Parametric Study of NCl($a^1\Delta$) and NCl($b^1\Sigma$) from the Reaction of $Cl/Cl_2/He + HN_3/He$

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By means of a microwave generator, chlorine diluted by helium was dissociated to chlorine atoms that subsequently reacted with hydrogen azide to produce the excited states of NCl($a^1\Delta$) and NCl($b^1\Sigma$). In this paper, the intensity of NCl($a^1\Delta$) and NCl($b^1\Sigma$) emission dependent on the flow rates of different gases was studied. Moreover, the production of NCl($a^1\Delta$) and NCl($b^1\Sigma$) along the reaction tube was also investigated. The results are presented and discussed. The optimum parameters for NCl($a^1\Delta$) and NCl($b^1\Sigma$) production are given, and the quenching rate of NCl($a^1\Delta$) by Cl_2 is obtained.

Introduction

Being the shortest wavelength chemical laser and the only laser based on electronic transition, the chemical oxygen−iodine laser (COIL) is of great interest owing to its potential applications in both industrial and military fields.[1] As the energy source of the laser, $O_2(a^1\Delta)$ is produced by the reaction of gaseous chlorine with liquid basic hydrogen peroxide (BHP) in the singlet oxygen generator (SOG), which is a main part of the COIL and occupies most of the COIL in size and weight, so power-volume or power-weight efficiency is limited by the gaseous−liquid reaction. Moreover, there are strong quenchers for excited atomic iodine, for example, water vapor and hydrogen peroxide, produced in the singlet oxygen generator (SOG). Consequently, it is necessary to look for metastable particles instead of $O_2(a^1\Delta)$ to pump iodine atoms.

Bower and Yang[2] reported the nearly resonant energy transfer from metastable NCl($a^1\Delta$) to atomic iodine in 1990 and obtained a reactive rate of $>1 \times 10^{-10}$ cm^3 s^{-1}, which is much faster than that of $O_2(a^1\Delta)$ to atomic iodine. The concept of NCl($a^1\Delta$)/I as a newly possible laser system is becoming a hot point. Many papers[3−9] about NCl($a^1\Delta$) energy transfer and quenching kinetics were reported. Yang et al.[10] achieved population inversion between $I(^2P_{1/2})$ and $I(^2P_{3/2})$ in 1992; Henshaw[11] and his group at the Air Force Research Laboratory measured the gain on the 1315 nm transition of atomic iodine in a subsonic flow of chemically generated NCl($a^1\Delta$) in 1999 and subsequently showed an output power of 180 mW from a new energy transfer chemical iodine laser pumped by NCl($a^1\Delta$) at 1315 nm in 2000.[12]

The mechanism of the system for a chemical atomic iodine laser pumped by NCl($a^1\Delta$) is generally as follows:

Production of NCl($a^1\Delta$)

$$Cl + HN_3 \rightarrow HCl + N_3 \qquad 8.9 \times 10^{-13\ 4} \qquad (1)$$

$$Cl + N_3 \rightarrow NCl(a^1\Delta) + N_2 \qquad 1.5 \times 10^{-11\ 4} \qquad (2)$$

Production of atomic iodine

$$Cl + HI \rightarrow HCl + I \qquad 1.0 \times 10^{-10\ 7} \qquad (3)$$

$$\text{or} \quad Cl + I_2 \rightarrow ICl + I \qquad 2.0 \times 10^{-10\ 15} \qquad (4)$$

$$\text{or} \quad Cl + ICl \rightarrow Cl_2 + I \qquad 8.0 \times 10^{-12\ 15} \qquad (5)$$

Production of excited atomic iodine

$$NCl(a^1\Delta) + I \rightarrow I(^2P_{1/2}) + NCl(X^3\Sigma) \qquad 1.8 \times 10^{-11\ 3} \qquad (6)$$

The above reactive rates are in units of cm^3/(s molecule).

