Measurement of CH2O in low and atmospheric pressure flames by Laser Induced Fluorescence and Cavity RingDown absorption

Document status and date:
Published: 01/01/2001

Document Version:
Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Download date: 16. Nov. 2023

MEASUREMENT OF CH$_2$O IN LOW AND ATMOSPHERIC PRESSURE FLAMES BY LASER INDUCED FLUORESCENCE AND CAVITY RINGDOWN ABSORPTION

Jorge Luque, Robert H. Klein-Douwel*, Jay B. Jeffries[#], Gregory P. Smith and David R. Crosley
Molecular Physics Laboratory, SRI International, Menlo Park, California 94025

*Present address: University of Nijmegen, Nijmegen, The Netherlands
[#]Present address: Stanford University, Stanford, California.

ABSTRACT

We have investigated the spatial structure of formaldehyde using laser-induced fluorescence (LIF), LIF imaging, and cavity ringdown spectroscopy (CRDS) in two flames. The first is an atmospheric pressure Bunsen flame, into which are inserted various metal to simulate different types of heat removal inserts in appliance flames. Here LIF imaging is used. The second is a low pressure flat flame that can be modeled with a one-dimensional code. All three techniques are used. The results in both cases show that CH$_2$O appears prior to CH, in lower pressure regions of the flame.

INTRODUCTION

Formaldehyde is an important intermediate in hydrocarbon combustion. It is formed by the oxidation reaction CH$_3$ + O, in low temperature regions, including where knock phenomena occur. It is also a toxic byproduct of incomplete combustion: it has been estimated that 50% of direct CH$_2$O emissions come from motor vehicles, especially with oxygenated fuels [1]. Incompletely burned CO can leak from household appliance burner [2] and it is possible that formaldehyde does too.

Previous workers have used the method of laser-induced fluorescence (LIF) to detect native formaldehyde in flames [3-5] and internal combustion engines [6,7]. The investigations were performed using the strong A-X 4_0^1 band near 355 nm. Although absolute absorption coefficients can be measured for this band, there is a considerable variation with temperature in the Boltzmann fraction (that is, the population in the particular rotational level(s) that absorb the laser light) for the 4_0^1 band. (Other higher lying vibrational bands in the excited state, such as the $4_0^1 2_0^1$ have also been used.) We have investigated and used a hot band of CH$_2$O, the A-X 4_1^0 band near 370 nm, for LIF detection of CH$_2$O in an atmospheric pressure flame [8]. This band, although weaker, has much less sensitivity to temperature than does the 4_0^1 band, and can provide more accurate results for fluorescence imaging and ring-down absorption measurements throughout a flame. Moreover, it lies close to the 1,0 B-X band of the CH molecule, and facilitates measurements of both these crucial compounds in a single flame with no change in laser dye.

We have applied this approach to two flames. The first is a study of the inner cone structure of a Bunsen burner flame, measured using laser-induced fluorescence (LIF) imaging.

The CH_2O appears inside CH for moderately rich stoichiometries typical of appliance flames, and the flame structure of the two intermediate species were also imaged with when a variety of inserts placed in the flame. The second is a combined LIF and cavity ringdown spectroscopy (CRDS) investigation in a methane/air flame at 25 Torr. The LIF is used to correct cavity ringdown spatial resolution limitations in this not quite flat flame. The peak concentration in this flame is 1500 ± 500 ppm at 1000K, with the large uncertainty arising primarily from inaccuracy in the absolute absorption coefficient.

SPECTROSCOPIC CONSIDERATIONS

The spectroscopy of the A-X band of the CH_2O molecule has been the subject of numerous studies, and sufficient information exists to assign many rovibrational lines for low lying vibrational levels. The origin band of formaldehyde is symmetry forbidden, so access to the A state can be made by absorption to an excited vibrational level (usually the 4_0^1) band or, as used here, from a hot band such as the 4_1^0.

