



Chemical Physics Letters 297 (1998) 335-342

CHEMICAL PHYSICS LETTERS

Generation of $NBr(a^{1}\Delta)$ by the reaction of N_{3} radicals with Br atoms: a flow reactor source for quenching rate constant measurements

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Received 3 August 1998; in final form 29 September 1998

Abstract

The reaction between azide radicals (N_3) and Br atoms is shown to produce electronically excited NBr($a^{1}\Delta$) molecules in a room temperature flow reactor. This chemical system provides adequate concentration of NBr($a^{1}\Delta$) so that this molecule can be systematically studied. The yield of NBr($b^{1}\Sigma^{+}$) is minor. The quenching reactions of NBr(a) with HCl, HBr, HI, NH₃, Br₂, CF₂Br₂, and O₂ were examined; the rate constants are $(22 \pm 5) \times 10^{-14}$, $(280 \pm 30) \times 10^{-14}$, $(2300 \pm 200) \times 10^{-14}$, $(35 \pm 3) \times 10^{-14}$, $(2600 \pm 300) \times 10^{-14}$, $(37 \pm 6) \times 10^{-14}$, and $(230 \pm 30) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, respectively. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Electronically excited molecules can serve as energy storage systems, provided that the radiative decay rate is small and that the generation of the excited state is easily accomplished by chemical means. The nitrogen monohalides (NX, X = F, Cl, or Br) have been proposed as candidates for such energy storage systems. The three lowest energy elec-

tronic states of NX are $X^3 \Sigma^-$, $a^1 \Delta$ and $b^1 \Sigma^+$, with the latter being 9281 and 14834 cm⁻¹ above the ground state of NBr, respectively [1,2]. The enthalpy of formation of NBr is -206 kJ mol⁻¹ [3]. Due to the forbidden nature of the $a^1 \Delta \rightarrow X^3 \Sigma^-$ transition, the $a^1 \Delta$ state is long-lived. The lifetimes are 5 s for NF(a) [4,5] and 2–3 s for NCl(a) [6–8]. The lifetime of NBr(a) seems to be 5–10 times smaller than that of NCl(a) based upon computations and observation of decay times in an Ar matrix [9,10]. Chemical generation of NX($a^1\Delta$) molecules is accomplished by the reaction of azide radicals (N₃) with halogen atoms, and in this Letter we show that Br + N₃ can be used as a source of NBr(a) in a flow reactor.

Azide radicals are produced by the reaction of hydrazoic acid with F atoms with a rate constant of

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 1.1×10^{-10} cm³ molecule⁻¹ s⁻¹ [11]. Recent measurements of the branching fraction of

$$F + HN_3 \rightarrow HF + N_3$$
, $\Delta_r H_{298}^o = -180 \text{ kJ mol}^{-1}$. (1)

Reaction (1) demonstrated conclusively that N_3 is the major product with a branching fraction of 0.97 [12]. The resulting azide radicals react with Br atoms to form NBr. Reaction (2),

 $Br + N_3$

$$\rightarrow N_{2} + NBr(X^{3}\Sigma^{-}), \quad \Delta_{r}H_{298}^{o} = -206 \text{ kJ mol}^{-1} \rightarrow N_{2} + NBr(a^{1}\Delta), \qquad \Delta_{r}H_{298}^{o} = -95 \text{ kJ mol}^{-1} \rightarrow N_{2} + NBr(b^{1}\Sigma^{+}), \qquad \Delta_{r}H_{298}^{o} = -29 \text{ kJ mol}^{-1},$$
(2)

has previously been observed to occur and produce NBr(a) and possibly some NBr(X) and NBr(b) [2,13]. A study by Liu et al. [13] reported rate constants for reactions between azide radicals and halogen atoms, however, recent work has shown that their reported rate constant for the reaction between $Cl + N_3$ was too large [6,14–17]. Their reported value [13] of $(3 \pm 2) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ can be considered an upper limit for reaction (2) and the true value is probably near 5×10^{-11} cm³ molecule⁻¹ s⁻¹, the accepted value for F + N₃ [13,18].

