

Absolute Concentration Measurement of Nitrogen Oxide in Flames by LIF Standard Addition Method

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Introduction

The establishment of practical measurement technique of NO is one of the most important issues in connection with the recent requirement of its global reduction. The technique of evaluating absolute NO concentration in practical combustion devices has not been well established yet. The difficulties come from the two reasons. The first is the complicated mechanisms of quenching effects. The quenching factors to NO drastically vary for different chemical species in combustion gases. The evaluation methods of the quenching effects are not at sufficient level neither theoretically nor experimentally. The second is the decrease of signal-to-noise ratio for measuring larger size objects. The S/N ratio is largely reduced, because the solid angle of collecting signal light becomes small.

Although there are many efforts to develop techniques for measuring the absolute concentration of NO molecules, quantitative reliability has not been established yet. One of the most reliable data was obtained using time-resolved LIF technique, in which quenching effects are evaluated monitoring the time decay of fluorescence intensity in nanoseconds [1].

The present paper reports a progress for developing reliable practical techniques of measuring the absolute concentration of NO molecules in burners. The results show that a quantitative measurement of NO concentration is established for laboratory-scale burners.

Experimental Apparatus and Method

The test burner was set on the central axial line of the 80 mm diameter tube, and the burner flame was stabilized by the surrounding air flow. The inner diameter of the burner is 30 mm, and a ceramic honeycombed cell was inserted inside the burner top. The methane-air premixed laminar flames of equivalence ratios 1, 0.8, and 1.2 were tested, and the LIF signal profiles at the height of 15, 25, 35, and 45 mm above the burner exit were obtained.

We used a set of excimer and dye lasers. A 308 nm beam in the XeCl excimer laser stimulates Coumarin2 dye in a dye laser to induce approximately 452 nm beam. The

frequency of the dye laser beam is further doubled in the SHG crystal to produce approximately 226 nm radiation. The fluorescence signal was collected perpendicular to the laser irradiation direction and collimated using a lens. The fluorescence intensity of approximately 247 nm along the incident laser beam was recorded by an image-intensified CCD camera through a narrow-band filter in front of the camera. Because the laser power decreases 10-50% during the measurement time, the signal output was normalized by carefully monitoring the laser power. The shutter timing of the CCD camera was controlled by a pulse delay generator, and the gate time of the camera was set 100 ns. The concentration profiles along the laser beam were obtained by accumulating the signals of 500 laser shots.

Evaluation of Temperature and Concentration

The governing equation of the LIF signals occurring by the electronic excitation from an energy level e_1 to an upper level e_2 is given below.

$$n_t = \frac{4\pi[(B_{12} + B_{21})U_L + Q_t]Z_E Z_V Z_R P(e_2, l)}{A_{21}(e_2, l)hc\nu(e_2, l)\epsilon\Omega V B_{12} U_L g_1 \exp(-E_1 / k_B T)} \quad (1)$$

$P(e_2, l)$ is the LIF signal intensity of the transition from the upper level e_2 to a lower l . n_t is number density of NO, B_{12} and B_{21} are the Einstein's coefficients of induced absorption and emission, respectively. U_L is the intensity of laser, and Q_t is the overall quenching coefficients. Z_E , Z_V , and Z_R are the partition functions of electronic, vibrational, and rotational energy levels, respectively. $A_{21}(e_2, l)$ is the Einstein's coefficient of spontaneous emission, and $\nu(e_2, l)$ is the wave number of observing fluorescence signal. The light speed is denoted by c , and h is Planck constant. Ω and ϵ are solid angle and efficiency factor of optical collection, respectively, and V is the volume of measurement. E_1 and g_1 are energy and degeneracy of energy level e_1 , respectively. Boltzmann constant k_B and temperature T appear in the above equation.

The condition of $Q_t \gg (B_{12} + B_{21})U_L$ holds in the present experiments. Further, a proper choice of e_1 level can give a simpler situation that factor of $g_1 \exp(-E_1 / k_B T) / Z_E Z_V Z_R$ in Equation (1) is approximately constant in high temperatures. The $P_{11}(36.5)$ line at 225.178 nm in $A^2\Sigma^+ \leftarrow X^2\Pi(0,0)$ transition provides the above condition in 10002000 K. The observed fluorescence were a few lines at different rotational levels in $A^2\Sigma^+ \rightarrow X^2\Pi(0,2)$ transition lines at approximately 247 nm. The influence of rotational levels is negligibly small, and the LIF lines are approximately a single line. The final approximate equation means that n_t is proportional to $P(e_2, l)$ in all the measurement points.

Mole fractions of nitrogen oxide are determined by a standard addition method. A calibrated gas mixture of 0.1% NO+N₂ gas was mixed with oxygen to make air. Under the assumption that the doped NO molecules do not react in the burnt parts of high temperature,

the comparison between the measurements of NO-doped and non-doped flames can provide the mole fractions. The NO mole fraction X is obtained by the following equation.

$$X = P(e_2, l) X_d / (P(e_2, l)_d - P(e_2, l)) \quad (2)$$

where X_d is the mole fraction of doped NO, and $P(e_2, l)_d$ is the fluorescence intensity of NO-doped flame. In addition to the methane-air gas mixtures, the air flow surrounding the flame was also doped with NO gas. The mole fractions of NO in equilibrium burnt gas of 1000-2000 K were calculated. The mole fractions are constant in these conditions. The value of X_d in Equation(2) of methane-air gas mixtures decreases 10-15% due to the chemical reactions, while the value of X_d in the surrounding air flow does not vary. For example, the initial value of 100 ppm in the flame of equivalence ratio 1 decreases to 89.9 ppm in the burnt gas. Therefore, the NO mole fraction was determined using the average value of burnt methane-air gas mixture and the surrounding air.