Our choice of a hot band was guided by two considerations. The overall excitation spectrum of the 4_1^0 band covers the region 368 to 373 nm, with K bandhead structure having alternating intensities and a large number of individual rotational lines. This region is close to the 1,0 band of the B-X system of the CH molecule, so both these important species could be measured using only a minor change in laser wavelength. One particular head at 386.2 nm, exists very close to the $P_1(8)$ and $P_2(8)$ rotational lines of CH, as shown in Fig. 1. The figure, which is a cavity ringdown spectrum in the low-pressure flame, also shows the rotational assignment of the K=4 bandhead of the 4_1^0 band of CH_2O. The fluorescence is to the red of the excitation, with bands extending from the excitation wavelength to over 500 nm.

A major advantage of the use of this hot vibrational band is its relative insensitivity to temperature, as calculated from Boltzmann fractions in various bands. If CH_2O behaves like OH or NH, it is polar enough that its quenching collision cross sections decrease with temperature; this suggests the net quenching rate is proportional to $T^{1/2}$. (No one has directly measured the relevant quenching cross section, although in a premixed atmospheric pressure flame the lifetime varied only between 17 and 12 ns over the height range 1.2 to 5 mm, and was the same within overlapping error bars [5].) Using this assumption and the Boltzmann fractions, we can calculate the temperature dependence of the relationship between signal and concentration. Between 700 and 1800K, the 4_1^0 band relationship varies a factor of 1.55; for the more commonly used 4_0^1 band, the variation is a factor of 4.7. On the other hand, the hot band population is much lower than for 4_0^1, by a factor of 10 at 700K and a factor of 2.5 at 1800K. However, because the 4_1^0 absorption band strength is higher than that for 4_0^1, absorbencies are comparable.

Further details on these spectroscopic aspects may be found in Ref. 8.

In the atmospheric pressure flame Bunsen type methane/air coflow flame, there was considerable background underlying the CH_2O LIF spectrum. We first attributed this to CH_2O hot bands in the flame. There are likely significant background contributions due to polycyclic aromatic hydrocarbons (PAHs), which have been found to cause interferences with CH_2O LIF in a Wolfhard-Parker nonpremixed flame [3]. In contrast, no such interference was found in the

premixed low-pressure flame on a McKenna burner; a background continuum was observed in the CRDS spectrum. PAHs might well be found in the continuum of mixing regions in a nonpremixed flame but not in the controlled stoichiometry in a fully premixed flame. Thus the background in the atmospheric pressure Bunsen flame is probably due to both causes, CH_2O hot bands and PAHs.

ATMOSPHERIC PRESSURE BURNER

A Bunsen burner designed for high stability is used in these experiments; premixed fuel and air are admitted via a steel tube 1.65 cm i.d., surrounded by a 20 cm diameter coflow of air. Further details about the burner have been previously reported [9]. LIF in both CH and CH_2O are excited with a excimer pumped dye laser operating between 365 and 370 nm; beam energies between 1 and 10 µJ/pulse were used to avoid saturation.

For the CH and CH_2O imaging measurements described here, the beam was formed into a 0.25 x 20 mm sheet; the fluorescence signal is collected by a uv-Nikkon lens with filters to admit only light at wavelengths longer than 380 nm. This efficiently collects a large fluorescence signal for both CH and CH_2O but flame luminosity and Raman scattering are also seen. This background signal is then observed with the laser tuned off resonance and subtracted from the flame image. Correction for inhomogeneities in the laser sheet and detector are normalized away using a Rayleigh signal in room air with no flame. Typical images require about 2500 laser shots.

Two-dimensional images of CH and CH_2O structures are shown in Fig. 2. This flame has a $\Phi = 1.36$ premixed inner cone. The inset at the bottom shows the intensity trace at 12 mm height, as marked by a line on the images. The formaldehyde occurs inside the inner cone, prior to the steepest thermal gradient, and is entirely contained within the CH structure. A similar pattern of CH_2O occurring before CH was observed earlier in a Wolfhard-Parker burner for the inner cone $\Phi = 1.79$ [3]. Neither CH nor CH_2O were found outside the premixed inner cone. We examined CH_2O to be present in flames with premixed Φ ranging from 1.3 to 3.0. As Φ increases, the flame becomes higher (slower flame velocity for richer mixtures) and the formaldehyde structure broadens significantly along the 12 mm height line. While CH diminishes considerably, becoming very faint for $\Phi = 2.2$, the integrated CH_2O signal is fairly constant.