The quenching rate constants of NBr(a) are important for the development of energy storage systems and for comparison with the other nitrogen monohalides NF($a^{1}\Delta$) [18,19] and NCl($a^{1}\Delta$) [20]. In this study we develop a method that is suitable for systematic studies employing a microwave discharge in CF₂Br₂ as the Br atom source. As a test of the method, we measured the magnitudes of the quenching rate constants of NBr(a) with the molecules NH₃, Br₂, CF₂Br₂, HCl, HBr, HI, and O₂ and compare them with those of NF(a) and NCl(a). The comparison with NCl(a) is especially interesting since the reported energies are 9280 ± 10 and 9281 ± 10 cm⁻¹ for NCl(a) and NBr(a), respectively [1,2].

2. Experimental methods

The production of NBr(a) by reaction (2) and the subsequent quenching reaction studies were carried out in a flow reactor at room temperature. The relative concentrations of NBr(a) and NF(a) were measured by monitoring the chemiluminescence intensity at 1077 and 874 nm of the $a \rightarrow X$ transitions, respectively. The flow reactor and the emission monitoring system, which are the same as previously used for the study of NCl(a) [20,21], are described below.

2.1. Flow reactor

The flow reactor was a 150 cm long, 7.4 cm diameter Pvrex tube. The surface of the flow reactor was coated with halocarbon wax (Halocarbon Products, series 600) to prevent the loss of F, Br, N₃ and other radical species by reaction with the reactor walls. The flow reactor consisted of two distinct regions: a pre-reactor where NBr was generated by reactions (1) and (2), and the reactor where the quenching reactions of NBr(a) occurred. The pre-reactor was 37 cm in length. The inlet tubes for the Ar carrier gas, the F atom source (CF_4 , the Br atom source (CF_2Br_2) , and HN_3 were located in an aluminum flange attached via ano-ring joint to the front end of the flow reactor. The majority ($\sim 90\%$) of the Ar carrier gas was added to the pre-reactor through a perforated ring; the F atoms and Br atoms were added with the remainder of the Ar through separate 10 mm o.d. quartz tubes; and the HN₃ was added through another perforated tube located at the exit of the F and Br inlets. The quenching reagent gases were added to the flow reactor via a perforated ring, which was located 37 cm downstream of the HN₃ inlet and marked the starting point of the reactor. The reactor was pumped using a mechanical pump/blower combination which provided a linear flow velocity of 1200 cm s⁻¹ at a typical Ar pressure of 0.4 Torr

The flow velocity in the reactor corresponds to a minimum reaction time of 35 ms in the pre-reactor. Under typical reaction conditions, this time was sufficient to allow reactions (1) and (2) to proceed to completion before the addition of the quenching reagent. The reactions of NBr(a) with added quench-

ing reagents then occurred during the 47 ms spent for travel down the flow reactor. The actual reaction time was determined by measuring the quenching rate of NF(a) with NH₃, which has an established rate constant of 3.6×10^{-12} cm³ molecule⁻¹ s⁻¹ [18]. The flow velocity could be reduced, if desired, by a throttling valve located before the pump.

The argon carrier gas was purified by passage through cooled (196 and 77 K for high and low pressure, respectively) molecular sieve filled traps. Approximately 10% of the Ar was used to dilute the CF_4 and Ar/CF_2Br_2 flows before they passed through the microwave discharges. The F atoms were produced by passing the resulting Ar/CF_4 mixture through a microwave discharge in an alumina tube. Under our experimental conditions, the CF_4 is nearly completely dissociated into $2F + CF_2$. The Ar/CF_2Br_2 mixture was passed through a second microwave discharge in an alumina tube to produce the Br atoms. The dissociation efficiency of CF_2Br_2 is not known; however, it was assumed to be similar to that of CF₂Cl₂ whose dissociation efficiency has been measured in our laboratory to be 1.5 Cl atoms per CF₂Cl₂ molecule [21].