Lasing

$$I(^2P_{1/2}) + h\nu \rightarrow I(^2P_{3/2}) + 2h\nu \qquad 7.8\ s^{-1\ 15} \qquad (7)$$

In addition, there is a sharp increase of NCl($b^1\Sigma$) emission upon iodine being injected into the system of NCl($a^1\Delta$)/Cl/He/Cl_2/HN_3, that is, a potential chemical laser at visible[13] is based on

$$NCl(X^3\Sigma) + I(^2P_{1/2}) \rightarrow NCl(a^1\Delta) + I(^2P_{3/2}) \qquad (8)$$

$$NCl(a^1\Delta) + I(^2P_{1/2}) \rightarrow NCl(b^1\Sigma) + I(^2P_{3/2}) \qquad (9)$$

In this paper, the intensity of NCl($a^1\Delta$) and NCl($b^1\Sigma$) emission dependent on the flow rates of different gases was studied. Moreover, the production of NCl($a^1\Delta$) and NCl($b^1\Sigma$) along the reaction tube was also investigated. The results were presented and discussed, and the quenching rate of NCl($a^1\Delta$) by Cl_2 is obtained. The optimum parameters for NCl($a^1\Delta$) and NCl($b^1\Sigma$) production are given finally.

Experimental Section

The diagram of the setup we used is shown in Figure 1. The reaction tube, which was made of silica glass and had an inner radius of 1 cm and a length of 1.2 m, the microwave generator of 1000 W, the gas supply system, the OMA4, and the pumping system are indicated. The mixture of chlorine measured by a flow meter and helium measured by a flow meter flowed through the MW generator to produce chlorine atoms, which then mixed

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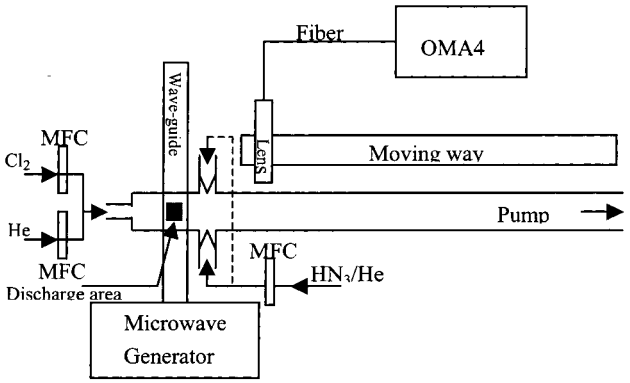

Figure 1. The schematic of the experimental setup.

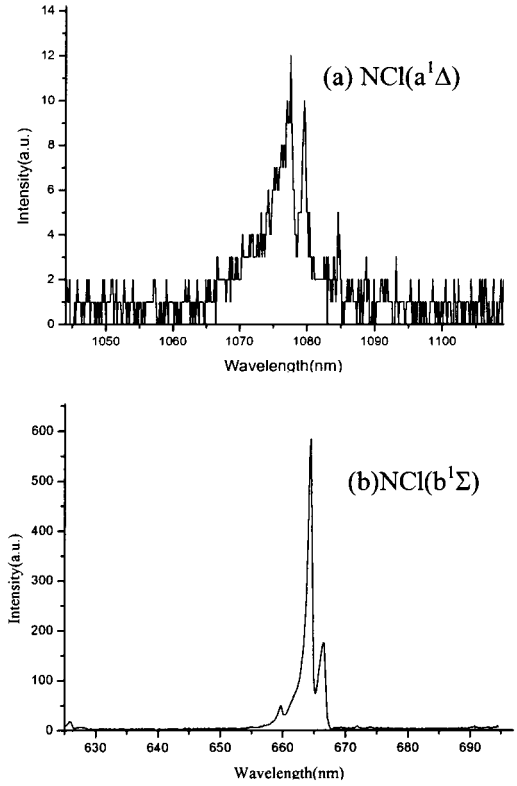

Figure 2. Spectra of NCl($a^1\Delta$) and NCl($b^1\Sigma$) emission.

and reacted with the mixture of hydrogen azide and helium at the ratio of 1:10. The chlorine and helium that we used have a purity of 99.99%. HN_3 was produced by the method described in ref 2 and stored in a 180 L steel container in which helium was input until the ratio of He/HN_3 was 10:1. The pressure of the reaction tube was about 10 Torr, and the linear velocity of the gases in the tube was around 100 m/s. NCl($a^1\Delta$) and NCl($b^1\Sigma$) emission was collected by an optical multichannel analyzer (OMA4) and processed by a computer.

