Quasi-simultaneous detection of CH$_2$O and CH by cavity ring-down absorption and laser-induced fluorescence in a methane/air low-pressure flame

Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025, USA

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ABSTRACT The combination of two-dimensional, planar laser-induced fluorescence (PLIF) and cavity ring-down (CRD) absorption spectroscopy is applied to map quantitatively the spatial distributions of CH$_2$O and CH in a methane/air flame at 25 Torr. Both species are detected in the same spectral region using the overlapping CH$_2$O $^1$A$_2$ $\rightarrow$ X $^1$A$_1$ 4$^0_i$ and CH $B$ $\rightarrow$ X (1, 0) bands. The combination of diagnostic techniques exploits the spatial resolution of LIF and the quantitative CRD absorption measure of column density. The spatially resolved PLIF provides the distribution of absorbers and line-of-sight CRD absorption the absolute number density needed for quantitative concentration images. The peak CH$_2$O concentration is (3.5 ± 1.4) x 10$^{14}$ cm$^{-3}$, or 1450 ± 550 ppm at 1000 K. The lack of precise absorption cross-section data produces these large error limits. Although a flame model predicts lower amounts, these large uncertainties limit this measurement’s usefulness as a test of the flame chemistry.

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1 Introduction

Detection of intermediates in flames by spectroscopic methods has provided a wealth of physical and chemical information to understand the combustion of hydrocarbons. Laser-induced fluorescence (LIF) is a well-established method [1], and cavity ring-down (CRD) absorption spectroscopy is also finding increased use as a flame diagnostic [2]. CRD techniques have already been demonstrated for quantitative measurements of important combustion intermediates (OH [3, 4], CH [5–8], $^1$CH$_2$ [9], CN [10], HCO [11]). The combination of both CRD and LIF techniques can extend the limits of laser optical diagnostics, thereby supplementing chemical and physical information that can be readily extracted.

CRD absorption offers the advantage of a simpler quantification of number density than LIF, because it does not require calibration or excited state collision rate data. However, CRD is sensitive to spatial resolution issues and to inhomogeneities of the sample in the optical path. Another advantage of CRD absorption spectroscopy is the ability to detect states with very low fluorescence quantum yields. Predissociation or collisional quenching at very high pressures can be responsible for very low fluorescence quantum yields, but these complications are minor in CRD absorption because collisions and predissociation only affect the lineshape and spectral bandwidth of an absorption line.

This work extends a previous laser-induced fluorescence study of CH$_2$O and CH in a partially premixed flame at atmospheric pressure [12–14] to a premixed low-pressure flame. We previously found that the CH $B$ $\rightarrow$ X (1, 0) $P$ and $Q$ branches overlap the CH$_2$O $A$ $\rightarrow$ X $^1$A$_1$ 4$^0_i$ band. This accidental overlap provides an advantageous scheme to measure both species almost simultaneously. We were able to measure the absolute concentration of CH in the Bunsen flame via LIF calibrated with Raman scattering of N$_2$. However, a determination of CH$_2$O was more challenging because of the complexity of the polyatomic molecule collisional processes and spectroscopic properties. Shin et al. [15] have overcome these problems by calibrating the CH$_2$O LIF signal in an atmospheric flame with the LIF signal from a known concentration of CH$_3$O in a quartz cell.

An alternate method is the combination of LIF and CRD to obtain a quantitative measure of the species [3, 7, 10, 16]. In this current low-pressure flame example, we report using CRD to quantify relative LIF CH$_2$O and CH concentrations and to detect CH $B$ $\nu'$ = 1 predissociative levels not accessible by LIF. Using LIF we can evaluate the effect of spatial resolution problems and inhomogeneities on the line-of-sight absorption measurements. Finally, experimental absolute number density profiles are compared to the predictions of the GRI-Mech 3.0 combustion kinetics mechanism [17], and some opinions are offered on the chemical significance of the LIF+CRD measurements that can be made for formaldehyde.

2 Experimental

2.1 Burner and flame details

Our standard CH$_4$/O$_2$/N$_2$ (O$_2$/N$_2$ + O$_2$) = 0.3 ) premixed laminar flame at 25 Torr pressure was burned on a porous McKenna burner in a pressure-controlled chamber with optical access. The stoichiometric ratio is 1.07 and the total flow rate is 3.22 slm. This flame has been investigated
with many previous combustion diagnostics measurements in our laboratory [18]. Thus, temperature and key intermediate species profiles (including CH) are well known, and meaningful comparisons can be made with results from different spectroscopic techniques. The burner is mounted on a motorized stage for vertical scans. The accuracy of this height scale is estimated to be 0.25 mm. The burner has four optical ports at 90° separation; two of them provide the laser path and employ either quartz windows for LIF or mirrors for CRD.

