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

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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 $\beta_1$ 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 $\sim$6 mm longitudinal] and with good signal-to-noise ratio in a rich ($\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, 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$_3$ through cavity ring-down spectroscopy, 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, and Raman and coherent Raman anti-Stokes spectroscopy 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. 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 $\beta_1$ 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 borate ($\beta$-BaB$_2$O$_4$) crystal and then mixed with the dye-laser fundamental in a second $\beta$-BaB$_2$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 $\sim$1 mJ near 216 nm and a bandwidth of $\sim$0.2 cm$^{-1}$. For the DFWM measurements we used a nearly phase-conjugate geometry in which the forward pump and the probe beams are crossed in a horizontal plane and the backward pump beam is directed downward at a small angle ($\sim$2°) 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 $\mu$J/pulse. The signal beam was directed through an $\sim$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 $I^4$ 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. 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.$^3$ 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 $\alpha^2(I/I_{sat})^2$ in the DFWM signal equation, where $\alpha$ 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 signal.$^{20}$ 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 ~2.1 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 ~4 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
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5. The reported value of $k_1$ 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).