# Efficient I(5 $^2P_{1/2}$) Production by the Reaction of $I_2$ with $NCl_3$ Flame

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When gaseous iodine was admitted into the $NCl_3$ autodecomposition flame, intense I(5 $^2P_{1/2}$) → I(5 $^2P_{3/2}$) emission was observed owing to direct pumping of iodine atoms by $NCl_3$ flame. It is found that the chemical environment of $NCl_3$ flame is benign for I(5 $^2P_{3/2}$). The mechanisms of I(5 $^2P_{1/2}$) production in the $NCl_3/I_2$ reactive gas flow are discussed for the first time. It is believed that Frank–Condon favored *E–E* energy transfer from $Cl_2$(B) to I(5 $^2P_{3/2}$) and the nearly resonant *V–E* energy transfer from $Cl_2$(X, $v = 15$) to I(5 $^2P_{3/2}$) respond for the production of excited state iodine atoms.

The first chemically pumped iodine laser oscillating on the I(5 $^2P_{1/2}$)–I(5 $^2P_{3/2}$) (hereafter I* and I) electronic transition was demonstrated by McDermott et al.[1] in 1978. Excited iodine atoms I* for use in iodine lasers has been produced photolytically[2] and by near resonant energy transfer between ground state iodine atoms and energy carriers, such as singlet oxygen $O_2$(a) (chemical oxygen iodine laser, COIL)[3] and NCl(a) ($HN_3$-based all gas-phase iodine laser, AGIL).[4] However, as the most successful iodine laser, COIL suffers from the on-demand preparation of basic hydrogen peroxide (BHP) that is unstable to long preservation, from the overall all weight ratio of singlet oxygen generator (SOG), and from water vapor, a relatively strong deactivator of excited iodine atoms.[5a] For $HN_3$-based AGILs, the difficulty lies in the highly explosives of gaseous $HN_3$ when condensed and in a high-temperature combustor to produce F or Cl.[5b]

Recently, McDermott et al.[6a] have observed NCl(a–X) emission spectrum in the $Cl/H_2/NCl_3$ flow system, and Davis et al.[6b] have observed I* transition in $H/NCl_3/HI$ flow system and the resulting significant decrease in the optical absorption of iodine atoms. More recently, McDermott et al.[6c] utilized the $NCl_3$ autodecomposition reaction as chlorine atom source to remove the necessity of a high-temperature combustor.

However, in spite of many thorough experiments on the $NCl_3$ system,[6] no laboratory has reported the achievement of laser oscillation based on $NCl_3/H/I$ reaction schemes. So, further deep studies on $NCl_3$ reactions to produce excited iodine atoms I* efficiently are needed. In the present study, the direct pumping of iodine atoms by $NCl_3$ autodecomposition flame was examined and studied.

A bright red flame in the gas-flow reactor due to surface-catalyzed branched-chain decomposition of $NCl_3$ was observed downstream the nozzle injector immediately after the gaseous mixture of $NCl_3$/He was expanded through the 140-μm diameter nozzle injector into the 1–10 Torr flow reactor. The red light is attributed to the B–X emission of $Cl_2$ molecules and $Cl_2$(B) is populated mostly on $v = 0$ vibrational level. The temperature increment of the reactor is less than 5 °C. This indicates that the wall losses of reactive species can be negligible at experimental conditions and that the energy librated by energetic $NCl_3$ molecules is mostly distributed on $Cl_2$(B) or higher vibrational levels of $Cl_2$(X).

