

LIF Measurements of Formaldehyde in Flame by YAG THG

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ABSTRACT

LIF is used to measure H_2CO which is a key intermediate species in reaction system of hydrocarbon flames and is a harmful exhaust constituent. As the excitation laser, YAG THG which is one of the most reliable high energy pulsed laser sources has been used and fluorescence spectra overlapped with Raman lines of major species have analyzed emissions. By comparison between observed spectra and the theoretical model, the prominent spectrum is identified as the fluorescence of H_2CO . And using the combined technique of LIF and spontaneous Raman scattering, we measured the temperatures and the concentrations of species in flame.

INTRODUCTION

Formaldehyde (H_2CO) is one of key intermediate species in early stage of combustion reaction and is also noted as a harmful exhaust constituent, for example, in alcohol combustion. A further detailed understanding of the reaction system of H_2CO can be obtained by comparison between measured and calculated density profiles. LIF (laser induced fluorescence) is highly sensitive method, often used for in-situ measurement of trace species but has a difficult problem of quenching at atmospheric pressure (1). The spontaneous Raman scattering is less sensitive but has an advantage of measuring multiple major species with single beam, which gives pertinent internal references for correcting uncertainties associate with the fluctuation of laser, optics and electricities. LIF and Raman complement each other quite well in measuring a wide range of molecules. As the excitation source, we use YAG THG which is one of the most reliable high power pulsed lasers (2). Analyzing emissions of LIF and Raman requires knowledge of interfering spectra in flame. The electronic band spectrum of H_2CO has been discussed in many papers (3,4,5). The absorption bands, extending from 230-350nm have been considerably

analyzed. Most spectral experiments of H_2CO were performed at low pressure and at low temperature conditions. The red shaded branch of 350nm band of H_2CO which is important for YAG THG excitation have been rarely discussed.

In this report, we present an observed emissions in flame at atmospheric pressure and have analyzed the red shaded fluorescence bands of H_2CO which overlap with Raman lines of major species. Using this bands we have measured the evolution of species and temperatures in laminar pre-mixed flame.

EXPERIMENTAL

Apparatus (2)

The LIF/Raman measurements were performed using the pulsed laser (DCR), the multi-channel detector (SMA), and the delay pulse generator. An exciting source is the third harmonics of the pulsed YAG laser with FWHM of 0.8cm^{-1} (5-6ns). The scattered light was collected from a section of the focused beam using Cassegrain type collector, perpendicularly to the incident axis. The diameter of laser beam focused at the measuring section was approximately $80\mu\text{m}$ and its image was focused at the slit with magnification ratio of 1.0. The collected light was dispersed with spectrometers ($f=50\text{cm}$, MEG50), when multiple species were measured. An entrance slit opening was $100\mu\text{m}$ in width and $200\mu\text{m}$ in height. The detector was a diode array type (18mm/512ch) cooled to -20C . The pulse of 5-7 ns was illuminated within the exposure period which was controlled by gate operation in order to reduce the background noise. The system was synchronized to the timing signal of the pulse generator triggered by the laser. The sensitivity was calibrated using the standard spectral lamp. The pre-mixed $\text{C}_2\text{H}_4/\text{air}$ supplied through mass flow controllers (Tyran) with accuracy of $\pm 1\%$ was burnt on a nozzle burner using tube diameter of 12mm. The total flow rate was 17l/min. The burner on a three-dimensionally movable stage was positioned with precision of $10\mu\text{m}$.

