



## Chemiluminescence from the Reaction of Iodine with Active Nitrogen

XIAO-SHUAN TANG<sup>1,\*</sup>, YUANKUI CHENG<sup>1</sup>, HONG-MEI WANG<sup>2</sup> and YAN-NAN CHU<sup>2</sup>

<sup>1</sup>College of Physics and Electronic Information, Anhui Normal University, WuHu 241000, P.R. China

<sup>2</sup>Laboratory of Environment Spectroscopy, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, P.R. China

\*Corresponding author: E-mail: x58929@mail.ahnu.edu.cn

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Active nitrogen has been prepared by hollow-cathode discharge of high pure nitrogen gas in a flow reactor. The emission spectra from the reaction of iodine with active nitrogen are studied. The strong emission spectra of  $\text{NI}(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$  in the range of 620-800 nm have been observed when iodine vapours carried by nitrogen gas were introduced into a stream of active nitrogen. This is the first experimental evidence for the generation of excited state of  $\text{NI}(b^1\Sigma^+)$  via the chemical reactions of iodine with active nitrogen. The results show that vibrationally unrelaxed emission spectra from the electronically excited state  $\text{NI}(b^1\Sigma^+)$  are observed and the production  $\text{NI}(b^1\Sigma^+)$  is formed directly by the reaction of excited nitrogen atom  $\text{N}(^2P)$  with  $\text{I}_2$ .

**Key Words:** Emission spectra, Active nitrogen, Iodine, Chemiluminescence.

### INTRODUCTION

Studies of nitrogen halide  $\text{NX}$  ( $X=\text{F}, \text{Cl}, \text{Br}, \text{I}$ ) radicals have attracted considerable interest because they are important intermediates in combustion and atmospheric chemical processes. They are iso(valence)electronic with  $\text{O}_2$ , which all exist in  $^3\Sigma^-$  ground states. The two low-lying electronically excited states,  $a^1\Delta$  and  $b^1\Sigma^+$ , result from the same electron configuration. Their low-lying metastable  $a^1\Delta$  and  $b^1\Sigma^+$  states make them potential candidates for chemical energy systems<sup>1,2</sup>. Transitions between these electronic states have been studied. Many spectroscopic investigations of the emission produced by adding halogen molecules to a flow of active nitrogen have been carried out. The spectrum of  $\text{NBr}$  was first reported by Elliott<sup>3</sup>. He photographed an orange flame produced by admitting molecular bromine into a stream of active nitrogen and observed banded structures. Colin and Jones observed the  $b^1\Sigma^+ \rightarrow X^3\Sigma^-$  bands of  $\text{NCl}$  in the after glow of a mild microwave discharge through a mixture of  $\text{N}_2$  and  $\text{Cl}_2$ <sup>4</sup>. Shestakov *et al.*<sup>5</sup> applied the LIF technique to study  $\text{NI}$  in a fast-flow system, because they did not observe  $b^1\Sigma^+ \rightarrow X^3\Sigma^-$  emission spectra of  $\text{NI}$  from the discharged  $\text{N}_2 + \text{I}_2/\text{I}$  chemiluminescence system and cw discharges in  $\text{N}_2 + \text{I}_2$  mixtures. Rice *et al.*<sup>6</sup> observed the emission spectra of  $\text{NCl}(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$  and  $\text{NBr}(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$  when  $\text{Cl}_2$  in  $\text{N}_2$  gas mixture and  $\text{Br}_2$  vapours were introduced into an atmospheric pressure active nitrogen, respectively. In contrast to  $\text{Cl}_2$  and  $\text{Br}_2$ , they did not observe the  $\text{NI}(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$  emission when iodine vapours were

introduced into the active nitrogen after glow<sup>6</sup>. Freeman and Phillips<sup>7</sup> studied the flame when iodine vapours were mixed with active nitrogen from a microwave discharge, where  $\text{I}_2$  vapours were carried by a stream of argon or nitrogen. They observed the blue emission which is due to the long-lived energetic specie production  $\text{N}_2(A^3\Sigma_u^+)$  and the mechanism  $\text{N}(^4S) + \text{I}_2(^1\Sigma) \rightarrow \text{NI}(X^3\Sigma^-) + \text{I}(^2P)$ ,  $\text{N}(^4S) + \text{NI}(X^3\Sigma^-) \rightarrow \text{N}_2(A^3\Sigma_u^+) + \text{I}(^2P)$  was proposed to account for this observation. No  $\text{NI}(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$  emission was observed in their experiment. Minkwitz and Froben<sup>8</sup> also observed the ground state  $\text{NI}(X^3\Sigma^-)$  product of a microwave discharge in an  $\text{N}_2$  and  $\text{I}_2$  mixture by IR absorption method. In these reactions of  $\text{I}_2$  with active nitrogen, the products include the ground state  $\text{NI}(X^3\Sigma^-)$ , but no electronically excited state  $\text{NI}(b^1\Sigma^+)$  was observed. Recently, emission spectra of  $\text{NI}(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$  were observed in our group when  $\text{C}_2\text{H}_5\text{I}$  vapours were introduced into a stream of active nitrogen prepared by DC hollow cathode discharge of high pure nitrogen gas<sup>9</sup>. In this paper, we aim to further study the reaction between active nitrogen and iodine vapours in our flowing after glow apparatus. The emission spectra of  $\text{NI}(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$  from the reaction of  $\text{I}_2$  with active nitrogen are measured and the possible formation mechanisms of excited  $\text{NI}(b^1\Sigma^+)$  are analyzed.