Structures of Bunsen flames with inserts were also examined. These inserts are commonly used in appliance flames, to cool the flame and reduce NO_x. Exhaust gas measurements in this flame show that inserts reduce NO but increase the output of CO. We perturbed the Bunsen flame with four inserts: (1) a flat plate pushed into on side of the outer diffusion flame; (2) a wire screen placed over the premixed flameholder; (3) a water-cooled tube transverse across the flame; and (4) a ring inserted just above and outside the premixed flame holder. Images of CH and CH_2O with these inserts are shown in Fig. 3.

Near the mesh screen CH is reduced and the CH_2O structure is broadened, much like that seen in a rich premixed flame cone. If CH_2O diagnoses the flame's temperature increase, then one can conclude that the mesh screen significantly spreads the reaction zone. Much higher in

the flame, far from the mesh, this flame is like the unperturbed one. The cooled tube produces much the same change. As with the mesh, reduced inner cone temperature owing to heat removal by the insert is the likely explanation. The flat plate produces interesting effects, which may mimic behavior on a gas stove or similar applications. CH and CH$_2$O both increase near the plate. This cannot be explained by simple heat removal, whereas additional preheat of the inner cone, or a higher flow rate due to flame stretch near the plate, are possible explanations. No CH$_2$O leakage beyond the premixed inner cone was observed.

LOW PRESSURE FLAME

The purpose of this experiment was quantification of the absolute amounts of CH and CH$_2$O in a low pressure premixed flame suitable for detailed chemical modeling. The ability of a model to accurately predict prompt NO depends upon its ability to predict absolute CH concentrations. This led to an absolute measurement using LIF in a similar flame [10]. Because of the importance of this measurement, absolute CH was also determined by CRDS [11,12]. The CH measurements agreed well with the LIF results. Here we discuss the measurement of CH$_2$O using both LIF and CRDS in the same flame.

We used our standard premixed laminar flame burnt on a McKenna burner at 25 Torr. The flame is CH$_4$/N$_2$/O$_2$ flame with O$_2$ 30% of the total N$_2$ + O$_2$; the stoichiometric ratio is 1.07 and the flow rate 3.22 slm. We have used this flame for many previous investigations [13] and it is well characterized including precise temperature profile measurements using LIF in both OH and CH. The burner is mounted on a motorized stage for vertical scans. The laser beam enters and exits through two ports, passing across the middle of the burner; the ports contain quartz windows for LIF measurements and mirrors for CRDS measurements. The fluorescence collection scheme is very similar to that in the atmospheric pressure flame.

The CH$_2$O 4^0 radiative lifetime is 4.8 ± 1.9 µs as measured experimentally [14] and 4.2 µs from theoretical calculations [15]; the estimated collision free quantum yield is 2% owing to predissociation [14]; so that the effective lifetime is 80 ns. However, at 25 Torr predissociation rates dominate, so that we expect the fluorescence quantum yield to vary significantly throughout the flame; see also the effective lifetimes in [5] as noted above. Absorption strength, related to radiative lifetime, is needed to analyze the CRDS signal, but quenching information is needed to interpret and quantify the LIF measurements.

In a CRDS experiment, a small portion of the laser light is admitted through the mirrors, which form a cavity. The beam intensity decreases with time due to losses on the mirrors, from scattering, and from absorption by the molecule of interest. The ringdown lifetime is given by

$$\tau(\nu) = (L/c)/(T + \Lambda + \sigma(\nu)Nd)$$

where L is the cavity length, T + Λ are the mirror and scattering losses, σ is the absorption cross section, N is the average absorber number density, and d is the effective distance in the path where the beam is absorbed homogeneously. The spectra are analyzed as L/cτ(ν) in terms of parts per million loss per pass. T + Λ appear as a continuous background, and thus, if σ and d are known, N can be determined. Spectra of the ringdown laser wavelength scans are exhibited

in Fig. 1. This brief discussion ignores the finite bandwidth of the laser pulse, which produces a nonexponential decay. For this work, the overlap integral between the finite bandwidths of the laser spectrum and the absorption line is treated as a first order correction only.

Fig. 4 shows LIF images of the CH and CH_2O structures in the flame, with absolute limits provided by the CRDS measurements as discussed below. Note that, as in the atmospheric pressure flame, the CH_2O appears well before the CH, in cooler regions of the flame. Some back diffusion at this low pressure accounts for the fact that some CH_2O is seen very close to the surface of the burner.

