

Detection of methyl radicals in a flat flame by degenerate four-wave mixing

Volker Sick,* Mary N. Bui-Pham, and Roger L. Farrow

Combustion Research Facility, MS 9057, Sandia National Laboratories, Livermore, California 94551

Received March 28, 1995

We report the spatially resolved detection of methyl radicals in a methane–air flat flame, using degenerate four-wave mixing (DFWM). A frequency-tripled dye laser pumped with a frequency-doubled Nd:YAG laser was used to access the Herzberg β_1 band of methyl near 216 nm. Using a nearly phase-conjugate geometry, we detected methyl with high spatial resolution [0.2 mm (0.3 mm) vertical (horizontal) and ~ 6 mm longitudinal] and with good signal-to-noise ratio in a rich ($\phi = 1.55$) flame. Compared with laser absorption spectra, DFWM spectra were much less influenced by a broad featureless background. From the absorption data, we measured the peak methyl concentration to be 650 parts in 10^6 , resulting in an estimated DFWM detection limit of 65 parts in 10^6 . © 1995 Optical Society of America

Owing to the importance of the methyl radical (CH_3) in combustion and in the growth of diamond by chemical-vapor deposition,^{1,2} the development of optical techniques for measuring CH_3 concentrations under high-temperature conditions and nonuniform spatial distribution has been widely pursued. Since the first demonstration of the existence of accessible UV transitions in CH_3 ,³ UV absorption methods,^{4–6} including cavity ring-down spectroscopy,⁷ have been widely used for line-of-sight measurements. Techniques with improved spatial precision, i.e., resolution in all three dimensions, have since been developed. Resonance-enhanced multiphoton ionization has been demonstrated for sensitive detection of CH_3 in flames,⁸ and Raman⁹ and coherent Raman anti-Stokes spectroscopy¹⁰ have been used to study CH_3 at much higher concentrations. Laser-induced fluorescence, commonly used for many combustion-relevant intermediate species, cannot be used because the B state of CH_3 is strongly predissociative, resulting in nondetectable fluorescence quantum yields.

Approaching the sensitivity of laser-induced fluorescence, degenerate four-wave mixing (DFWM) has been shown in recent years to be a useful technique for the detection of combustion-relevant species.¹¹ In this Letter we describe the use of a DFWM scheme for sensitively probing the concentration distribution of CH_3 radicals in a rich methane–air flat flame and compare the results with absorption measurements. To our knowledge, this is the first example of the detection of a polyatomic radical by DFWM.

The Herzberg β_1 band near 216 nm is accessible with common laser sources and is what we study here. We used a tunable dye laser (Lambda Physik FL 2002) pumped with a frequency-doubled injection-seeded Nd:YAG laser (Positive Light) for excitation. With DCM dye operation, the output was frequency doubled in a beta-barium metaborate ($\beta\text{-BaB}_2\text{O}_4$) crystal and then mixed with the dye-laser fundamental in a second $\beta\text{-BaB}_2\text{O}_4$ crystal. The second-harmonic and fundamental radiation was then removed with mirrors coated for 216 nm and a spatial filter (diamond pinhole with a focusing telescope). Final output pulses had energies of ~ 1 mJ near 216 nm and a bandwidth

of ~ 0.2 cm⁻¹. For the DFWM measurements we used a nearly phase-conjugate geometry¹² in which the forward pump and the probe beams are crossed in a horizontal plane and the backward pump beam is directed downward at a small angle ($\sim 2^\circ$) with respect to the forward beams while it remains in a vertical plane containing the forward pump beam. This causes the emerging signal to propagate downward at the same angle, thus permitting very efficient collection of the signal beam with a mirror rather than a beam splitter. Scattered light caused by the probe beam passing through the beam splitter is also avoided. For most of the experiments all beams had vertical polarizations. Each beam had the same energy of 10–20 μJ /pulse. The signal beam was directed through an ~ 2 -mm iris, focused through a 25- μm pinhole, and detected with a UV-sensitive photomultiplier tube (Hamamatsu 955) without any additional filtering. We typically averaged measurements from 20 laser pulses, normalizing the DFWM signals to I^3 on a single-pulse basis, where I is the total input pulse energy. We simultaneously recorded absorption data by measuring the transmitted pulse energy of the probe beam and normalizing by I . (Optimized absorption measurements were performed separately.) The signal-to-noise ratio in our experiments was 22 for the DFWM and 5 for the absorption data.