Results and Discussion

1. Spectrum of NCl($a^1\Delta$) and NCl($b^1\Sigma$) Emission. Upon HN_3/He being injected into Cl/Cl_2/He, the red fluorescence can be seen immediately. Spectra of NCl($a^1\Delta$) and NCl($b^1\Sigma$) emission recorded by OMA4 are shown in Figure 2. The peaks of NCl($a^1\Delta$) emission around 1077 nm and NCl($b^1\Sigma$) emission around 665 nm are the same with the results in ref 14.

The OMA4 was calibrated by a standard tungsten lamp at 665 nm and 1077 nm, and the coefficients were 5.73×10^7 s^{-1} $counts^{-1}$ and 2.99×10^8 s^{-1} $counts^{-1}$, respectively. By means of Einstein emission coefficients, the solid angle, and the collected volume, we determined that the densities of NCl($a^1\Delta$) and NCl($b^1\Sigma$) at the experimental parameters were in the range of $10^{10}-10^{11}$ cm^{-3} and 10^7-10^8 cm^{-3}, respectively. The ratio of the densities of NCl($a^1\Delta$) and NCl($b^1\Sigma$) was about 10^3-10^4, which is well-accordant with the results of 6500 in ref 10 and agrees with a NCl(a) fraction of $\geq 0.5\%$[4] and a NCl(b) fraction of $\leq 1\%$.[5] However, it is the fact that the intensity counts of NCl($b^1\Sigma$) emission look much stronger than those of NCl($a^1\Delta$) emission (see Figure 2). This is completely due to the fact that the Einstein emission coefficient of NCl($b^1\Sigma$) (1600 s^{-1})[13] is much larger than that of NCl($a^1\Delta$) (0.7 s^{-1})[13] and the sensitivity of OMA4 is more sensitive at visible than at IR ranges.

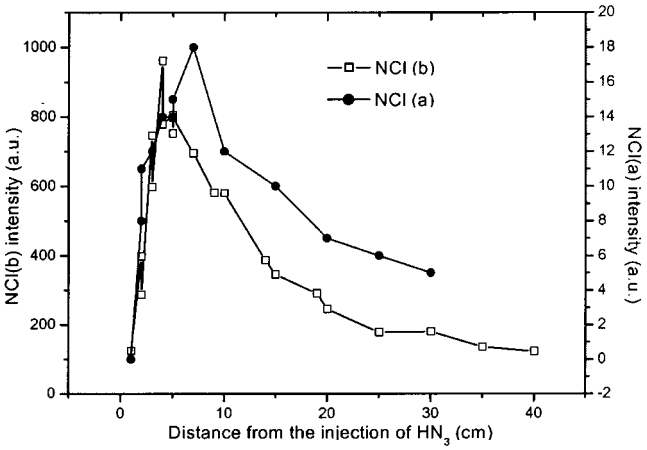

Figure 3. The intensity of NCl($a^1\Delta$) and NCl($b^1\Sigma$) emission along the reaction tube.

2. NCl($a^1\Delta$) and NCl($b^1\Sigma$) Emission along the Reaction Tube. The intensity of NCl($a^1\Delta$) and NCl($b^1\Sigma$) emission along the reaction tube is shown in Figure 3. It can be seen that there is a maximum at the range of 4−5 cm along the reaction tube at the experimental conditions of the helium flow rate of 19.7 SLM, chlorine flow rate of 0.42 SLM, HN_3/He mixture flow rate of 1.6 SLM and the pressure of the reactor at 10 Torr. This is easily understood because the production of NCl($a^1\Delta$) and NCl($b^1\Sigma$) increases with the mixing, which is better and better with the distance and, on the other hand, the quantity of NCl($a^1\Delta$) and NCl($b^1\Sigma$) decreases with the distance owing to the quenching by many particles, for example, NCl($a^1\Delta$) quenched by the following particles.