Curvature of this nominally one-dimensional flat flame is clearly present in the images. Analysis of the CRDS data must account for this inhomogeneity in the absorption path. Fig. 5 shows the CH_2O CRDS absorption profile plus two obtained from LIF (CH CRDS absorption is also shown for reference). One of the LIF height profiles is taken at the center of the flame, and the other integrates it along the line of sight, taken from the image in Fig. 4. The two LIF profiles are identical for heights up to 1.3 mm, but deviate above that owing to the flame curvature. We calibrate the CRDS data at 1.5 mm above the burner. Here the path length uncertainty is small, because the flame shows only a bit of curvature at this height. Then the distance d is determined by the ratio of the flame-center LIF to the line-of-sight-integrated LIF. $\sigma(\nu)$ is calculated from the radiative lifetime, Boltzmann fraction, and laser and absorption linewidth overlap.

Quantification of the CH_2O number density is complicated by poor knowledge of σ for the hot band. The oscillator strength has been determined only theoretically, although experimental evidence on the 4_0^1 band shows that the calculated oscillator strengths are perhaps 15% too low; we adopt a higher value of f=0.000021. We estimate the uncertainty in the oscillator strength at ± 25%; this is the major contributor to the uncertainty in the absolute number density of CH_2O.

We must also consider the rotational structure of the transition. We are exciting CH_2O in a band head for most measurements; see Fig. 1. There are three incompletely resolved lines near the head. We calculate an overlap integral using the spectrum and a Gaussian approximation; taking into account the intensity alternation associated with the H atom symmetries. Hönl-London factors are taken from Herzberg [16]. We find an effective σ at the bandhead of 2.4 x $10^{-20} cm^2$. Given uncertainties in the oscillator strength, linewidths, and other factors involved in the calculation, the total error in the effective cross section is estimated to be 35%.

The resulting peak number density is (3.5 ± 1.4) x 10^{14} cm^{-3}. This number density corresponds to 1500 ± 500 ppm, where most of the uncertainty comes from the oscillator strength. We checked the consistency of this value, determined by the bandhead measurements, by probing two resolved rotational lines in the same branch: $^RR(10)$ and $^RR(13)$. The number densities from these lines are about 20% than the bandhead value.

A flame model using GRI-Mech 3.0 [17] predicts about half the observed CH_2O, and is mostly sensitive to the CH_3 + O reaction product branching ratio. The large measurement uncertainty precludes a rigorous test of the model.

CONCLUSIONS

We have made measurements of CH_2O in both atmospheric pressure Bunsen flames and a low pressure "flat" flame using LIF imaging, LIF point measurements, and CRDS. The structure of formaldehyde exists prior to CH, in cooler flame regions, in both flames. The absolute CRDS measurement in the low pressure flame has a large uncertainty owing to lack of an accurate oscillator strength and forms only a limited test of flame chemistry models. The CH_2O hot band diagnostic provides a good marker for the premixed combustion region in Bunsen flames of all stoichiometries, and a means of examining effects of inserts.

ACKNOWLEDGEMENTS

REFERENCES

1. C. P. Koshland, "Impacts and Control of Air Toxics from Combustion," Proc. Combust. Inst. 26, 2049 (1996).

2. A. V. Mokhov, H. DeVries, and H. B. Levinsky, "A LIF and CARS Study of CO and NO_x Formation in Two Optically Accessible Household Appliances," Proc. Inter. Gas Res. Conf., Vol. 4, p. 526 (1998).

3. J. E. Harrington and K. C. Smyth, "Laser-Induced Fluorescence Meaurements of Formaldehyde in a Methane/Air Diffusion Flame," Chem. Phys. Lett. 202, 196 (1993).

4. R. Bombach and B. Käppeli, "Simultaneous Visualisation of Transient Species in Flames by Planar-Laser-Induced Fluorescence using a Single Laser System," Applied Physics B 68, 251 (1999).

5. D. L. Shin, T. Drier, and J. Wolfrum, "Spatially Resolved Absolute Concentration and Fluorescence Lifetime Determination of H_2CO in Atmospheric-Pressure CH_4/Air Flames," Applied Physics B 72, 257 (2001).