The absolute number density is finally obtained by an additional measurement of temperature of two-line method. The two-line method includes two different excitation lines with the common upper excitation energy level. In addition to P_{11} (36.5) line, Q_{22} (10.5) line at 226.576 nm in (0,0) transition band was used. Although the upper level is not exactly same, the difference is so small that the above assumption holds. Although the fluorescence lines are also slightly different, the effects are negligibly small. The temperature is determined using the equations below.

$$T = (E_1^a - E_1^b) / (k_B \ln \Lambda) \quad (3)$$

$$\Lambda = P(e_2, l)^b (2J+1)^a B_{12}^a / (P(e_2, l)^a (2J+1)^b B_{12}^b) \quad (4)$$

J is rotational quantum number, and the superscripts a and b correspond to the two different excitation lines. The two-line method of doping NO gas has been successfully applied to flame thermometry [2]. The number density n_t is determined by the equation below.

$$n_t = pX / k_B T \quad (5)$$

In the above equation, p is the atmospheric pressure in the present experiments.

Results and Discussion

The appropriate conditions of doping concentration and laser power were first searched for ensuring a linear relation between the LIF intensity and doping concentration. The relatively lower laser power cases gave approximate linear relations, while the higher cases gave increasing deviations for higher concentrations of nitrogen oxide. The reason for this tendency may be attributed to photochemical reactions occurring under the conditions of high laser power and high NO concentration. The doping mole fraction of 100 ppm was chosen, and the laser power was set below 0.6 mJ/pulse.

Figure 1 shows the profiles of mole fraction, temperature, and number density for the

stoichiometric flame. The mole fraction profiles show that the value of approximately 30 ppm at the top of the flame reaction cone increases to 40-60 ppm in the burnt gas. The temperature profiles are acceptable in comparison with the calculated adiabatic flame temperature of 2226 K. The number density profiles show that the value of $1.2 \times 10^{14} \text{ cm}^{-3}$ near the flame reaction zone increases to $2.2 \times 10^{14} \text{ cm}^{-3}$ in the burnt gas. This result is in good agreement with the data of $1.5\text{-}2.2 \times 10^{14} \text{ cm}^{-3}$ obtained by time-dependent LIF method [1].

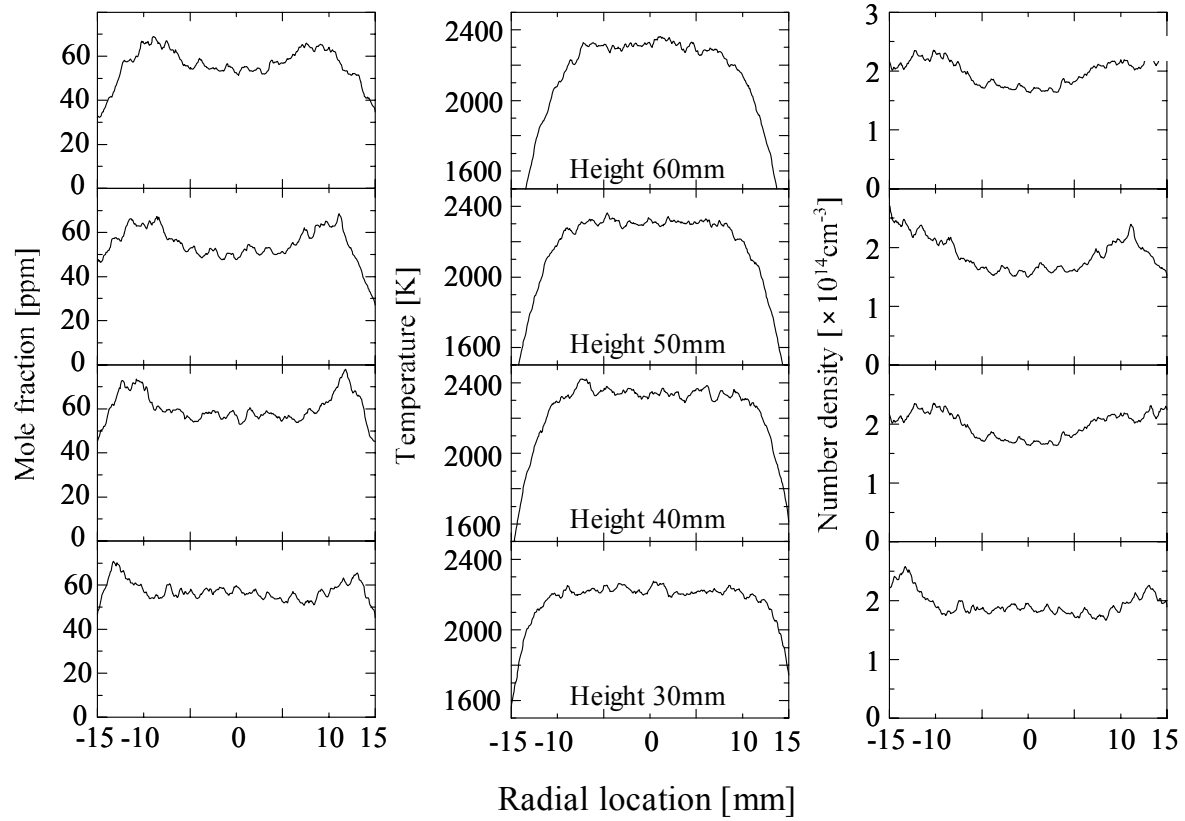


Figure 1 Profiles of Mole Fraction, Temperature, and Number Density

References

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- [2] M. Tamura, J. Luque, J. E. Harrington, P. A. Berg, G. P. Smith, J. B. Jeffries, and D. R. Crosley, *Applied Physics B*, Vol.66(1998), pp. 503–510.