The gases CF_2Br_2 , HCl, HBr, and NH₃ were obtained from commercial vendors, purified via freeze-pump-thaw cycles, and stored as pure gases or as dilute mixtures in Ar. The O₂ and CF₄ were obtained from commercial vendors and used without purification. The HI was synthesized by the reaction of iodine with boiling tetrahydronaphthalene [22], distilled and stored as a mixture in Ar. The HN₂ was prepared by the reaction of excess stearic acid with sodium azide (NaN₃) heated to 363 K under vacuum [18]. The product, which was collected in a 12 1 Pyrex reservoir, was diluted to 10% with argon. The flow rates of Ar, CF_4 , and CF_2Br_2 were controlled by needle valves and measured by Hastings mass flow meters. The flow rate of HN₃ and the quenching gases were controlled by needle valves and measured by the rate of pressure rise in a calibrated volume.

2.2. Detection system

The emission from the NBr(a) was monitored by a photomultiplier tube (PMT) attached to the exit slit

of a 0.5 m monochromator. The PMT was an S-1 type (Hamamatsu R1767) cooled to -80° C. The monochromator has a 600 lines/mm grating blazed at 1000 nm. Typical dark current was <15 pA. The current was monitored using an electrometer (Keithley, model 614) and recorded by a computer. The slit width was typically 0.5 mm.

The monochromator was attached to a movable platform, allowing it to travel along the length of the flow reactor and thus changing the reaction time at which observations were made. The monochromator could be scanned to produce continuous spectra or it was set to a fixed wavelength to monitor the maximum of the NBr(a) or NF(a) emission. For the fixed wavelength measurements, the computer read the output from the electrometer at ~ 0.5 s intervals. The collection time was typically 20 s for each data point.

3. Proof of method

Previous work by Pritt et al. [2] determined that the formation of excited NBr molecules occurs upon reaction of azide radicals with Br atoms. They detected chemiluminescence from both the NBr(a) and NBr(b) electronic states using F atoms, Br_2 and HN_3 as reactants. We set out to determine experimental conditions under which emission from NBr(a) was strong enough to measure and relatively constant along the length of our flow reactor, so that quenching rate constants could be measured.

Using the method developed for studying NCl($a^{1}\Delta$) [20,21], we replaced the CF₂Cl₂ precursor gas by CF₂Br₂, thus switching from production of Cl atoms to Br atoms. Using concentrations of [F] $\approx 2 \times 10^{12}$, [HN₃] $\approx 3 \times 10^{12}$, and [Cl or Br] $\approx 2 \times 10^{12}$ molecule cm⁻³, ~4 times higher emission intensity was observed from NCl(a) than from NBr(a). The NBr(a)/NCl(a) intensity ratio, when both NBr(a) and NCl(a) are produced under their respective optimum conditions for the same [HN₃]₀, is 1:2. The relative intensities and the difference in Einstein coefficients suggest that the yield of NBr(a) is considerably lower than for NCl(a). This implies that [NBr(X)] is significant in the reactor. Optimum conditions for production of NBr(a) were obtained using

initial reactant concentrations of $[F] \approx 2.0 \times 10^{12}$, $[Br] \approx 4.5 \times 10^{11}$, and $[HN_3] \approx 3.0 \times 10^{12}$ molecule cm⁻³. The atom concentrations are based upon $[F] = 2[CF_4]$ and $[Br] = 1.5[CF_2Br_2]$. Using these conditions, the emission intensity profiles of NBr(a), NBr(b) and NF(a) as a function of time were measured and they are shown in Fig. 1. The emission intensity from NBr(a) decreased by ~ 35% from 35–100 ms which is satisfactory for quenching stud-



Fig. 1. The emission intensity of NBr($a^1\Delta$) [\blacktriangle], NBr($b^1\Sigma^+$) [\bullet], and NF($a^1\Delta$) [\blacksquare] as a function of time. The initial reactant concentrations were [Ar] = 1.4×10^{16} , [CF₄] = 1.0×10^{12} , [CF₂Br₂] = 2.3×10^{11} , and [HN₃] = 3.5×10^{12} molecule cm⁻³. The NBr(a) emission reaches its maximum intensity in 35–40 ms and then begins to slowly decay. NBr(b) and NF(a) reach their maximum intensity in 15–20 ms. The quenching agents were added 35 ms after the start of the Br+N₃ reaction.