6. N. L. Garland, "Assignment of Formaldehyde Laser-Induced Fluorescence Spectrum from the Sandia Engine Experiment," SRI International Report MP 84-033, February 1984.

7. B. Bauerle, J. Warnatz, and F. Behrendt, "Time Resolved Investigation of Hot Spots in the End Gas of an S. I. Engine by Means of 2-D Double Pulse LIF of Formaldehyde," Proc. Combust. Inst. 26, 2619 (1996).

8. R. J. H. Klein-Douwel, J. Luque, J. B. Jeffries, G. P. Smith, and D. R. Crosley, "Laser-Induced Fluorescence of Formaldehyde Hot Bands in Flames," Appl. Opt. 39, 3712 (2000).

9. N. H. Heberle, G. P. Smith, J. B. Jeffries, D. R. Crosley, and R. W. Dibble, "Simultaneous Laser-Induced Fluorescence and Rayleigh Scattering Measurements of Structure in Partially Premixed Flames," Appl. Phys. B 71, 733 (2000).

10. J. Luque and D. R. Crosley, " Absolute CH Concentrations in Low Pressure Flames Measured with Laser-Induced Fluorescence," Appl. Phys. B 63, 91 (1996).

11. J. Luque, G. P. Smith, J. B. Jeffries, D. R. Crosley and J. J. Scherer, "Absolute Concentration of CH in a Low Pressure Methane Flame using Cavity Ringdown Spectroscopy in the A-X System," Appl. Phys. B., to be submitted, 2001.

12. . J. Luque, G. P. Smith, J. B. Jeffries, D. R. Crosley and J. J. Scherer, "Combined Cavity Ringdown Absorption and LIF Imaging Experiments of CN(B-X) and CH(B-X) in Low Pressure $CH_4/O_2/N_2$ and $CH_4/NO/O_2/N_2$ Flames," Combust. Flame, submitted, 2001.

13. P. A. Berg, D. A. Hill, A. R. Noble, G. P. Smith, J. B. Jeffries, and D. R. Crosley, "Absolute Concentration Measurements in Low-Pressure Methane Flames: Comparison with Model Results," Combust. Flame **121**, 223 (2000).

14. R. G. Miller and E. K. C. Lee, "Photochemistry of Formaldehyde," J. Chem. Phys. 68, 4448 (1978).

15. M. J. H. Kemper, J. M. F. vanDijk, and H. M. Buck, J. Chem. Phys. 70, 2854 (1979).

16. G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, D. Van Nostrand, Princeton, 1996.

17. G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarity, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. Gardiner, V. V Lissanski, and Z. Qin, GRI-Mech 3.0 Web site: http://www.me.berkeley.edu/gri_mech/, 1999.
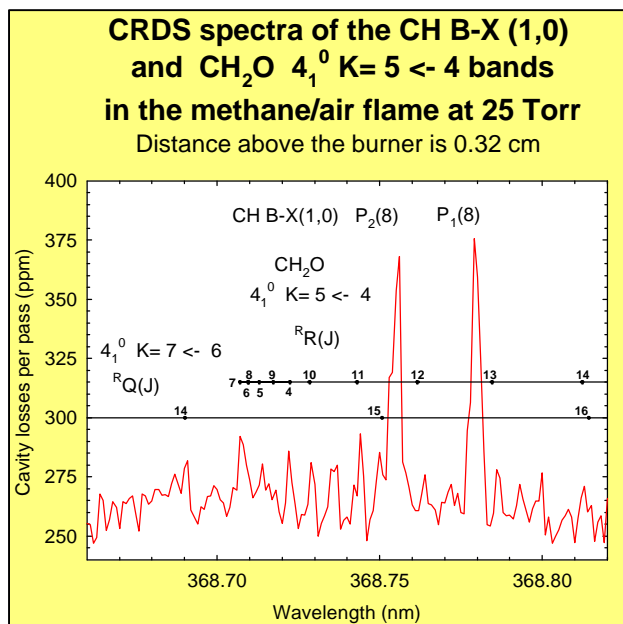
CRDS spectra of the CH B-X (1,0)
and CH$_2$O 4$_1^0$ K= 5 <- 4 bands
in the methane/air flame at 25 Torr
Distance above the burner is 0.32 cm