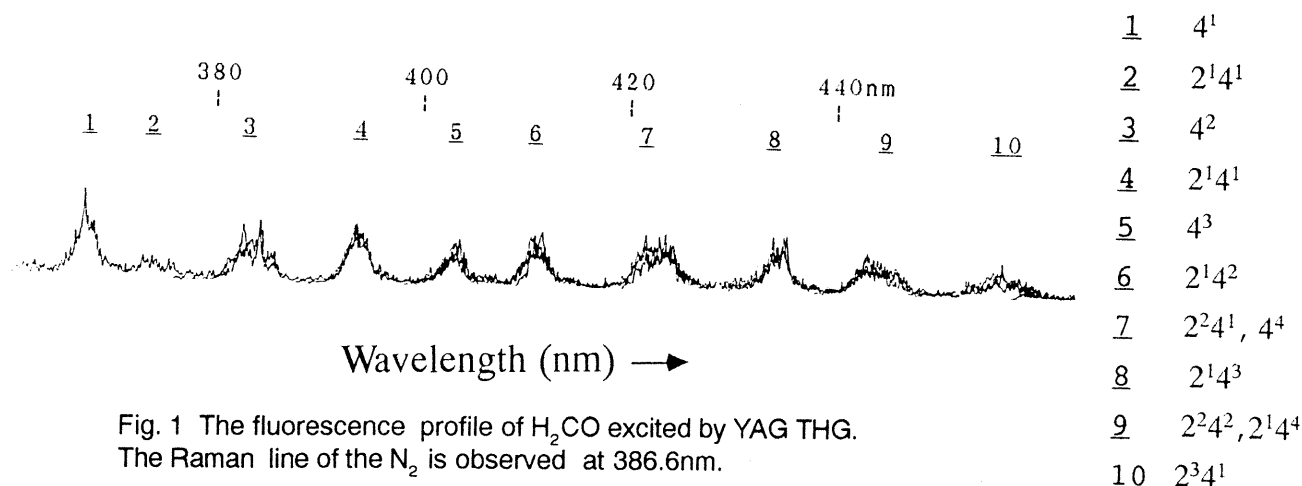


Fig. 1 The fluorescence profile of H₂CO excited by YAG THG. The Raman line of the N₂ is observed at 386.6nm.

OBSERVED SPECTRUM

Fluorescence

We performed measurements in flame on a single nozzle burner, and confirmed spectra using each sample gas in cell at NTP. Prominent band which overlapped with Raman spectra of major species, is shown in Fig. 1. (2) This band spectrum has been identified as the fluorescence of H₂CO by comparing with the predicted vibrational system(3,4). Fig. 2 shows integral intensities of each branch versus excitation energy. Intensities of all branches are proportional to the excitation energy without saturation. Fig. 3 shows the comparison between observed rotational spectra of H₂CO and its calculated absorption profile (6). Quite good agreement is attained, so we apply this calculated profile to correct the overlapping of H₂CO with other spectra.

Absorption

H₂CO of 350nm band has a red shaded band which contains large number of closely spaced lines where YAG THG line exists. The simulation indicates that a few lines which has been broadened by Doppler and collisional effect under atmospheric pressure, overlap with the laser line and the situation do not greatly vary with temperature. Fig.4 confirms that the spectrum in flame are almost equal to that in the cell at normal temperature. So we could estimate the equivalent cross section of H₂CO in flame from that at normal temperature for the concentration measurement.

Decay time

Fig. 5 shows decay times of H₂CO fluorescence branches measured at NTP. The decay characteristic time is almost equal for each branch, $\tau=33\text{nsec}$ and the fluorescence signal fades about 200nsec which determines our exposure period of the detector. Typically rates for collisions causing a change in energy levels are $> 10^9 \text{ sec}^{-1}$ at 1 atm., the most fate of an

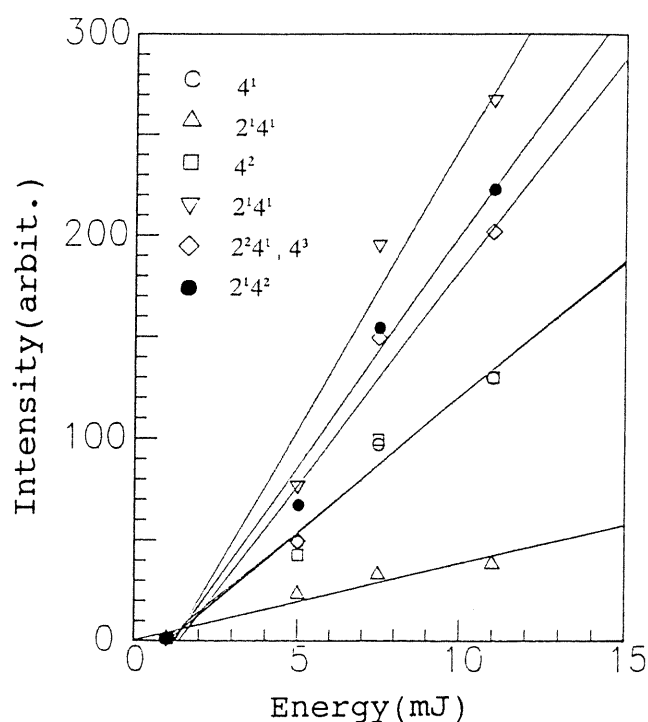


Fig. 2 LIF intensity of H₂CO versus the excitation energy. The H₂CO of 49ppm balanced with the N₂ was measured at NTP.