Fig. 2. The emission spectrum, corrected for detector response, from the flow reactor after a reaction time of 40 ms. The reactant concentrations were $[Ar] = 1.4 \times 10^{16}$, $[CF_4] = 1.1 \times 10^{12}$, $[CF_2Br_2] = 3.0 \times 10^{11}$, and $[HN_3] = 3.0 \times 10^{12}$ molecule cm⁻³. Emission was observed from NBr(a¹\Delta), NBr(b¹\Sigma⁺), NF(a¹\Delta) and N_2(B³\Pi_g).

ies. The fast rise of the NF(a) emission intensity results from the excess [HN₃], which removes the [F] early in the pre-reactor. The slow rise of NBr(a) emission indicates that the magnitude of the rate constant for reaction (2) is comparable to that for the $F + N_3$ reaction, 5×10^{-11} cm³ molecule⁻¹ s⁻¹. We cannot assign a better estimate because the [Br] was not measured. It was observed that higher CF_2Br_2 flows actually reduced the NBr(a) emission intensity, this is believed to be the result of quenching of NBr(a) by Br atoms, since CF_2Br_2 has a negligible quenching rate at this concentration.

Fig. 2 shows a spectrum, corrected for detector response, recorded after a reaction time of 40 ms. The ratio of emission intensity from NBr(a) and NBr(b) is about 24:1, which corresponds to a concentration ratio of 28000:1 using the Einstein A coefficients 6.57 and 7651.4 s⁻¹ for NBr(a) and NBr(b), respectively [9,10]. Even after a reaction time of only 5 ms, when the emission intensity ratio of NBr(a) and NBr(b) is approximately unity, the concentration ratio is 1165:1. The A coefficient for NBr(b) is large enough that [NBr(b)] reaches a steady-state value and does not accumulate in the reactor. As a result, the [NBr(b)]/[NBr(a)] ratio is always small, much less than 1%. The main source of NBr(b) at each time is believed to be from the excitation of NBr(a) by vibrationally excited HF

molecules formed by reaction (1); this NBr(b) excitation mechanism is analogous to the mechanism for production of NF(b) and NCl(b) [6]. The $N_2(B)$ emission seen in Fig. 2 is from nitrogen impurity passing through the microwave discharges.

4. Rate constants

After determining the optimum conditions for producing NBr(a), we set out to determine some quenching rate constants. The optimum conditions for NBr(a) production gave well-behaved, pseudofirst-order decay kinetics for the addition of a reagent. The molecule NH₃ was used as a standard reference in previous work on NF(a) and NCl(a) [6,18,20], and we utilized it to calibrate the reaction time based upon the residual NF(a) quenching. Quenching by Br_2 was examined since $F + Br_2$ has previously been used as a Br atom source [2]. We also examined CF_2Br_2 , our Br atom source. We chose the hydrogen halides to give a systematic comparison with NF(a) and NCl(a) reactions. The quenching of NBr(a) by oxygen was also measured because this should be an excitation-transfer reaction.

4.1. Ammonia

The reaction between NBr(a) and NH₃ was examined by adding [NH₃] $\leq 4 \times 10^{13}$ molecule cm⁻³ to the flow reactor and monitoring the NBr(a) emission intensity after 45 ms. The NF(a) emission was also monitored under the same conditions. Fig. 3 shows the Stern–Volmer plot for the quenching of NF(a) and NBr(a) by NH₃; both reactions follow pseudofirst-order kinetics. The reaction time was set by using the accepted value for NF(a) quenching rate constant of 360×10^{-14} cm³ molecule⁻¹ s⁻¹ [18]. The rate constant for NBr(a) was determined to be $k_{\rm NH_3} = (35 \pm 3) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ based upon two separate measurements.