Fig. 1. CRD absorption spectrum of CH B-X (1,0) P(8) lines, and the ^{R}R(4) bandhead of the CH$_2$O (A-X) 4$_1^0$ band in a methane/air flame at 25 Torr. Distance is 0.28 cm above the burner surface where the temperature is 1350K.
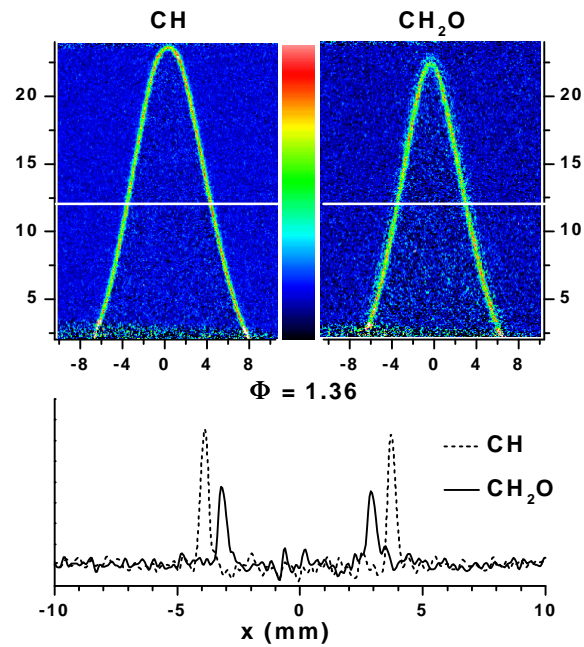
Fig. 2. Images of CH and CH_2O LIF in the atmospheric pressure methane/air Bunsen flame with premixed stoichiometry 1.36. Lower trace is at 12 mm height, as indicated by the line in the images.
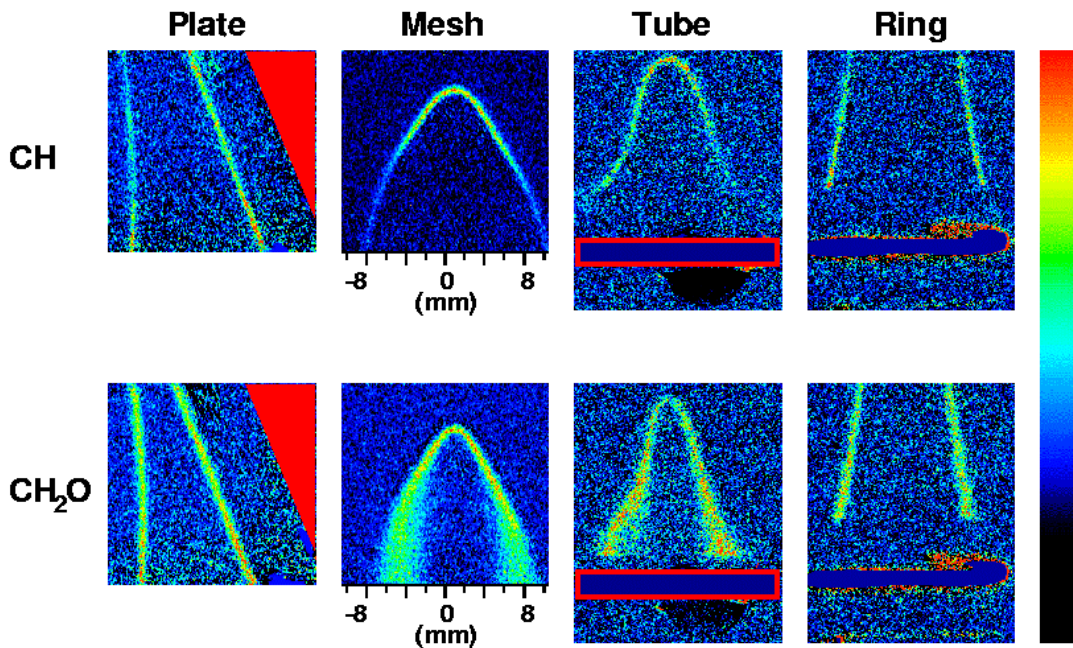

