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Measurements of dissociation efficiency of molecular chlorine through microwave discharge*

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Abstract: For the system of $Cl/Cl_2/HN_3/He$ which is the basis of concept of $NCl(a^1\Delta)/I$ as a newly possible laser system, the amount of the production of chlorine atoms is essential and important to the system. In this paper, the dissociation efficiency of chlorine by a Microwave Generator is investigated by a versatile titration technique. The intensity of $NCl(a^1\Delta)$ and $NCl(b^1\Sigma)$ emission is monitored by an OMA with the titration of mixture of He and HN_3. The dissociation efficiency of chlorine by Microwave Generator is not low as expected, it is up to 100% at lower flow rate of chlorine and decreases with increasing chlorine flow rates.

Key words: Microwave discharge; Molecular chlorine; Dissociation efficiency

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After being reported the nearly resonant energy transfer from metestable $NCl(a^1\Delta)$ to atomic iodine by Bower and Yang[1] in 1990, the concept of $NCl(a^1\Delta)/I$ as a newly possible laser system is becoming a hot point. It is certified for production of $NCl(a^1\Delta)$ via two steps as follows[2],

$$Cl + HN_3 \rightarrow HCl + N_3, \qquad 8.9\times10^{-13}$$

$$Cl + N_3 \rightarrow NCl(a^1\Delta) + N_2, \qquad (2.8\pm0.4)\times10^{-10}$$

Later, the reaction rate of the second step is verified in order of $10^{-11}cm^3/s$. For the system of $Cl/Cl_2/HN_3/He$ as the basis of the concept of $NCl(a^1\Delta)/I$ as a newly possible laser system, the amount of the production of chlorine atoms is very essential and important to the system. A large amount of metastable particles $NCl(a^1\Delta)$ can be possible to obtain via directly or indirectly generated large atomic chlorine[3~5]. T L·Henshaw[6] and his group at Air Force Research Laboratory measured the gain on the 1315nm transition of atomic iodine in a subsonic flow of chemically generated $NCl(a^1\Delta)$ in 1999 and subsequently got an output power of 180mW from a new energy transfer chemical iodine laser pumped by $NCl(a^1\Delta)$ at 1315nm in 2000[7] based on the indirect method to generate atomic chlorine which is a displacement of hydrogen chloride or deuterium chloride by atomic fluorine produced by DC discharge. And exactly due to the limited amount of atomic fluorine and consequently the limited atomic chlorine, the output power of the new laser system does not scale up, then[7]. At the latest publication, MankeII G C, T L·Henshaw and his group[8] studied the dissociation efficiency of fluorine and chlorine by DC discharge and obtained the dissociation efficiency of 100% for F_2 flow rates less than 0.5mmol/s and the efficiency with chlorine less than 50%.

1 Experimental

The diagram of the experimental setup used is shown in figure 1. A silica tube with inner diameter of 2cm goes through a microwave cavity and then extends to a 2cm×5cm rectangular cell which is melt with a tube of 5cm diameter to pumps. The total length of 1.2m, the Microwave generator of 1kW, the supply of gas system, 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 reacts

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with the mixture of hydrogen azide and helium at the ratio of 1 ∶10 injected at the exit of the microwave cavity. The chlorine and helium used have a purity of 99.99 %. HN_3 was produced by the method described in reference [1] and stored in an 180L steel contaner in which helium was input till the ratio of He/HN_3 reached 10 ∶1. The pressure of the reaction tube was about 267Pa and the linear velocity of the gases in the tube was around 150m/s. $NCl(a^1\Delta)$ and $NCl(b^1\Sigma)$ emission was collected by OMA4 and processed by a computer.