4.2. Bromine and CF_2Br_2

Two sources of Br atoms in flow reactors have been utilized in studies on NBr; $F + Br_2$ was used by Fig. 3. Stern–Volmer plot for the quenching of NBr($a^{1}\Delta$) [•] and NF($a^{1}\Delta$) [•] by NH₃. The reactant concentrations were [Ar]=1.4 × 10¹⁶, [CF₄]=1.1 × 10¹², [CF₂Br₂]=2.7 × 10¹¹, [HN₃]=2.5 × 10¹², and [NH₃] ≤ 3 × 10¹³ molecule cm⁻³. The emission was monitored 45 ms after the addition of NH₃. The time was calculated from the NF(a) quenching plot and the known rate constant 360×10^{-14} cm³ molecule⁻¹ s⁻¹ (see text). The NBr(a) quenching rate constant from the plot was determined to be 37×10^{-14} cm³ molecule⁻¹ s⁻¹. The average value obtained from two experiments was $(35 \pm 3) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

Pritt et al. [2] and we used the microwave discharge of CF₂Br₂. Erroneous results can be obtained if the residual precursor gases cause significant quenching of NBr(a). Reagent concentrations of $[Br_2] \le 2 \times 10^{12}$ or $[CF_2Br_2] \le 7 \times 10^{12}$ molecule cm⁻³ were added to the reactor. Measuring the NBr(a) emission after 47 ms for various Br₂ and CF₂Br₂ concentrations gave quenching rate constants of $k_{Br_2} = (2600 \pm 300) \times 10^{-14}$ and $k_{CF_2Br_2} = (37 \pm 6) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

4.3. Hydrogen halides

Quenching of NBr(a) upon addition of hydrogen halides into the reactor was also studied. Reagent concentrations of $[\text{HCl}] \le 3 \times 10^{14}$, $[\text{HBr}] \le 8 \times 10^{13}$, and $[\text{HI}] \le 5 \times 10^{12}$ molecule cm⁻³ were added to the reactor. The quenching rate constants





Fig. 4. Stern–Volmer plot for quenching of NF($a^{1}\Delta$) [•], NCl($a^{1}\Delta$) [•], and NBr($a^{1}\Delta$) [•] by HBr. The reactant concentrations were [Ar] = 1.4 × 10¹⁶, [CF₄] = 1.1 × 10¹², [CF₂Br₂] = 2.7 × 10¹¹, [HN₃] = 2.5 × 10¹², and [HBr] \leq 7 × 10¹³ molecule cm⁻³. The reaction time was 47 ms. The quenching rate constants obtained from this plot are 10.2 × 10⁻¹⁴, 187 × 10⁻¹⁴, and 368 × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ for NF(a), NCl(a) and NBr(a), respectively.

were determined by monitoring the emission intensity of NBr(a) after a reaction time of 45 ms. Fig. 4 compares the quenching of NF(a), NCl(a) and NBr(a) by HBr. The rate constants obtained are 10.2×10^{-14} , 187×10^{-14} , and 368×10^{-14} cm³ mole-

Table 1 Comparison of quenching rate constants of NBr(a) with NF(a) and NCl(a)

cule⁻¹ s⁻¹ for NF(a), NCl(a), and NBr(a), respectively. The rate constants for NF(a) and NCl(a) are within the uncertainty of the previously reported values [20]. The NBr(a) rate constants with the hydrogen halides are $k_{\rm HCI} = (22 \pm 5) \times 10^{-14}$, $k_{\rm HBr} =$ $(280 \pm 30) \times 10^{-14}$, and $k_{\rm HI} = (2300 \pm 300) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹. In each case, the decay also was measured for NF(a) to ensure that conditions were satisfactory. For HI, the NF(a) quenching rate constant has not been reported and we determined it to be $(380 \pm 50) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹. The fast F + HBr reaction could be used as an alternative source of Br atoms for reaction (2) in a carefully designed flow reactor [6].

4.4. Oxygen

The final quenching study was between O₂ and NBr(a). Concentrations of $[O_2] \le 6 \times 10^{12}$ molecule cm⁻³ were added to the reactor and the NBr(a) emission monitored after 45 ms. The rate constant from a good first-order plot was $k_{O_2} = (230 \pm 30) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

5. Conclusions

The chemiluminescence of NBr has been detected in a flow reactor from the reaction of azide radicals

NF(a)^a NCl(a)^b NBr(a)^c Reagent $(10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ $(10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ $(10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ $35 + 3^{d}$ NH₃ 360 + 2011 + 2 $2600 \pm 300^{\mathrm{f}}$ 3800 ± 600^{e} 1600 ± 200 Br_2 37 ± 6^{d} CF₂Br₂ O_2 0.70 + 0.07300 + 20 $230 + 30^{d}$ 0.16 + 0.03 22 ± 5^{d} HC1 4.0 + 0.4 9.0 ± 2.0^{b} 180 ± 30 280 ± 30^{d} HBr HI $380 + 50^{\circ}$ 2900 + 500 $2300 + 300^{f}$

^aRef. [18].