Fig. 3. Images of CH and CH_2O LIF in the atmospheric pressure Bunsen flame with premixed stoichiometry 1.57, using various metal inserts as described in the text.
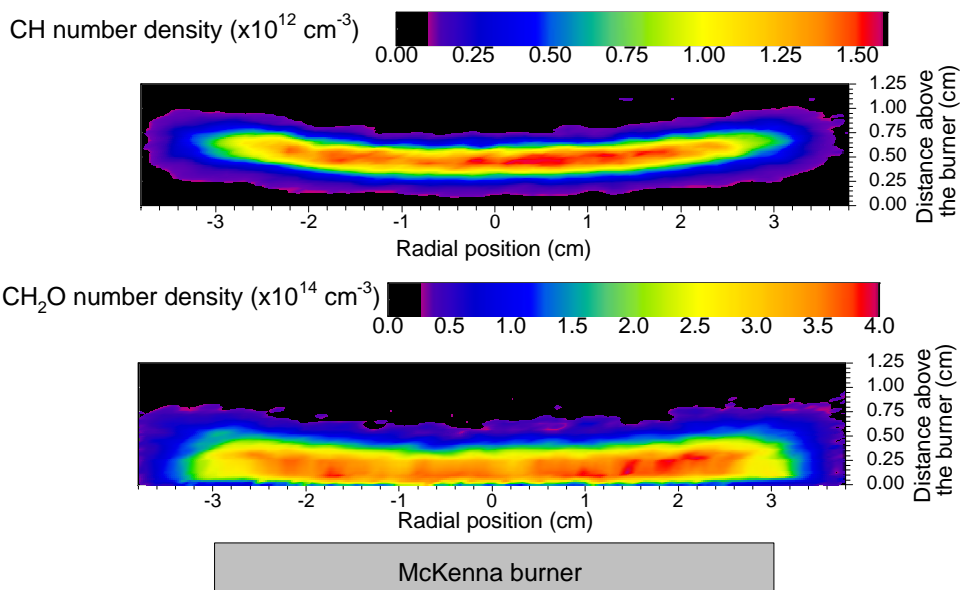
Fig. 4. Two dimensional LIF images of CH (upper panel) and CH$_2$O (lower panel) in the premixed methane/air flame at 25 Torr.
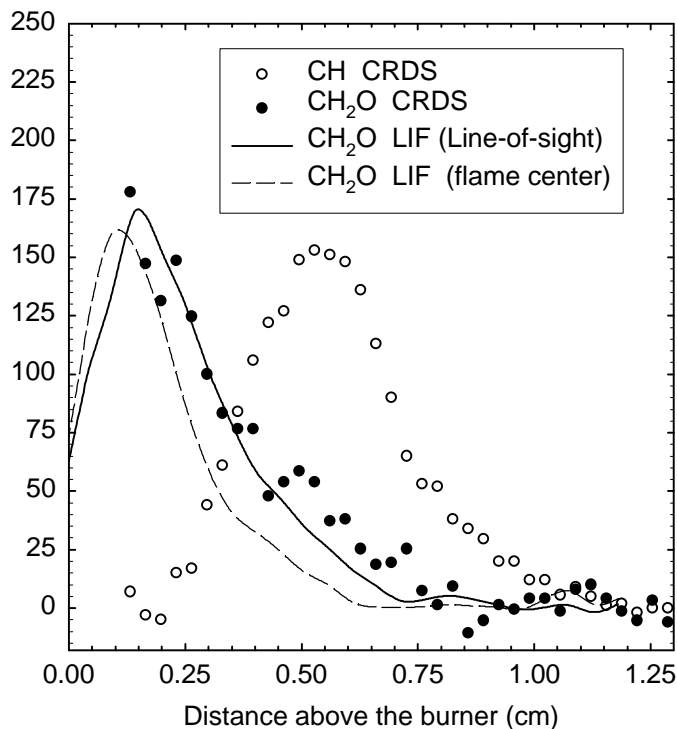

Fig. 5. CRDS profiles of CH$_2$O (solid circles) and CH (open circles) in the 25 Torr methane/air flame. Two CH$_2$O profiles are shown, taken by averaging the fluorescence signal parallel to the burner surface along the burner diameter and CRDS path (continuous line), and by integrating along a 0.5 cm path at the center of the flame (dashed line).