### 2.2 Laser-induced fluorescence

The CH \( B - X(1, 0) \) and CH\(_2\)O \( A \rightarrow X \) lines at 368 nm are excited with a dye laser (Lambda Physik FL-2002, temporal width ∼ 7 ns, spectral bandwidth ∼ 0.13 cm\(^{-1}\), vertically polarized), pumped by a tripped Nd:Yag laser at 355 nm. Laser energies between 1 µJ and 100 µJ were measured with a microjoulemeter (RJ-7200, Laser Precision Corp.). The laser tunability range and energy per pulse are limited because of the proximity of the Nd:Yag pumping wavelength. The laser pulse is spatially filtered and coupled TEM\(_{00}\) into the optical cavity. We imaged the path of the laser beam through the flame to a spectrograph SPEx 270M (f/4, 500 nm blaze angle) and onto a gated intensified CCD camera (Princeton Instruments, ICCD-576G/RGB, 14-bits dynamic range, 384 × 576 pixels, pixel size 23 µm). One CCD pixel corresponds to 130 µm in the flame, but the imaging of a test card indicates the spatial resolution of our optical collection system is approximately 3 pixels or 400 µm. A glass filter KV-370 cuts off the light below 385 nm, and the fluorescence collection scheme is similar to the previous Bunsen flame LIF experiment [12].

Single-pass laser-induced fluorescence measurements are performed using the CCD camera as a one-dimensional array detector. The laser beam diameter is 1 mm and images are composed of a series of 0.6 mm horizontal slices (sums of 4 center camera pixels) taken every 0.35 mm above the burner up to a height of 16 mm. The intensifier gate is slightly delayed from the laser pulse to avoid detecting scattered light, and the integration time is 20 ns to minimize any effects of fluorescence yield variations versus height by measuring only prompt fluorescence. Images of the flame are taken with the laser on-resonance at the selected transition and without any laser excitation. The final LIF image has the flame chemiluminescence removed by subtraction of the flame image without laser excitation.

### 2.3 Cavity ring-down absorption spectroscopy

The laser beam is spatially filtered with a telescope (2:1) and pinhole (100 µm diameter) for better mode matching in the CRD cavity. The burner is equipped with optical access arms. At both ends, mirrors with reflectivity better than 99.99% and a 6-m radius of curvature (Los Gatos Research) are set in kinematic mounts, forming a cavity of 0.92 m length. The CRD light at the far side of the exit mirror is measured by a 9558QB EMI photomultiplier, digitized with a 500 MHz Tektronix 520C oscilloscope. A Labview program handles data acquisition and laser synchronization. The transients, averaged over 10–20 laser shots, are fit to a single exponential decay between 90% and 10% of the maximum signal intensity. We use CCD camera images of the ring-down laser light scattering in the chamber to calibrate the distance above the burner. In previous CRD experiments, we could optimize the cavity alignment by imaging the LIF distribution while simultaneously monitoring the CRD decay and achieve only TEM\(_{00}\) coupling. However, in the present experiment the LIF signal is too weak for this approach to be practical because of the very low laser energies available at 368 nm. Therefore, we optimize the alignment by first adjusting the time decay to the longest possible decay time. Then we check the width of the CH CRD absorption height profile, which is known to be 3.2 ± 0.2 mm (FWHM) in this flame from optimized CRD measurements in the CH \( A - X(0, 0) \) and \( B - X(0, 0) \) bands [10, 16]. If transverse modes were coupled, our previous work shows the CH structure would be significantly broadened. Finally, we maximize the CRD absorbance at the peak of the CH distribution. Under these conditions, the beam waist is < 1 mm FWHM.

In a cavity ring-down experiment, the monochromatic light pulse coupled into the cavity decreases in intensity with time due to mirror, scattering, and absorber losses. The light intensity collected beyond the exit mirror on every other pass decays exponentially with a ring-down lifetime \( \tau \) given by:

\[
\tau(v) = (L/c)/(T + A + \sigma(v)Nd),
\]

where \( L \) is the cavity length, \( T + A \) are mirror and scattering losses, \( \sigma \) is the cross section for the absorber, \( N \) is the number density of the absorber, and \( d \) is the distance in the path where the absorber is distributed homogeneously. The spectra are analyzed in terms of total losses per pass \( \sigma = L/c\tau(v) \). Within this description, mirror and scattering losses appear as a background in the spectrum, and absorption peaks depend on number densities and absorption cross sections.

Linearity of LIF is a function of the optical pumping and depopulation rates. CRD is generally insensitive to this kind of optical saturation because the signal size does not depend on laser spectral irradiance and very modest laser powers are enough to obtain CRD absorption spectra with no optical saturation. Wide laser bandwidth can, however, prove a problem for CRD [19, 20] as this produces a distribution of ring-down times over the laser bandwidth. When the laser bandwidth becomes comparable to or larger than the absorption linewidth, multiexponential decays and lower sensitivity are observed. Under these circumstances, without calculating correction factors, concentrations of the absorption are underestimated. For the present experimental conditions, such deviations due to the finite laser bandwidth should be less than 10%.

### 3 CH \( B - X(1, 0) \) and CH\(_2\)O \( A - X \) \( 4^0 \) CRD spectra

Figure 1 shows a typical cavity-ring down absorption spectrum of the CH \( B - X(1, 0) \) \( P_1(8) \) and \( P_2(8) \) rotational lines together with \( R \) bandhead of the CH\(_2\)O \( A - X \) \( 4^0 \) \( 5 ← 4 \) (\( K^′ ← K^″ \)) band. The assignment of the formaldehyde rovibrionic lines is based on Dyne’s work [21]. We find several strong lines near the bandhead not identified in the only available spectroscopic tabulation. Dyne’s experiment spectrum was taken at 430 K, but our temperature is \( \sim 1300 \) K in