

## LIF measurement of OH radicals in coaxial cylinder barrier discharge for clarification of toxic gas decomposition

有害ガス処理の機構解明に向けた同軸円筒バリア放電下のOH-LIF計測

Yusuke Nakagawa, Ryo Ono and Tetsuji Oda

中川雄介, 小野亮, 小田哲治

The University of Tokyo

7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

東京大学 〒113-8656 東京都文京区本郷7-3-1

Behaviour of radicals in non-thermal plasma is worth clarifying in order to interpret the chemical reaction processes in the plasma gas treatment. Inside the coaxial cylinder dielectric barrier discharge (DBD) reactor, the spatial distribution of relative density and rotational temperature of OH radicals are measured in pulsed barrier discharge under atmospheric pressure using laser-induced fluorescence (LIF) method. OH radicals are produced in the secondary streamer region. The OH rotational temperature increases within tens-hundreds of microseconds, caused by vibrational energy relaxation. The temperature in the coaxial DBD reactor rises slower and reaches lower than that in needle-plane corona discharge. There is a difference in temperature rising pace between near the anode and center of the discharge gap. It indicates that the acceleration of vibrational energy transfer mainly occurs in the secondary streamers.

### 1. Introduction

Since air pollution with gaseous contaminants is a serious problem today, it is desirable that decomposition technique of toxic gas with non-thermal plasma (NTP) be put to practical use[1,2]. Our group has been developed the NTP technique for decomposition of VOCs (volatile organic compounds). In this field, recent reports have shown that radicals play a major role in chemical reactions inside NTP. However, the radical measurement in the coaxial cylinder DBD reactor is under development yet. In this study, laser-induced fluorescence (LIF) measurement of OH(X) is performed in the coaxial cylinder DBD reactor with the injection of decomposing target, evaluating the effect of OH radicals on VOC decomposition.

### 2. Experiments

#### 2.1 Laser-induced fluorescence

An optical parametric oscillator (OPO) is used to excite OH radicals in the  $X^2\Sigma(v=0)$  ground state to the  $A^2\Pi(v=1)$  excited state by 282 nm transition [3-5]. We measure the fluorescence of 309 nm and 315nm. The fluorescence intensity  $I_{LIF}$  is proportional to the incident laser intensity  $I_L$  and ground state density  $n_0$ ,

$$I_{LIF} = cBI_L n_0 \left( \frac{A_0 Q_v}{\Gamma_1 \Gamma_0} + \frac{A_1}{\Gamma_1} \right) \quad (1)$$

where  $c$  is experimental constant,  $B$  represents the absorption coefficient of  $X^2\Pi(v=0)$ - $A^2\Sigma(v=1)$  transition,  $A$  and  $\Gamma$  represent emission and relaxation coefficients. the indices 0 and 1 are

related to  $A^2\Sigma(v=0)$  and  $A^2\Sigma(v=1)$ , respectively.  $Q_v$  is vibrational relaxation constant. With these coefficients of each state [5-8], we can determine the OH density from fluorescence intensity.

#### 2.2 Experimental setup

Experimental system is represented in Fig. 1. Optical parametric oscillator (OPO laser) generates 562 nm fundamental laser beam, which is converted to 282 nm by SHG. The trigger of the laser pulse is obtained from pulse generator and delayed  $\tau$  [s] from the trigger of the discharge so that we can observe the OH density in afterglow period. The fluorescence passes through frequency filter and is detected by photon-multiplier tube (PMT).

#### 2.3 Structure of the reactor

The reactor consists of high voltage (HV) central

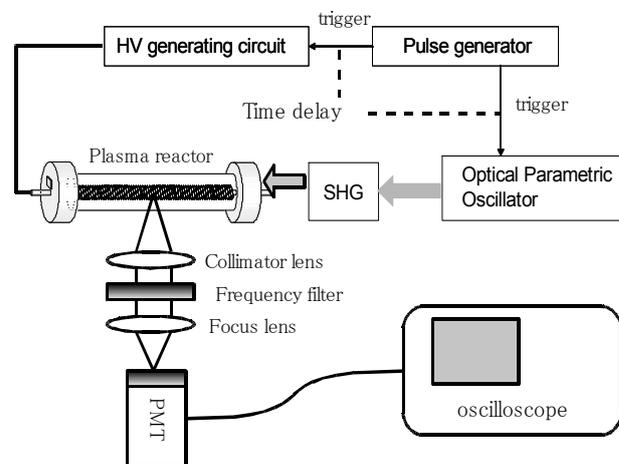


Fig.1 Experimental setup.

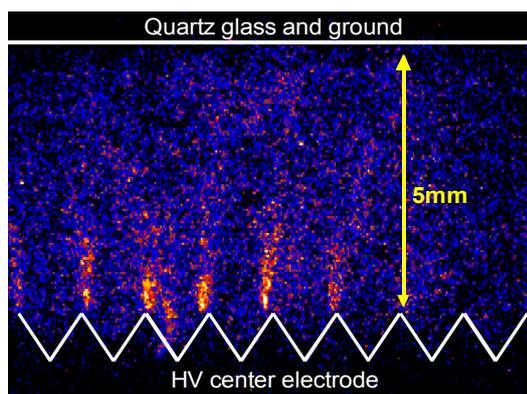


Fig.2 Photograph of barrier discharge.