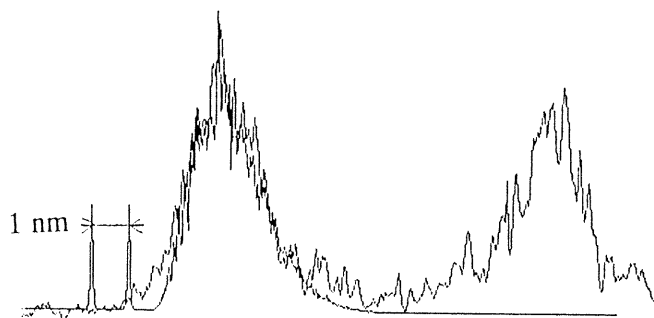


Fig. 3 Comparison between the observed fluorescence spectrum and the simulation. (Kmax=20, Jmax=50)

excited molecule is to undergo collisional transfer to some other levels. The collisions are qualitatively, separated into two cases: quenching collisions, and energy transfer collisions (1,7). Considering that the characteristics of observed H₂CO system shows very wide fluorescence spectrum, the excited molecule seems to undergo the rapid energy transfer to various excited energy levels before quenching.

CALIBRATION

Thermometry

Reaction of H₂CO in flame goes rather in low temperature range. For the low temperature measurements, the line fitting method is not convenient because higher vibrational branches can not obviously be observed under 1000K. Then we have calculated the temperature from the integrated line intensity of N₂ Raman line (1) by the following equation, on the assumption that the ideal gas law and the constant pressure.

$$T = \frac{T_r I_r f_r(\Delta v, T)}{I} \quad (1)$$

where T is the temperature, f_r is the correction function depending on spectral resolution and temperature. Suffix r indicates the calibrated state. The calibration measurements are performed over a range of known temperature and species concentrations, from these data we generate the correction functions which account for the variation in signal due to cross-talk between detector channels.

Concentration

We have calculated the species concentration from the following equation.

$$N = N_r \frac{I \left(\frac{d\sigma}{d\Omega} \right)_{cr} f_{cr}(\Delta v, T)}{I_r \left(\frac{d\sigma}{d\Omega} \right)} \quad (2)$$

where N is the concentration of the specie, I is the integrated line intensity, r indicates the calibrated state, (dσ/dΩ) is the differential cross section, f_{cr} is the correction factor depending the spectral resolution and temperature. For LIF measurement of H₂CO, differential cross section data are not available, we determined the concentration of sample by comparing with that of known concentration. We have also measured the equivalent cross section of the sample gas which contained H₂CO of 49ppm in N₂ at NTP. Table 1 shows the equivalent cross section of H₂CO compared to N₂ Raman at NTP. Fluorescence intensity is stronger than N₂ Raman by order of 3 to 5.

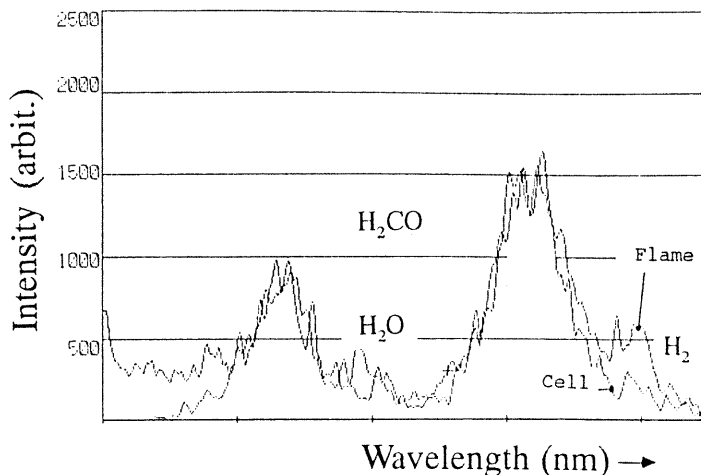


Fig. 4 LIF of H₂CO (excited by YAG THG) in flame was compared with that in cell at normal temperature. Both spectra are alike except small peaks of Raman spectra.