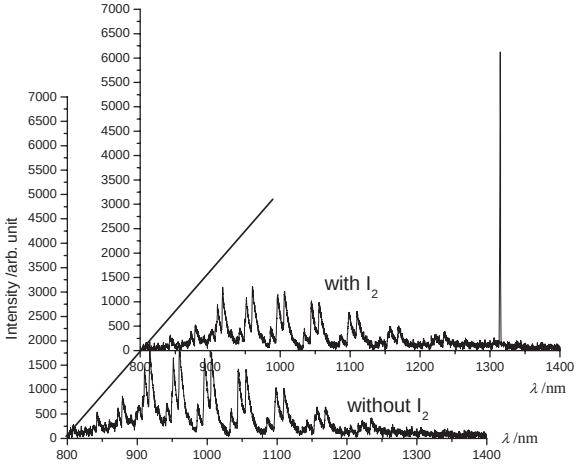


**Figure 1.** IR spectra of $NCl_3$ combustion flame with and without iodine.

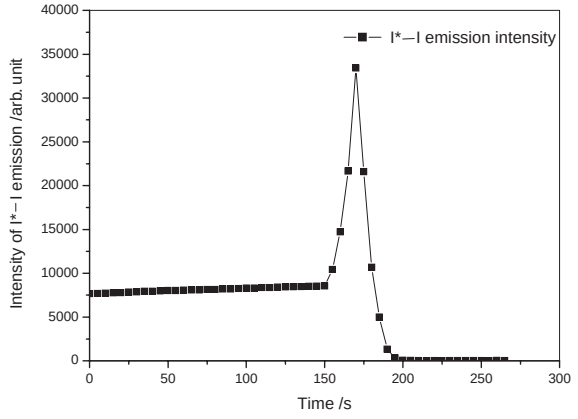


**Figure 2.** Flashed increase of I*–I emission before its extinguishing when $I_2$ flow is turned off.

As is shown in Figure 1, intense I*–I emission at 1315 nm is observed immediately after the admission of $I_2$/He gas mixture into the $NCl_3$ flame. It can be seen in Figure 1 that the intense I*–I emission is always accompanied by a little reduction of $Cl_2$(B–X) emission intensity.

It is found that when the $I_2$/He gas mixture is injected downstream to the $NCl_3$ flame, no I*–I emission at 1315 nm could be observed. When the $I_2$/He gas flow is injected upstream to the $NCl_3$ flame, the I*–I emission can be observed in the flame and after the flame. These results indicate that excitation of iodine atoms results from $Cl_2$(B) energy carrier or some species in $NCl_3$ flame related with $Cl_2$(B). To date, however, there is no reference that discusses the mechanisms of the energy transfer between

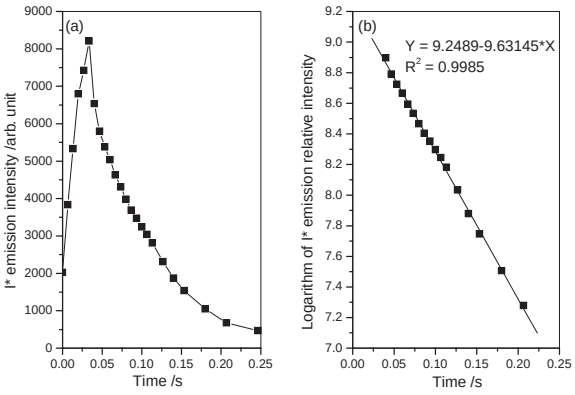


**Figure 3.** Rapid production and slow decay of excited iodine atoms I*. (a) The time decay of I* along the gas-flow reactor; (b) Logarithmic plot for the time decay of I*.

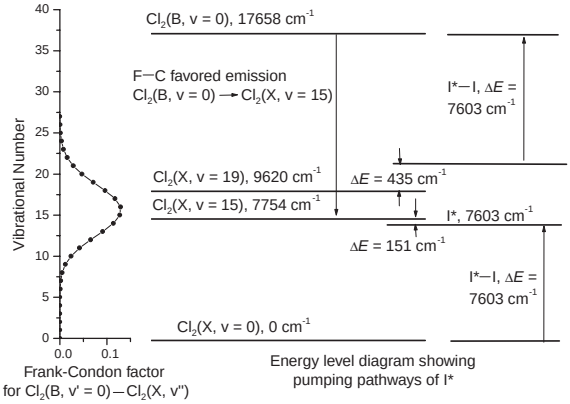


**Figure 4.** The most probable mechanism proposed for the production of excited state iodine I* in $NCl_3/I_2$ reactive flow system.

$NCl_3$ flame and iodine atoms.