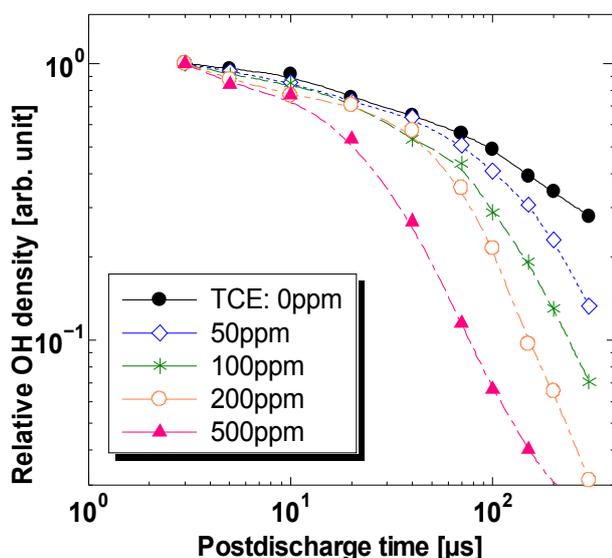


Fig.3 Time evolution of OH radicals  
( $V = 28\text{kV}$ ,  $r = 2.5\text{ mm}$  and humidity is 2.3%).

electrode, discharge space, quartz glass tube and outer ground electrode. The pulsed high voltage  $V$ [kV] is supplied with spark-gap switch. The stainless M8 screw shaft is used for the central electrode in order to be favourable for discharge. The quartz tube has 18 mm inside diameter, the gap between anode and glass is 5 mm, the length of the reactor is 190 mm. The 282 nm excitation laser beam is parallel to the electrodes and has rectangular cross section of  $1\text{ mm} \times 3.5\text{ mm}$ . The fluorescence is collected perpendicularly to the laser beam direction. The distance between the HV electrode and the laser beam is defined as  $r$  [mm]. The spatial distribution of OH can be obtained by measuring LIF signal at various  $r$ . Humid air ( $\text{O}_2(20\%)/\text{N}_2$ ) flows in the reactor at a rate of 2L/min. Decomposing target is injected to the gas flow with its boiling temperature. The discharge emission photograph at  $V = 28\text{ kV}$ , humidity: 2.3% is shown in Fig. 2.

### 3. Results and discussions

Previous study often reports that humidity in the decomposition background suppresses the decomposition efficiency of trichloroethylene (TCE)[9]. Therefore it may be suggested that OH radicals does not decompose TCE. In order to clarify the OH influence upon TCE decomposition, we measured the time evolution of OH radicals with various TCE densities in the background gas. The results are shown in Fig. 3. The discharge condition is  $V = 28\text{kV}$ ,  $r = 2.5\text{ mm}$  and humidity is 2.3%. The OH decay rate is quickened with increasing TCE concentration. This indicates OH radical definitely reacts with TCE.

The reason for suppression of TCE decomposition with increasing humidity is estimated below;

1. OH radicals decompose TCE.
2. However, OH radicals strongly react with O radicals which significantly decompose TCE.
3. As a consequence, O reduction by OH has more influence than direct TCE decomposition by OH, leading to suppression of decomposition efficiency.

### 4. Conclusion

Time evolutions of OH density are measured by LIF in pulsed barrier discharge under atmospheric pressure. The practical coaxial cylinder DBD reactor is used in order to simulate the discharge form in the gas treatment. LIF using 282nm excitation reveals that OH radicals react with TCE.

### References

- [1] H. H. Kim, *Plasma Process. Polym.*, Vol.1, 91-110 (2004)
- [2] T. Oda, *J. Electrostat.*, Vol.57, 293-311 (2003)
- [3] S. Kanazawa, H. Tanaka, A. Kajiwara, T. Ohkubo, Y. Nomoto, M. Kocik, J. Mizeraczyk and J. S. Chang, *Thin Solid Films*, Vol.515, 4266-4271 (2007)
- [4] L. Magne and S. Pasquiers, *C. R. Physique*, Vol.6, 908-917 (2005)
- [5] J. Luque and D. R. Crosley, *SRI International Report*, MP-99-009 (1999)
- [6] C. Y. Chan, R. J. O'Brien, T. M. Hard, and T. B. Cook, *J. Phys. Chem.*, Vol.87, pp.4966-4974 (1983)
- [7] G. P. Smith and D. R. Crosley, *Applied Optics*, Vol.22, No.10, pp.1428-1430 (1983)
- [8] L. R. Williams and D. R. Crosley, *J. Chem. Phys.*, Vol.104 No.17, 1 (1996)
- [9] Futamura S, Zhang A. H, Yamamoto T, *J. J. Electrostat.*, Vol.42, 51(1997)