### EXPERIMENTAL

Experiments were performed in a flowing after glow apparatus in Anhui institute of optics and fine mechanics,

Chinese academy of sciences, which is shown schematically in Fig. 1 and basically identical to that described in earlier works<sup>10,11</sup>. Nitrogen gas (99.999 %) was further purified by three molecular sieves in series cooled by liquid nitrogen traps and then entered the hollow-cathode discharge tube, where active nitrogen was generated by applying a DC discharge with a voltage of 300 V at a low current of 2 mA. Iodine vapours are carried through a glass flask by a stream of nitrogen and enter the active nitrogen stream through the reagent inlet 2 on the flow reactor. Analytical reagent grade iodine, commercial 99.9 % is used.

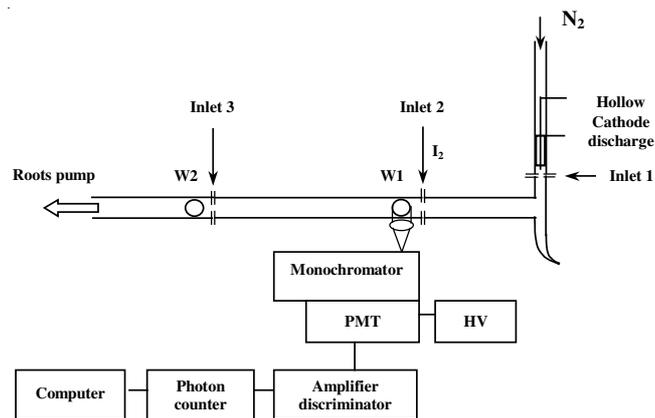


Fig. 1. Schematic diagram of the flowing after glow apparatus and the spectroscopic detection system

Flame spectra have been collected into and dispersed by a 0.75 m monochromator (1200 grooves/mm) located at the optical window W1 and detected by a cooled photomultiplier tube (RCA C31034) fitted to an amplifier discriminator (EG&G 1120) and a photon counter (EG&G 1109). A computer was used to record and process the spectral data. The whole flow reactor was evacuated by a 150 L/s roots pump downstream and the typical pressure in the flow tube was around 1 Torr. A low pressure Hg lamp light source was used to calibrate the wavelength of the monochromator and the wavelength accuracy is  $\pm 0.2$  nm over the region of 600-900 nm.

## RESULTS AND DISCUSSION

When only the iodine vapours in room temperature (not with the carrier gas of nitrogen) were introduced into a stream of active nitrogen through reagent inlet 2, no perceptible change was found in the mixing zone. The vapour pressure of solid iodine is low in room temperature (about 1 Torr) and the rates of deactivation of the active nitrogen [ $N_2(A^3\Sigma_u^+)$ ,  $N(^2D)$ ,  $N(^2P)$ ] by  $N_2$  molecule are relatively low<sup>12</sup>. So a nitrogen flow ( $10 \mu\text{mol s}^{-1}$ ) was used as a carrier gas of iodine vapours. When the iodine vapours with the carrier gas of nitrogen were introduced into a stream of active nitrogen through reagent inlet 2, a yellow-orange flame appeared instantly in the mixing zone, extending for about 10 cm downstream. The spectra of this flame measured at the first optical window (W1) are shown in Fig. 2. All of the banded features shown in the spectrum can be attributed to the  $b^1\Sigma^+ \rightarrow X^3\Sigma^-$  transitions in NI, ranging from 620-800 nm. The bands around 740-840 nm are over-

lapped by nitrogen bands [ $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$ ]. The wavelengths of all vibrational transitions are identical with those that obtained from the reaction between active nitrogen with  $C_2H_5I$ , in which the experimental parameters and the spectrum detection conditions are the same. For comparison purposes the emission spectra from the reaction between active nitrogen and  $C_2H_5I$  are shown<sup>9</sup> in Fig. 3. Thus the vibrational transitions in Fig. 2 can be readily attributed to the  $b^1\Sigma^+ \rightarrow X^3\Sigma^-$  transitions in NI. Specifically, there was no change in the relative intensities of the transitions when the pressure in the flow tube was increased to 3 Torr.