In the case that $I_2$ is excessive, an interesting flashed-increase of I*–I emission before its extinguish is observed in our experiments when the $I_2$ flow is turned off, as is shown in Figure 2. The I* emission is stable under fixed flow rate of $NCl_3$ and $I_2$. However, it was found that the I* emission intensity would always increased sharply and multiply before its final extinguishing. It may be explained by the efficient quenching of I* by $I_2$.[7]

Figure 3a shows the rapid production of I* and the I*–I emission intensity decay curve along the flow reactor. Fast production of I* indicates that the energy-transfer process is efficient and the a compact iodine laser is feasible. Figure 3b is a logarithmic plot for the time decay of excited-state iodine atoms. A slow total decay rate, $k_d = 9.6\,s^{-1}$, is obtained by a least-squares fitting. It is comparable with the radiation rate, $k_r = 7.8\,s^{-1}$.[7] Consequently, when $I_2$ is almost completely converted into I by reacting with Cl, the quenching decay rate of I*, $k_q = k_d - k_r$, is virtually negligible at experimental conditions. These indicate that the chemical environment in the $NCl_3$ autodecomposition reaction is benign for I* and that a scalable chemical laser system may be feasible.

In order to explain the efficient production of I*, the following probable mechanisms are proposed.

Iodine atoms can be generated by the rapid reaction of $I_2$ with Cl atoms in $NCl_3$ flame. Then, iodine atoms reacting with $NCl_3$ flame can produce excited iodine atoms I*.

$$Cl + I_2 \rightarrow ICl + I \quad (1a)$$

$$Cl + ICl \rightarrow Cl_2 + I \quad (1b)$$

One probable mechanism is the energy transfer between energy carriers and iodine atoms. The Frank–Condon factor of $Cl_2(B, v = 0)$–$Cl_2(X)$[8] and the energy level diagrams of $Cl_2(B)$, $Cl_2(X, v)$ and I* are shown in Figure 4. As is seen in Figure 4, the electronic transition of $Cl_2(B, v = 0)$ to $Cl_2(X, v = 15–19)$ is Frank–Condon favored. The electronic transition of $Cl_2(B, v = 0)$ to $Cl_2(X, v = 19)$ and vibrational transition of $Cl_2(X, v = 15)$ to $Cl_2(X, v = 0)$ is virtually in energy resonance with the electronic transition from I to I*, and these energy-transfer rates are expected to be extremely efficient. Therefore, it is possible that the high vibrational levels of the X state of $Cl_2$, $Cl_2(X, v = 15–19)$ participate in the production of I*. It includes two pathways, i.e., (i) *E–E* energy transfer:

$$Cl_2(B, v = 0) + I \rightarrow Cl_2(X, v = 19) + I^* \quad (2)$$

and (ii) *V–E* energy transfer:

$$Cl_2(B, 0) \rightarrow Cl_2(X, v = 15) + h\nu(1007\,nm) \quad (3a)$$

$$Cl_2(X, v = 15) + I \rightarrow Cl_2(X, v = 0) + I^* \quad (3b)$$

As aforementioned, the flow tube studies show that the intense I* emission could be produced only in the presence of $Cl_2(B)$. It also can be seen in Figure 1 that the intense I*–I emission is always accompanied by a little reduction of $Cl_2(B$-$X)$ emission intensity. These suggest that $Cl_2(B)$ or some excited state species related with $Cl_2(B)$ must participate in the efficient production of I*.

Another probable mechanism may be due to $Cl_3(AL)$. Linear type $Cl_3$ intermediate has a strongly bound state AL, located about $8900\,cm^{-1}$ above the ground state XL, which is in nearly resonance with I*–I transition.[9] The $Cl_3(AL)$ intermediate may be produced in $NCl_3$ flame by the recombination of Cl and $Cl_2(B)$. More mechanisms can be seen in detail in Supporting Information.[10]

In summary, intense I*–I emission could be observed by the reaction of $I_2$ with $NCl_3$ flame. I* was produced only in the presence of $Cl_2(B)$. The chemical environment of the $NCl_3$ autodecomposition flame is benign for I*. The $NCl_3/I_2/He$ system can be a scale efficient iodine laser system. Finally, the most probable mechanisms for I* production are proposed for the first time. They include nearly resonant energy-transfer processes from $Cl_2(B)$ and $Cl_2(X, v = 15)$ to $I(5\,^2P_{3/2})$.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) June 7, 2008; doi:10.1246/cl.2008.738