All experiments used an axisymmetric honeycomb burner (50-mm diameter) operated at atmospheric pressure with methane–air mixtures of $\phi = 1.55$. The flow conditions were chosen so that the flame front was nearly flat and lifted, permitting access to the region in which the peak CH_3 concentration was expected based on calculations.¹³ The beam diameters used in the experiments ranged from 800 (FWHM) to 200 μm , obtained by downcollimation with a telescope and by additional insertion of 1-m focal-length lenses, respectively.

We used absorption spectroscopy to initially locate and characterize CH_3 distributions in the flame. Tuning the laser frequency from 45 800 to 46 500 cm⁻¹, with the probe beam passing just below the visible flame zone, we obtained spectra such as that shown

by the top trace of Fig. 1. (We found it necessary to correct for slowly varying but significant changes in beam-splitter and mirror reflectivities as a function of frequency.) To confirm that the observed broad absorption features are due to CH_3 , we calculated the spectrum, using a symmetric top model as described by Herzberg.¹⁴ Details for calculating the term energies and the spectroscopic constants for the ground state were found in Ref. 15. Since constants for the excited state are not well known, except for the electronic term energy and the rotational constants,¹⁶ we varied the former for best fit. With a predissociative broadening of 100 cm^{-1} (Ref. 4) the calculated (solid curve at the top of Fig. 1) and measured spectra are in good agreement if a strong baseline absorption (dashed line) that increases linearly with frequency is added.⁴ Using a band oscillator strength of 0.0137,¹⁷ we can reproduce the absorption coefficient as measured by Davidson *et al.*⁵ Consequently, we calculated a peak CH_3 concentration of 650 parts in 10^6 occurring at a beam height of 2.1 mm for our flame, assuming a path length of 4 cm (confirmed with DFWM as described below).

Intense DFWM signals were observed when the beam height was set to 2.1 mm and the laser was tuned to either of the CH_3 absorption peaks. From a comparison of the resulting DFWM spectra (bottom trace of Fig. 1) with the absorption results it is evident that the broad DFWM features originate from CH_3 . The spectral positions of the two broad peaks, caused by the combined P and Q as well as the separated R branch, are present in both spectra. This, together with our observation of the DFWM signals at the flame height corresponding to maximum CH_3 absorption, and in agreement with flame-chemistry calculations (discussed below), confirms that the detected signals originate from CH_3 . Interestingly, the strong sloping background dominating the absorption measurements is not present in the DFWM spectra. However, we did observe a nonresonant underlying DFWM signal that was less than 10% of the peak CH_3 signal. Narrow lines are also observed in the DFWM signal that are present in the absorption data to a much lesser extent. All the narrow lines can be assigned to Schumann–Runge $B-X$ transitions in molecular oxygen (O_2), mainly from $v'' = 3-5$.¹⁸ Differences in the relative intensities of spectral features between the absorption and the DFWM spectra can be attributed to the factor $\alpha^2(I/I_{\text{sat}})^2$ in the DFWM signal equation, where α is the peak absorption coefficient.¹¹ For example, we measured I_{sat} for the DFWM background to be roughly 50 times greater than that of CH_3 or O_2 , explaining the relatively reduced background signals in DFWM compared with absorption. Different (calculated) saturation intensities are also expected to reverse the DFWM peak intensities for the CH_3 P/Q and R branches compared with absorption.

An attempt to model the CH_3 DFWM spectra with a two-level model based on the theory of Abrams *et al.*¹⁹ and our theoretical absorption database did not yield satisfactory agreement with the measurements for the overall shape of the spectrum. Calculating the spectrum by simply squaring the calculated absorption spectrum less the background yielded somewhat better

results (though judged too preliminary for publication). We also observed that using a crossed (horizontal) polarization of the forward pump beam decreased the CH_3 DFWM signal by a factor of 20 ± 5 . Both of these results suggest a contribution from a thermal grating.²⁰ A two-color experiment is currently in progress to investigate this possibility.