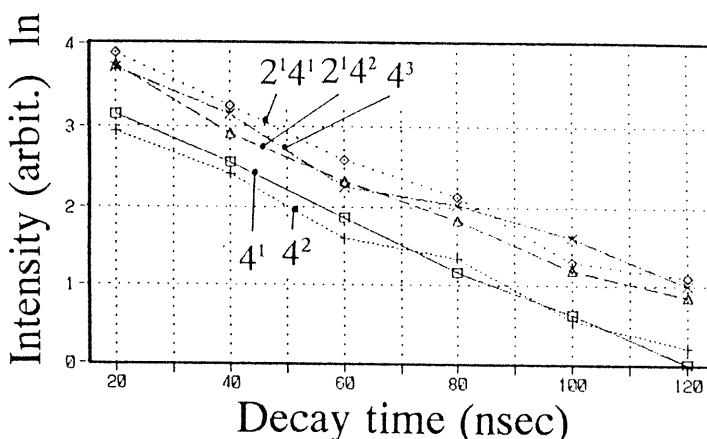


Fig. 5 Decay time of H₂CO fluorescence measured at NTP. Decay characteristic times are almost equal for each branches, τ=33.2nsec.

Table 1 Fluorescence intensities of H₂CO branch compared with the N₂ Raman.

NO.	σ/σ _{N₂} (x10 ³)	Δλ(Å)
<u>1</u>	142	66
<u>2</u>	47.3	50
<u>3</u>	74.4	70
<u>4</u>	12.5	67
<u>5</u>	73.9	55
<u>6</u>	119	67
<u>7</u>	171	75
<u>8</u>	105	53
<u>9</u>	121	74
<u>10</u>	92.6	82

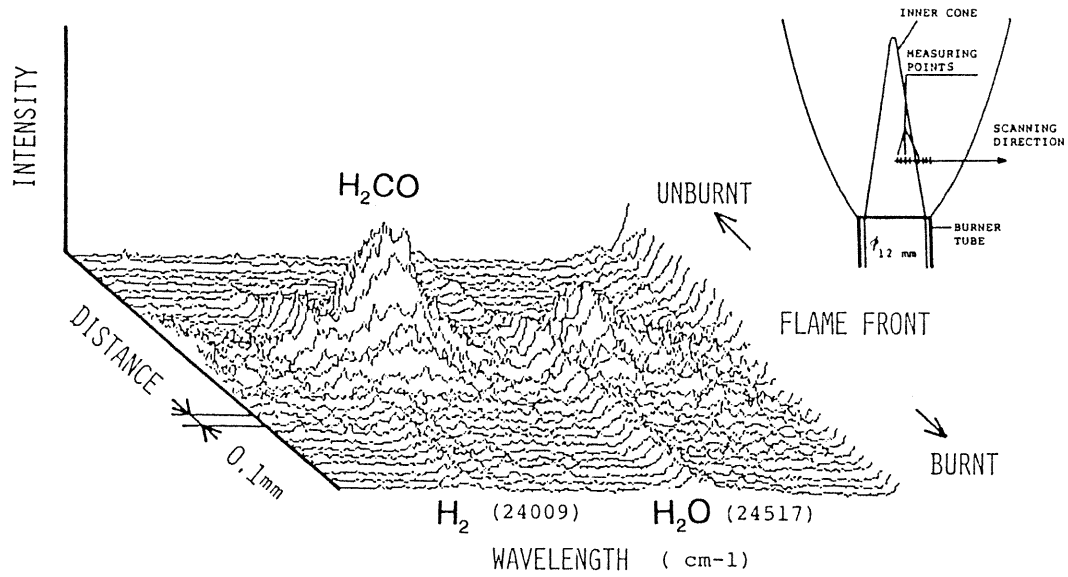


Fig. 6 Raman spectra of H_2O and H_2 and LIF of H_2CO in 400 nm spectral region, measured across the reaction zone of C_2H_4 /air flame.

FORMALDEHYDE IN FLAME

Interfering spectra

Fig. 6 shows the spectra of H_2O , H_2 , and H_2CO in 400-430 nm region, which are observed across the reaction zone of C_2H_4 /air flame. In Fig. 7, the Stokes-Raman spectra of O_2 , C_2H_4 , CO , CO_2 and N_2 in 370-390nm region of the above mentioned flame at various zone are overlaid. At normal temperature, there is little interfering signal with these lines, but at higher temperature the strong fluorescence of H_2CO spectra overlap with N_2 Raman. Hence the rotational structure of H_2CO can be estimated by the simulation, the integral Raman intensities of N_2 and other major species have been corrected. Fig. 8 shows the results of measurements. Temperature, H_2CO , C_2H_4 , O_2 , H_2O , H_2 concentration are shown as function of the radial distance from arbitrary point in inner cone of C_2H_4 /air flame. H_2CO has its peak in under 1000K region and almost disappears before maximum temperature.