$$\mathrm{NCl}(a^1\Delta) + \mathrm{M} \rightarrow \mathrm{NCl}(X^3\Sigma) + \mathrm{M}$$

$$\mathrm{M} = \mathrm{Cl_2} \qquad (4 \pm 1) \times 10^{-13}\ ^2 \tag{10}$$

$$= \mathrm{He} \qquad \leq 1 \times 10^{-15}\ ^{16} \tag{11}$$

$$= \mathrm{Cl} \qquad 1 \times 10^{-12}\ ^3 \tag{12}$$

Because the pressure in the reaction tube is low, the quenching of NCl($a^1\Delta$) by the silicon tube wall is too small to be considered. Considering the reaction formulas of eqs 1, 10, 11, and 12 and denoting the [Cl_2], [He], and [Cl] as [M], we can obtained the following kinetics equation:

$$\frac{\mathrm{d}[\mathrm{NCl}(a^1\Delta)]}{\mathrm{d}t} = k_1[\mathrm{Cl}][\mathrm{HN_3}] - \sum k_m[\mathrm{M}][\mathrm{NCl}(a^1\Delta)] \tag{13}$$

If we input the linear velocity of the gas (denoted as u), the

equation can be written as a function of the distance (denoted as x):

$$\frac{d[NCl(a^1\Delta)]}{dx} = \frac{1}{u}\{k_1[Cl][HN_3] - \sum k_m[M][NCl(a^1\Delta)]\} \quad (14)$$

Assuming $[HN_3]$, [M], and the reactive rates of k_1 and k_m as constants and integrating the above equation, we obtain the following:

$$[NCl(a^1\Delta)] = \frac{A}{B}(1 - e^{-Bx}) \quad (15)$$

where $A = (1/u)(k_1[HN_3]_0[Cl])$ and $B = (1/u)(\sum k_m[M])$.

If only considering the dominant reaction step (eq 1), we can obtain that [Cl] goes down with the distance according to the reaction kinetics equation

$$\frac{d[Cl]}{dx} = -\frac{1}{u}\{k_1[Cl][HN_3]\}$$

So,

$$[Cl] = [Cl]_0 e^{-cx} \quad (16)$$

where $c = (1/u)k_1[HN_3]_0$. So eq 15 becomes

$$[NCl(a^1\Delta)] = \frac{A_0}{B} e^{-cx}(1 - e^{-Bx}) \quad (17)$$

where $A_0 = (1/u)(k_1[HN_3]_0[Cl]_0)$. The maximum of NCl($a^1\Delta$) along the distance can be easily obtained on the basis of making the differential equation of formula 17 equal zero.

Also, both profiles have almost the same trend, and the emission of NCl($a^1\Delta$) and NCl($b^1\Sigma$) spreads all over the tube inside according to spectrum measurements as well as sights. In the following, we studied the relationship of the intensity of the NCl($b^1\Sigma$) emission and the parameters of gaseous flow rates because NCl($a^1\Delta$) has the same trend with NCl($b^1\Sigma$), and the OMA4 has a higher signal-noise ratio in the visible wavelengths.

3. NCl($a^1\Delta$) and NCl($b^1\Sigma$) Emission Dependent on the Ratio of He and Cl_2. The intensity of NCl($b^1\Sigma$) emission dependent on the ratios of He and Cl_2 was studied at the position of 5 cm and is indicated in Figure 4. The ratio of He and Cl_2 was changed by adjusting the flow rates of chlorine at a fixed flow rate of helium. The intensity of NCl($b^1\Sigma$) emission is almost completely stronger at the ratios of He and Cl_2 of more than 30:1 in the cases of several flow rates of helium. In more detail, it also can be seen that the ratio of He and Cl_2 for the maximum intensity of NCl($b^1\Sigma$) emission increases with the flow rate of He. Even so, the ratio of helium and chlorine at 30:1 is enough to protect atomic chlorine Because it is not easy to charge for more diluent helium by means of the microwave generator.