We also investigated the applicability of DFWM for real-time spatially resolved CH_3 detection. Setting the laser frequency to the peak CH_3 signal in a region free of O_2 interference (46185 cm^{-1}), we translated the burner vertically and observed a distinct peak in the signal at $\sim 2.1 \text{ mm}$ above the burner surface. Similar measurements with the laser tuned away from resonance with CH_3 and O_2 transitions indicated that the CH_3 signal was the dominant contribution to the total signal by at least a factor of 20. We found that the transverse spatial resolution defined by the focused laser beams easily resolved the CH_3 signal profile, which was asymmetric and approximately 1 mm thick. From geometric considerations we estimated the longitudinal resolution to be 6.5 mm in this configuration. This estimate was consistent with comparisons of CH_3 profiles that we obtained by horizontally translating the burner first parallel and then perpendicular to the laser beams. We found the CH_3 signal strength to be relatively constant—and to peak at the same height—across $\sim 4 \text{ cm}$ of the visible flame diameter of 5 cm. Based on these results we used 4 cm as the effective absorption path length for analyzing the absorption measurements.

Figure 2 shows a CH_3 spatial profile measured by DFWM in comparison with flame-model calculations. The square root of the DFWM signal was taken following subtraction of the nonresonant background, but the

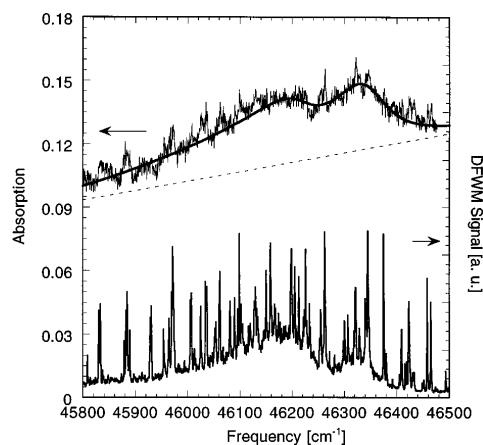


Fig. 1. Single-pass absorption spectrum of CH_3 measured 2.1 mm above the burner surface (top trace). A concentration of 650 parts in 10^6 CH_3 radicals is calculated for this flame position. The dashed line indicates the broadband background absorption, dominating the overall absorption in this spectral range. This background has been added to the simulation of the spectrum (thick solid curve). The bottom trace shows a DFWM spectrum of CH_3 measured with 200- μm beams at the same position. The two underlying broad features result from CH_3 , and the overlapping narrow peaks correspond to O_2 Schumann–Runge transitions. Note that there is region at 46185 cm^{-1} at the peak of the stronger CH_3 band that is free of O_2 interference.

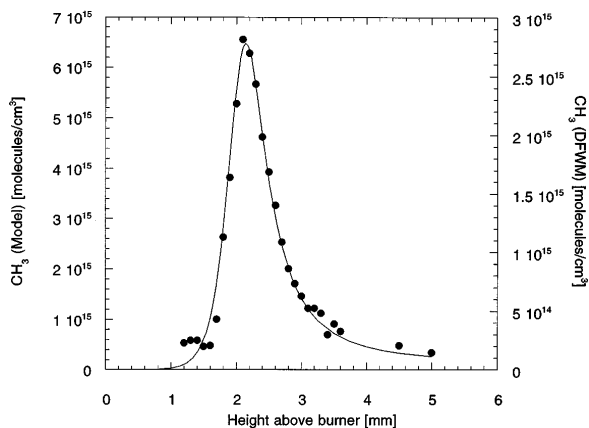


Fig. 2. Spatial CH_3 profiles in a laminar methane-air flame at $\phi = 1.55$. The measured profile (filled circles) was taken with 200- μm -diameter focused laser beams.

data have not been corrected for temperature effects, important only on the left side of the profile. Excellent agreement is observed for the shape of the profiles, with the peak concentration measured by DFWM being roughly a factor of 2 lower (this discrepancy may result from uncertainties in the absorption coefficient based on the large background).

In comparison with other techniques for measuring CH_3 we note the following advantages of DFWM: Resonance-enhanced multiphoton ionization measurements, which have been shown to be quite sensitive,⁸ suffer from the need to insert electrodes in the flame, which can be intrusive or impractical. Also, interferences that completely obscured the CH_3 signals occurred in some regions of the flame.⁸ Compared with line-of-sight methods (cavity ring-down and conventional absorption techniques), DFWM provides spatial resolution in three dimensions, which is required in many applications. The estimated CH_3 detection limit with our current DFWM setup is ~ 65 parts in 10^6 , calibrated by absorption measurements. This is comparable with 90 parts in 10^6 for cw ring-laser absorption,⁵ assuming a detection limit of 0.2% for I_0 and a path length equal to our interaction length of ~ 6.5 mm. A detectivity of 16 parts in 10^6 for the same path length at 20-Torr total pressure has been reported for cavity ring-down absorption spectroscopy⁷; however, in atmospheric-pressure flames this method has been demonstrated only for detecting OH.²¹

Our results show that DFWM is a promising technique for measuring CH_3 concentrations with high spatial and temporal resolution and high sensitivity, even within 0.5 mm of surfaces. In contrast to those with absorption and resonance-enhanced multiphoton ionization techniques, interfering background signals are substantially reduced and are independent of frequency. Because of this, real-time measurements with a single laser wavelength appear possible, provided that the temperature is known. The use of a standard tunable dye laser provides sufficient spectral resolution to avoid simultaneous detection of O_2 . Future study is aimed at developing a quantitative DFWM spectral model for CH_3 and at investigating multicolor four-wave mixing approaches.