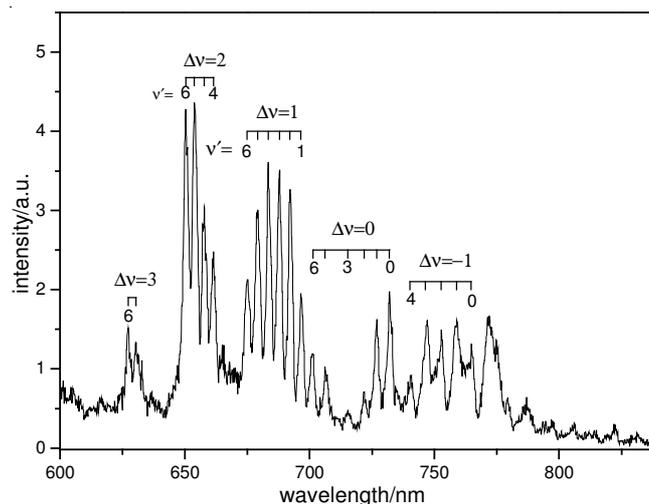


Fig. 2. Emission spectra of  $NI(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$  obtained when the iodine vapours with the carrier gas of nitrogen are added to a flow of active nitrogen

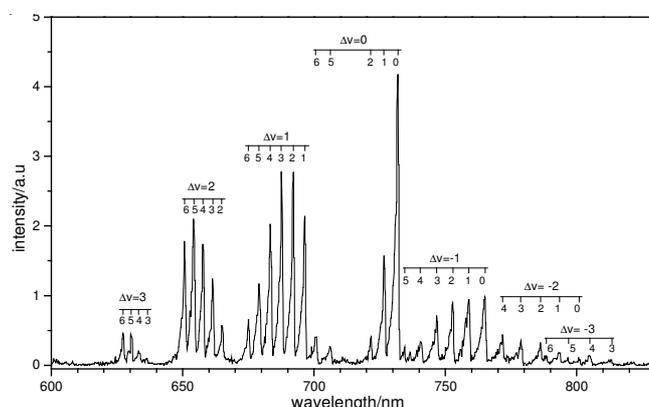
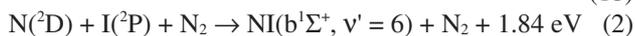
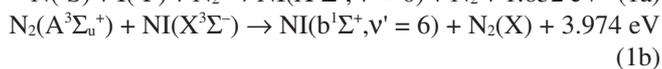
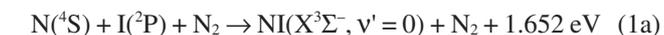


Fig. 3. Emission spectra of  $NI(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$  obtained when  $C_2H_5I$  is added to a flow of active nitrogen

Emission from vibrational level as high as  $v' = 6$  of the  $NI(b^1\Sigma^+)$  state is evident in Figs. 2 and 3. The sharp cutoff of the transition at  $v' = 7$  suggests that vibrational predissociation would take place over the  $v' = 6$  level of the excited  $NI(b^1\Sigma^+)$  state. The intensity of the 0-0 transition in the active nitrogen/ $C_2H_5I$  system is the highest among all the vibrational transitions, where the Franck-Condon factor of the 0-0 vibrational transition in  $NI(b^1\Sigma^+ \rightarrow X^3\Sigma^-)$  is the largest. However, in the active nitrogen/iodine system, the intensity of the 0-0 vibrational transition is lower than other vibrational transitions. There are obvious differences about the vibrational distributions of the  $NI(b^1\Sigma^+)$  state between the spectra obtained from

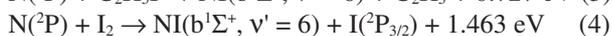
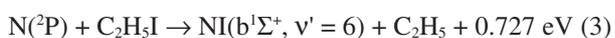
the two reaction systems. It shows that the unrelaxed emission character is more obvious in the active nitrogen/iodine system than in the active nitrogen/C<sub>2</sub>H<sub>5</sub>I system.

