant for  $N_2(A^3\Sigma_u^*)$  quenching by BrN<sub>3</sub> was determined to be  $1.2 \pm 0.2 \times 10^{-12}$  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup>. The overall appearance of this process is that of an upconversion in which molecular nitrogen is excited by the energy carried by  $BrN_3$ . In reality, the mechanism likely involves collisional excitation of BrN<sub>3</sub> to a triplet dissociative state correlating to  $N_2(B^3\Pi_e) + NBr(X^3\Sigma^-)$ . This pseudo-first order process dominates the decay of  $N_2(A^3\Sigma_u^*)$  for photolysis at 222 nm. The second order process produces intense  $\operatorname{Br}_2 D'({}^3\Pi 2_{\mu}) \rightarrow A'({}^3\Pi 2_{\mu})$  emission. The  $\operatorname{Br}_2$  may be generated by reaction of BrN3 with bromine atoms produced as a photolysis product. The observation of this emission suggests the possibility of a photochemically pumped laser operating on the Br<sub>2</sub> transition, if the yield of  $N_2(A^{3}\Sigma_{\mu}^{\bullet})$  from the photolysis is high.

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