The authors acknowledge helpful discussions with P. H. Paul of Sandia National Laboratories (SNL). This research was sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division. V. Sick is grateful to the Deutsche Forschungsgemeinschaft for a grant permitting the visit to SNL.

*Present address, Physikalisch-Chemisches Institut, Universität Heidelberg, Heidelberg, Germany.

References

1. J. Warnatz and C. Chevalier, "Reactions in the C/H/C system," in *Combustion Chemistry*, W. C. Gardiner, Jr., ed. (Springer-Verlag, New York, to be published).
2. S. J. Harris, *Appl. Phys. Lett.* **23**, 2298 (1990).
3. G. Herzberg and J. Shoosmith, *Can. J. Phys.* **34**, 523 (1956).
4. D. F. Davidson, A. Y. Chang, M. D. Di Rosa, and R. K. Hanson, *J. Quant. Spectrosc. Radiat. Transfer* **49**, 559 (1993).
5. The reported value of k_λ was later revised. See D. F. Davidson, M. D. Di Rosa, E. J. Chang, and R. K. Hanson, *J. Quant. Spectrosc. Radiat. Transfer* **53**, 581 (1995).
6. T. Etzkorn, J. Fitzer, S. Muris, and J. Wolfrum, *Chem. Phys. Lett.* **208**, 307 (1993).
7. P. Zalicki, Y. Ma, R. N. Zare, E. H. Wahl, J. R. Dadamio, T. G. Owano, and C. H. Kruger, *Chem. Phys. Lett.* **234**, 269 (1995).
8. K. C. Smyth and P. H. Taylor, *Chem. Phys. Lett.* **122**, 518 (1985).
9. P. B. Kelly and S. G. Westre, *Chem. Phys. Lett.* **151**, 253 (1988).
10. P. L. Holt, K. E. McCurdy, R. B. Weisman, J. S. Abrams, and P. S. Engel, *J. Chem. Phys.* **81**, 3349 (1984).
11. R. L. Farrow and D. J. Rakestraw, *Science* **257**, 1894 (1992), and references therein.
12. R. L. Vander Wal, R. L. Farrow, and D. J. Rakestraw, in *Twenty-Fourth Symposium (International) on Combustion* (Combustion Institute, Pittsburgh, Pa., 1992), p. 1653.
13. M. N. Bui-Pham and J. A. Miller, in *Twenty-Fourth Symposium (International) on Combustion* (Combustion Institute, Pittsburgh, Pa., 1994), p. 1309.
14. G. Herzberg, *Molecular Spectra and Molecular Structure III. Electronic Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1966).
15. C. Yamada, E. Hirota, and K. Kawaguchi, *J. Chem. Phys.* **75**, 5256 (1981).
16. K. Glänzer, M. Quack, and J. Troe, in *Sixteenth Symposium (International) on Combustion* (Combustion Institute, Pittsburgh, Pa., 1977), p. 949.
17. A. B. Callear and M. P. Metcalfe, *Chem. Phys.* **14**, 275 (1976).
18. V. Sick and M. Szabadi, "Einstein coefficients for oxygen $B-X$ transitions used in laser-induced fluorescence experiments with tunable KrF excimer lasers," *J. Quant. Spectrosc. Radiat. Transfer* (to be published).
19. R. L. Abrams, J. F. Jam, R. C. Lind, and D. G. Steel, in *Optical Phase Conjugation*, R. A. Fischer, ed. (Academic, New York, 1983).
20. S. Williams, L. A. Rahn, P. H. Paul, J. W. Forsman, and R. N. Zare, *Opt. Lett.* **19**, 1681 (1994).
21. G. Meijer, M. G. H. Boogaarts, R. T. Jongma, D. H. Parker, and A. M. Wodtke, *Chem. Phys. Lett.* **217**, 112 (1994).