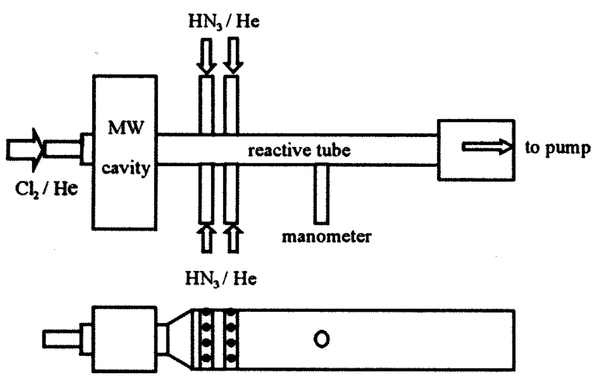

Fig. 1 Schematic of the experimental set

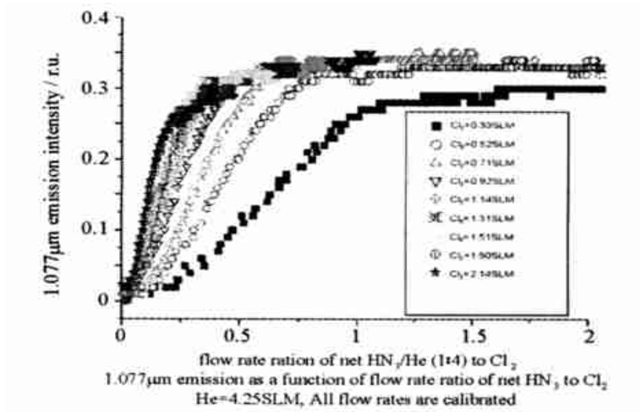

Fig. 2 Relationship of the emission intensity of $NCl(a^1\Delta)$ and the ratio of HN_3/Cl_2

2 Results and Discussion

Owing to the same trend of $NCl(a^1\Delta)$ and $NCl(b^1\Sigma)$ emission intensity[9], the emission of $NCl(b^1\Sigma)$ was first collected. Later emissions of $NCl(a^1\Delta)$ are also collected at several chlorine flow rates as shown in figure 2 in which we keep the flow rate of Cl_2 as a constant and change that of HN_3 at a flow rate of He. It can be seen from figure 2 that the maximum intensities are mostly around 1 of the HN_3/Cl_2 ratio at lower flow rates of chlorine less than 0.5 SLM (Standard Liter per Minute).

For the system of $Cl/Cl_2/HN_3/He$, the reactive mechanism is described as follows:

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

$$Cl + HN_3 \rightarrow HCl + N_3, \quad 8.9\times10^{-13} \tag{1}$$

$$Cl + N_3 \rightarrow NCl(a^1\Delta) + N_2, \quad 1.5\times10^{-11} \tag{2}$$

(2) Quenching of $NCl(a^1\Delta)$

$$NCl(a) + M \rightarrow NCl(X) + M$$
$$M = Cl_2, \quad k_{Cl_2} = (4\pm1)\times10^{-13} \tag{3}$$

$$M = He, \quad k_{He} \leq 1\times10^{-15} \tag{4}$$

$$M = Cl, \quad k_{Cl} = 1\times10^{-12} \tag{5}$$

$$M = HN_3, \quad k_{HN_3} = ? \tag{6}$$

Considering reaction formulas of (1), (2), (3), (4), (5) and denoting $[Cl_2]$, $[He]$, $[Cl]$, $[HN_3]$ as $[M]$, we can obtain the following kinetics equation of $NCl(a^1\Delta)$ reactions

$$\frac{d[N_3]}{dt} = k_1[Cl][HN_3] - k_2[Cl][N_3] \tag{7}$$

$$\frac{d[NCl(a^1\Delta)]}{dt} = k_2[Cl][N_3] - \sum k_m[M][NCl(a^1\Delta)] \tag{8}$$

Introducing the linear velocity of the gas (denoted as u), the equation can be written as a function of the distance (denoted as x). Considering the emission intensity collected at a specific position ("l" from HN_3 injectors), and $k_2[Cl]l/u \approx 10^{-3}\times10^{-3} \ll 1$, $[N_3]$ can be written as

$$[N_3]_l = \{k_1[Cl][HN_3]\frac{l}{u}/(k_2[Cl])\}(1 - e^{-k_2[Cl]l/u}) = k_1[Cl][HN_3]\frac{l}{u} \tag{9}$$

So, $NCl(a^1\Delta)$ can be as follows

$$\frac{d[NCl(a^1\Delta)]}{dx} = \frac{1}{u}\{k_1 k_2 [Cl]^2 [HN_3] \frac{l}{u} - \sum k_m [M][NCl(a^1\Delta)]\} \quad (10)$$

Assuming [Cl], $[HN_3]$, [M] and the reactive rates of k_1, k_2 and k_m as constants, and integrating the above equation as follows

$$[NCl(a^1\Delta)] = \frac{A}{B}(1 - e^{-Bl}) \quad (11)$$

Where, $A = \frac{l}{u^2}(k_1 k_2 [HN_3][Cl]^2)$, $B = \frac{1}{u}(\sum k_m [M])$

Since the linear velocity is about 150～200m/s and the distance is around 15cm, "Bl" is a small value.