It is well known that active nitrogen includes the ground state nitrogen atom N(<sup>4</sup>S) and molecule N<sub>2</sub> and the metastable N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>), N(<sup>2</sup>D) and N(<sup>2</sup>P)<sup>13,14</sup>. From the Figs. 2 and 3, it is observed that the mechanisms for production of the NI(b<sup>1</sup>Σ<sup>+</sup>) state in two reaction systems are not the same. Therefore the following two production mechanisms of excited NI(b<sup>1</sup>Σ<sup>+</sup>) can be ruled out.



where iodine atoms in mechanism 1 and mechanism 2 can be produced by the collisional dissociation of C<sub>2</sub>H<sub>5</sub>I (or I<sub>2</sub>) molecules with the N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>) metastable in active nitrogen. Mechanism 1 includes that a three-body recombination process and an energy transfer process. However the energy transfer process has too large energy-defect to occur. Mechanism 2 is a three-body recombination process involving in metastable excited atom N(<sup>2</sup>D). If mechanism 1 or 2 were effective, the emission spectra of NI(b<sup>1</sup>Σ<sup>+</sup> → X<sup>3</sup>Σ<sup>-</sup>) obtained in the active nitrogen/iodine system and the active nitrogen/C<sub>2</sub>H<sub>5</sub>I system would be identical.

In the active nitrogen/C<sub>2</sub>H<sub>5</sub>I system, the formation mechanism of the excited NI(b<sup>1</sup>Σ<sup>+</sup>) is proposed to be the reaction of N(<sup>2</sup>P) in active nitrogen with C<sub>2</sub>H<sub>5</sub>I molecule<sup>9</sup>. In reaction (3), the N(<sup>2</sup>P) can be generated by the interaction between N(<sup>4</sup>S) and N<sub>2</sub>(A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>) with the rate coefficient of 4 × 10<sup>-11</sup> cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup><sup>15</sup>.



Thus the formation mechanism of the excited NI(b<sup>1</sup>Σ<sup>+</sup>) in the active nitrogen/iodine system can also be proposed that NI(b<sup>1</sup>Σ<sup>+</sup>) is the reaction production between the N(<sup>2</sup>P) atom in active nitrogen and the iodine molecule. The reaction energy of reaction (4) is 1.463 eV, which is more than that of reaction (3). It is consistent with the experimental observations. More

heat energy released in exothermic reaction (4) results in higher vibrational levels distribution of nascent NI(b<sup>1</sup>Σ<sup>+</sup>) molecules in the active nitrogen/iodine system. The one-step reaction mechanism is also consistent with the experimental fact that the yellow-orange flame appears instantly in the mixing zone.

## Conclusion

The reaction of active nitrogen with iodine molecule can efficiently generate electronically excited state NI(b<sup>1</sup>Σ<sup>+</sup>) in a traditional flowing after glow reactor, where the active nitrogen is produced through a hollow discharge of high pure nitrogen gas. The emission spectra of NI(b<sup>1</sup>Σ<sup>+</sup> → X<sup>3</sup>Σ<sup>-</sup>) obtained in the active nitrogen/iodine system show obvious unrelaxed emission character. The results show that the excited state NI(b<sup>1</sup>Σ<sup>+</sup>) is produced directly through the one-step reaction between iodine molecule and N(<sup>2</sup>P) atom in active nitrogen.

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## REFERENCES

1. A.J. Ray and R.D. Coombe, *J. Phys. Chem.*, **99**, 7849 (1995).
2. T.L. Henshaw, G.C. Manke, T.J. Madden, M.R. Berman and G.D. Hager, *Chem. Phys. Lett.*, **325**, 537 (2000).
3. A. Elliot, *Proc. R. Soc. (London) A*, **169**, 469 (1938).
4. R. Colin and W.E. Jones, *Canadian J. Phys.*, **45**, 301(1967).
5. O. Shestakov, R. Gielen, K. Setzer and E. Fink, *J. Mol. Spectrosc.*, **192**, 139 (1998).
6. G.W. Rice, A.P. D'silva and V.A. Fassel, *Appl. Spectrosc.*, **38**, 149 (1984).
7. C.G. Freeman and L.F. Phillips, *J. Phys. Chem.*, **68**, 362 (1964).
8. R. Minkwitz and F.W. Froben, *Chem. Phys. Lett.*, **39**, 473 (1976).
9. X.S. Tang, H.M. Wang, Y.N. Chu, W.J. Zhang, S.K. Zhou, *Chem. Phys. Lett.*, **423**, 174 (2006).
10. H.M. Wang, X.S. Tang, S.K. Zhou, W.J. Zhang and Y.N. Chu, *Chem. Phys. Lett.*, **407**, 78 (2005).
11. X.S. Tang, H.M. Wang, H.Y. Han, J.Q. Li, S.P. Jin, G.D. Huang, Y.N. Chu, W.J. Zhang and S.K. Zhou, *Acta Phys.-Chim. Sin.*, **21**, 392 (2005).
12. J.T. Herron, *J. Phys. Chem. Ref. Data*, **25**, 1453 (1999).
13. B. Brocklehurst and K.R. Jennings, *Prog. React. Kinet.*, **4**, 1 (1967).
14. J.T. Herron and R.E. Huie, *J. Phys. Chem.*, **72**, 2235 (1968).
15. L.G. Piper, *J. Chem. Phys.*, **90**, 7087 (1989).