4. NCl($a^1\Delta$) and NCl($b^1\Sigma$) Emission Dependent on Cl_2. The intensity of NCl($b^1\Sigma$) emission dependent on the flow rates of Cl_2 is shown in Figure 5 in which the maximum intensity of NCl($b^1\Sigma$) emission was in the range of 0.25−0.4 SLM for the flow rate of chlorine. More or less chlorine can cause a decrease in the production of NCl($a^1\Delta$) and NCl($b^1\Sigma$) because less chlorine only produces less chlorine atoms and consequently produces less excited particles; in contrast, excessive chlorine can quench the excited particles of NCl($a^1\Delta$) and NCl($b^1\Sigma$). The

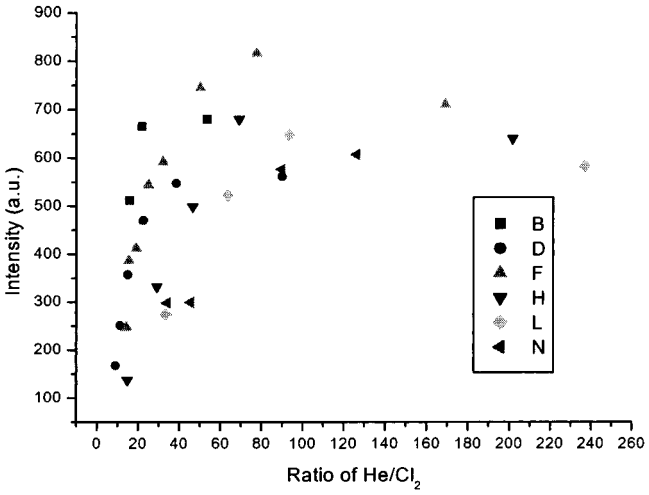

Figure 4. The intensity of NCl($b^1\Sigma$) emission dependent on the ratios of He and Cl_2: (B) He 4.8 SLM, HN_3/He (1:10) 0.5 SLM; (D) He 8.1 SLM, HN_3/He (1:10) 1 SLM; (F) He 18.6 SLM, HN_3/He (1:10) 2.5 SLM; (H) He 24.2 SLM, HN_3/He (1:10) 1 SLM; (L) He 30 SLM, HN_3/He (1:10) 1 SLM; (N) He 39.2 SLM, HN_3/He (1:10) 2 SLM.

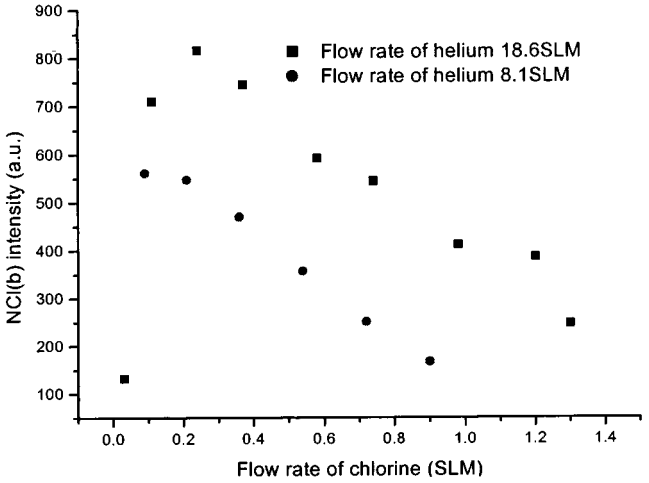

Figure 5. The intensity of NCl($b^1\Sigma$) emission dependent on the flow rates of Cl_2.

relationship of the density of NCl($a^1\Delta$) and the density of Cl_2 is display in Figure 6.