$$e^{-Bl} = 1 - Bl$$

Formula (11) can be simplified as

$$[NCl(a^1\Delta)] = Al = \frac{l^2}{u^2}(k_1 k_2 [HN_3][Cl]^2) \quad (12)$$

The values of "l, u, k_1, k_2" can be considered as constants, and $(l^2/u^2) k_1 k_2$ is denoted as a constant "C", $[NCl(a^1\Delta)$ as $f(x_1, x_2)$, $[HN_3]$ as x_1, [Cl] as x_2. Equation (12) is rewritten as

$$f(x_1, x_2) = C x_1 x_2^2 \quad (13)$$

thus

$$df(x_1, x_2) = C x_2^2 dx_1 + 2 C x_1 x_2 dx_2 \quad (14)$$

make formula (14) equal zero, then

$$df(x_1, x_2) = C x_2^2 dx_1 + 2 C x_1 x_2 dx_2 = 0$$

$$C x_2^2 dx_1 = - 2 C x_1 x_2 dx_2$$

if $dx_1 = - dx_2$, then, $x_2 = 2 x_1$

That is

$$[Cl] = 2[HN_3] \quad (15)$$

The maximum point of $[NCl(a^1\Delta)]$ is located at [Cl] twice as $[HN_3]$.

If the flow rate of chlorine as a constant $[Cl_2]_m$ and assuming the dissociation efficiency of molecular chlorine as η defined as follows

$$\eta = [Cl]/2[Cl_2] \quad (16)$$

So, the equation (16) can be presented as

$$2\eta[Cl_2]_m = 2[HN_3]_m, \qquad \eta = [HN_3]_m/[Cl_2]_m \quad (17)$$

From figure 2, we can obtain that the dissociation efficiency of molecular chlorine by Microwave Generator is up to 100 % at lower flow rates of chlorine and decreases with increasing chlorine flow rate.

3 Conclusion

The dissociation efficiency of chlorine by a Microwave Generator is investigated by a versatile titration technique. We keep the flow rate of Cl_2 as constant and change that of HN_3, or make the flow rate of HN_3 as constant and change that of Cl_2 at a flow rate of He. The intensity of $NCl(a^1\Delta)$ or $NCl(b^1\Sigma)$ emission is monitored by an OMA. The dissociation efficiency of chlorine by Microwave Generator is up to 100 % at lower flow rates of chlorine and decreases with increasing chlorine flow rates.

References:

[1] Yang T T, Bower R D. $I(^2P_{1/2})$ produced from the energy transfer from $NCl(a^1\Delta)$ to $I(^2P_{3/2})$ [A]. SPIE[C]. 1990, **1225**:430.

[2] MankeII G C, Setser D W. Kinetics of NCl(a and b) Generation: The Cl + N_3 Rate Constant, the NCl(a) Product Branching Fraction, and Quenching of NCl(a) by F and Cl Atoms[J]. *J Phys Chem A*, 1998, **102**:7257.

[3] Coombe R D, Patel D, Pritt A T, et al. Photodissociation of ClN_3 at 193 and 249nm[J]. *J Chem Phys*, 1981, **75**:2177.

[4] Pritt A T, Coombe R D. Azide Mechanisms for the Production of NCl Metastables[J]. *Intern J Chem Kinetics*, 1980, **12**:741.

[5] Exton D B, Gilbert J V, Coombe R D. Generation of excited nitrogen monochloride by the reaction of hydrogen atoms with nitrogen trichloride[J]. *J Phys Chem*, 1991, **95**:2692.

[6] Henshaw T L, Madden T J, Herbelin J M, et al. Measurement of gain on the 1.315μm transition of atomic iodine produced from the NCl(a) + I energy transfer reaction[A]. SPIE[C]. 1999, **3612**:147.

[7] Henshaw T L, Manke II G C, Madden T J, et al. A new energy transfer chemical laser at 1.315μm[J]. *Chem Phys Lett*, 2000, **325**:537.

[8] Manke II G C, Henshaw T L, Madden T J. Characterizing fluorine and chlorine atom flow rates using iodine atom spectrometry[J]. *AIAA Journal*, 2001, **39**:447.

[9] Duo L P, Tang S K, Li J, et al. Parametric study of NCl($a^1\Delta$) and NCl($b^1\Sigma$) from the reaction of Cl/Cl_2/He + HN_3/He[J]. *J Phys Chem A*, 2002, **106**:743.

微波放电解离氯分子解离效率的测量

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摘 要: 以 Cl/Cl_2/HN_3/He 为基础的 NCl($a^1\Delta$)/I 作为一种化学激光新的体系,氯原子产生的多少对该体系的研究是至关重要的。利用滴定法研究了微波解离氯分子的解离效率。用 HN_3/He 滴定 Cl,由光学多通道分析仪监测 NCl($a^1\Delta$)和 NCl($b^1\Sigma$)辐射的荧光。发现微波解离氯分子的效率并不是想象的那样低,在较小的氯流量下,最高的解离效率可以达到 100 %。

关键词: 微波放电; 氯分子; 离解效率