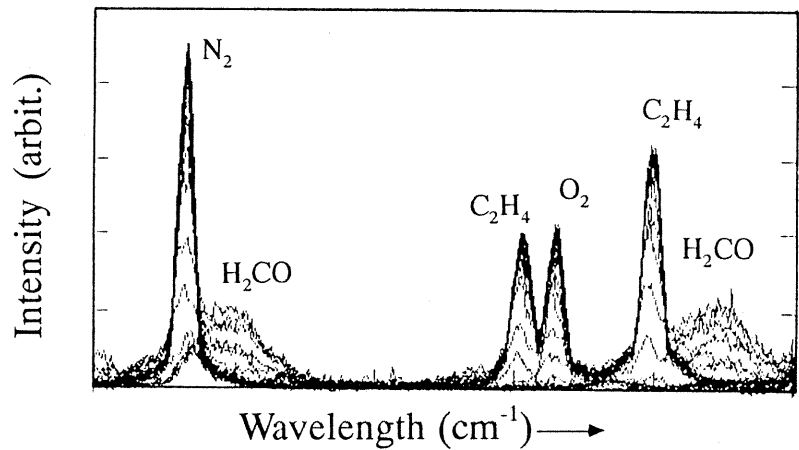


Fig. 7 Raman spectra of major species and LIF of H_2CO in 380nm spectral region of various zone of the flame are overlaid, measured across the reaction zone of C_2H_4 /air flame.

SUMMARY

Prominent spectra in hydrocarbon flame excited by YAG THG has been identified as the fluorescence of H_2CO which overlap with the Raman spectra. The observed wide fluorescence spectrum of H_2CO indicates that the energy transfer rate in excited state is larger than the quenching rate. And the rotational profile of formaldehyde at NTP is not greatly changed under about 800K in the flame. Conferring the obtained knowledge of the interfering spectra in flame, the combined techniques of LIF and Raman can be applied for measuring the temperature and the concentration of H_2CO with major species in hydrocarbon flame.

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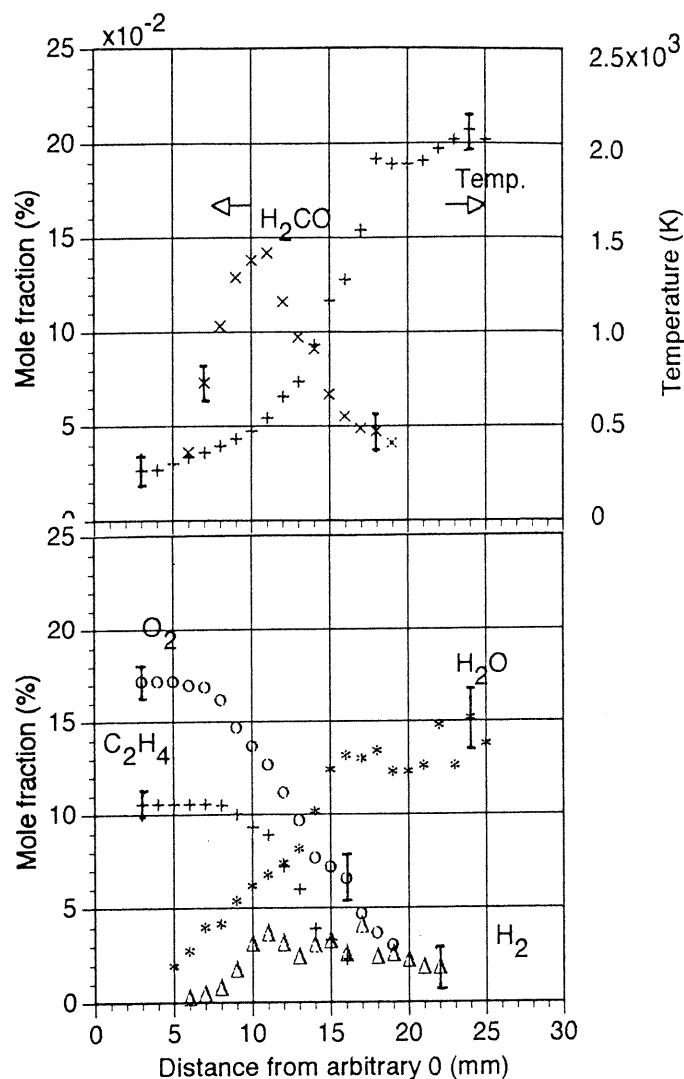


Fig. 8 The evolution of H_2CO , major species and the temperature in C_2H_4/air ($\Phi=1.7$) flame.