Now, we only consider the quenching by Cl_2 because k_{He} is much less than k_{Cl_2} and the atomic chlorine is much less; the kinetics equation can be written as

$$\frac{d[NCl(a^1\Delta)]}{dx} = \frac{1}{u}(-k_{Cl_2}[Cl_2][NCl(a^1\Delta)])$$

$$[NCl(a^1\Delta)] = -[NCl(a^1\Delta)]_0 e^{-(1/u)k_{Cl2}x[Cl_2]} \quad (18)$$

From the fit of the experimental data in Figure 6, the exponential coefficient of $(1/u)k_{Cl_2}x$ is simulated as 2×10^{-16}. Based on the linear velocity of ca. 10 000 cm/s and the collecting position of 5 cm, the quenching rate of NCl($a^1\Delta$) by chlorine (denoted as k_{Cl_2}) is around 4×10^{-13} cm^3/(s molecule), which is in good agreement with the result in ref 6.

5. NCl($a^1\Delta$) and NCl($b^1\Sigma$) Emission Dependent on HN_3/He. The intensity of NCl($b^1\Sigma$) emission dependent on the flow rate of HN_3/He at different flow rates of helium and chlorine is

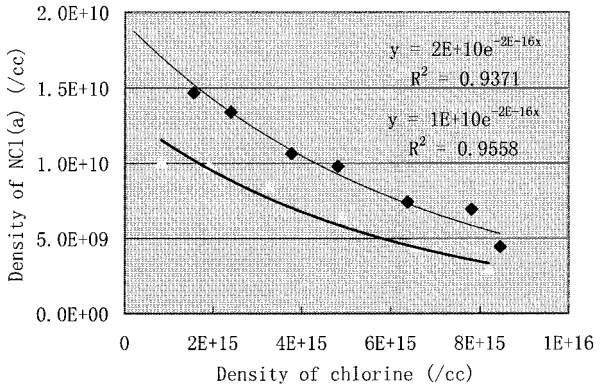

Figure 6. The dependence of the density of NCl($a^1\Delta$) on the density of Cl_2.

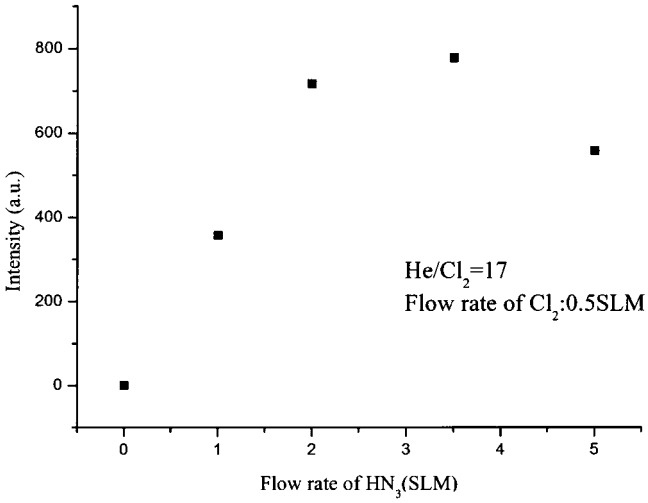

Figure 7. The intensity of NCl($b^1\Sigma$) emission dependent on the flow rate of HN_3/He.

shown in Figure 7 in which it can be seen that the maximum NCl($b^1\Sigma$) was produced at the flow rate of 2.5−3.5 SLM of HN_3/He. Excess or less HN_3/He can cause the decrease of the production of NCl($a^1\Delta$) and NCl($b^1\Sigma$) because less hydrogen azide only produces limited excited particles and extra hydrogen azide similarly quenches the excited particles of NCl($a^1\Delta$) and NCl($b^1\Sigma$) though the reaction rate of NCl($a^1\Delta$) quenched by HN_3 is unknown to us so far.

$$NCl(a^1\Delta) + HN_3 \rightarrow NCl(X^3\Sigma) + HN_3 \qquad k_x = ?$$

$$\frac{d[NCl(a^1\Delta)]}{dt} = k_1[Cl][HN_3] - k_x[HN_3][NCl(a^1\Delta)] + k_m[M][NCl(a^1\Delta)]$$

If we assume that the mixing efficiency is unity, we can obtain that the dissociation efficiency of chlorine based on the maximum flow rate of hydrogen azide,

$$\eta_{diss} = \frac{[HN_3]_{max}}{[Cl_2]}$$

is 50%−75%. In summary, the optimum operating parameters for the present setup are listed in Table 1.