^bRef. [20].

^cThis Letter, see text.

^dUncertainty is the standard deviation of multiple runs.

^eRef. [19].

^fUncertainty is from a least-squares fit to a pseudo-first-order plot.

with Br atoms. The Br atoms were generated by a microwave discharge through the precursor gas CF_2Br_2 . The emission spectra correspond to the previously detected NBr($a^{1}\Delta$) and NBr($b^{1}\Sigma^{+}$) [1,2]; the yield of NBr(b) is < 1% of the NBr(a) yield. For the same [F], [HN₂], and $[CF_2X_2]$ concentrations, the ratio of the NBr(a)/NCl(a) emission intensity was approximately 1:4. For optimum experimental conditions of each case, the NBr(a)/NCl(a) ratio was approximately 1:2. The present data strongly suggest that the branching fraction for NBr(a) formation is substantially smaller than for NCl(a) in the $Cl + N_2$ reactions: the latter has been assigned as > 0.5 [6]. The NBr(a) emission is very sensitive to the CF_2Br_2 flow rate, as increasing flow drastically decrease the emission intensity, probably because of quenching by Br atoms. Conditions could be optimized to produce a NBr(a) concentration that slowly decreased over 50 ms. Using these optimized conditions. quenching rate constants were measured for several molecules. The values obtained are $k_{\rm NH_2} = (35 \pm 3)$ $\begin{array}{l} \times 10^{-14}, \ k_{\rm O_2} = (230 \pm 30) \times 10^{-14}, \ k_{\rm HCl} = (22 \pm 5) \times 10^{-14}, \ k_{\rm HCl} = (22 \pm 5) \times 10^{-14}, \ k_{\rm HBr} = (280 \pm 30) \times 10^{-14}, \ k_{\rm HI} = (2300 \pm 300) \times 10^{-14}, \ k_{\rm Br_2} = (2600 \pm 300) \times 10^{-14} \text{ and} \ k_{\rm CF_2Br_2} = (37 \pm 6) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \end{array}$

Comparing the magnitude of the quenching rate constants of NF(a), NCl(a) and NBr(a) with NH_3 , shown in Table 1, one notices that they lie in the order NF(a) > NBr(a) > NCl(a). The rate constant for NBr(a) is three times larger than the corresponding value for NCl(a). However, the magnitude of the rate constant for NF(a) is the largest because of its stronger base property [18]. The magnitudes of the rate constants for the hydrogen halides follow a systematic pattern, NF(a) < NCl(a) < NBr(a), increasing as the halogen in the NX molecule increases in mass, with the exception of HI for which NCl(a) and NBr(a) have nearly equal rate constants.

The magnitudes of the rate constants with oxygen are ordered NF(a) \ll NBr(a) \approx NCl(a). The excitation-transfer reaction between NX(a) and O₂ produces excited oxygen molecules. The NX(a) molecules all have more energy than required to excite oxygen. The excitation-transfer reaction between NF(a) and O₂ has 3553 cm⁻¹ of excess energy, while the reaction between NCl(a) or NBr(a) and O₂ only has 1398 cm⁻¹ of excess energy. The larger energy defect is the cause of the smaller rate constants between NF(a) vs. NCl(a) or NBr(a). A systematic study of the crossing of the potential energy surfaces for reaction (3) would be interesting [23].

$$NX(a^{1}\Delta) + O_{2}(X^{3}\Sigma) \rightarrow NX(X^{3}\Sigma^{-}) + O_{2}(a^{1}\Delta).$$
(3)

Acknowledgements

This work was supported by the US Air Force under Grant F49620-96-1-0110 from the Air Force Office of Scientific Research.

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