TABLE 1: The Optimum Operating Parameters for the Present Setup

HN_3 flow rate (SLM)	0.25−0.35
Cl_2 flow rate (SLM)	0.25−0.4
He flow rate (SLM)	11−14
pressure (Torr)	10
diameter of the tube (cm)	2
Cl_2 dissociation efficiency (%)	50−75
linear velocity (m/s)	100

Conclusion

Through the parametric study of NCl($a^1\Delta$) and NCl($b^1\Sigma$) emission, it can be seen that the branch ratio of NCl($a^1\Delta$) and NCl($b^1\Sigma$) is about 10^3-10^4 in the reaction system of Cl/Cl_2/He + HN_3/He. The ratio of helium and chlorine of about 30:1 is enough to protect atomic chlorine because it is not easy to charge for more diluent helium by means of the microwave generator. Also, we obtained that the optimum parameters for the production of NCl($a^1\Delta$) and NCl($b^1\Sigma$) were the flow rates of chlorine in the range of 0.25−0.4 SLM, hydrogen azide in the range of 0.25−0.35 SLM, and helium in the range of 11−14 SLM and the pressure of the reaction tube at about 10 Torr in our present experimental conditions. Moreover, the quenching rate of NCl($a^1\Delta$) by Cl_2 is about 4×10^{-13} cm^3/(s molecule).

References and Notes

(1) Zhuang, Q.; Sang, F.; Zhou, D. *Short Wavelength Chemical Laser*, 1st ed.; The Publishing House of the National Defense and Industry: Beijing, China, June 1997 (in Chinese).
(2) Yang, T. T.; Bower, R. D. *Proc. SPIE—Int. Soc. Opt. Eng.* **1990**, *1225*, 430.
(3) Henshaw, T. L.; Herrera, S. D.; Schlie, L. A. *J. Phys. Chem. A* **1998**, *102*, 6239.
(4) Manke, G. C., II; Setser, D. W. *J. Phys. Chem. A* **1998**, *102*, 7257.
(5) Henshaw, T. L.; Herrera, S. D.; Haggquist, G. W.; Schlie, L. A. *J. Phys. Chem. A* **1997**, *101*, 4048.
(6) Hewett, K. J.; Manke, G. C., II; Setser, D. W.; Brewood, G. *J. Phys. Chem. A* **2000**, *104*, 539.
(7) Manke, G. C., II; Henshaw, T. L.; Madden, T. J.; Hager, G. D. *Proc. SPIE—Int. Soc. Opt. Eng.* **2000**, *3931*, A-12.
(8) Ray, A. J.; Coombe, R. D. *J. Phys. Chem.* **1993**, *97*, 3475.
(9) Ray, A. J.; Coombe, R. D. *J. Phys. Chem.* **1995**, *99*, 7849.
(10) Yang, T.; Gylys, V. T. *Opt. Lett.* **1992**, *24*, 1803.
(11) Henshaw, T. L.; Madden, T. J.; Herbelin, J. M.; Manke, G. C., II; Anderson, B. T.; Tate, R. F.; Hager, G. D. *Proc. SPIE—Int. Soc. Opt. Eng.* **1999**, *3612*, 147.
(12) Henshaw, T. L.; Manke, G. C., II; Madden, T. J.; Berman, M. R.; Hager, G. D. *Chem. Phys. Lett.* **2000**, *325*, 537.
(13) Yang, T. T. *Proc. SPIE—Int. Soc. Opt. Eng.* **1994**, *2119*, 122.
(14) Pritt, A. T.; Coombe, R. D. *Int. J. Chem. Kinet.* **1980**, *XII*, 741.
(15) Perram, G. P.; Hager, G. D. *The Standard Chemical Oxygen—Iodine Laser Kinetics Package*; Report AD-A208643; 1988.
(16) Ray, A. T.; Coombe, R. D. *J. Phys. Chem.* **1994**, *98* (36), 8940−8945.