

## DETECTION OF THE METHYL RADICAL IN A METHANE/AIR DIFFUSION FLAME BY MULTIPHOTON IONIZATION SPECTROSCOPY

Kermit C. SMYTH and Philip H. TAYLOR<sup>1</sup>

*Center for Fire Research, National Bureau of Standards, Gaithersburg, MD 20899, USA*

Received 6 September 1985

Methyl radicals have been detected in an atmospheric pressure, methane/air diffusion flame by three-photon ionization. The origin band of the transition between the  $\bar{X}^2A_2'$  ground electronic state and the  $3p^2A_2''$  Rydberg state is observed at 333.5 nm via two-photon excitation. A second peak at 340.8 nm is likely due to both a methyl radical hot band in the same electronic transition and three-photon ionization of carbon atoms produced by photolysis. Spatial profiles are presented as a function of height above the burner and are discussed in terms of resonant and non-resonant ionization processes.

### 1. Introduction

The methyl radical is an important species in hydrocarbon combustion, particularly in the initial pyrolysis reactions. Once these radicals are formed, subsequent recombination to yield ethane



is one of the key steps which produces heavier hydrocarbons, including polycyclic aromatic compounds and soot. Absolute concentration measurements of the methyl radical are essential for understanding its role in hydrocarbon combustion kinetics.

Methyl radicals have been detected in premixed flames using absorption [1] and mass spectrometric sampling [2,3] methods. Neither of these approaches is well suited for diffusion flame studies. Absorption measurements are restricted in terms of sensitivity and spatial resolution, while molecular beam sampling causes severe perturbations of the chemical structure in a diffusion flame. Therefore, a new optical method for observing methyl radicals would be most useful.

Recently, multiphoton ionization has been utilized to detect a variety of flame species, including H [4–6], O [6,7], NO [8,9], PO [10], CO [11], C<sub>2</sub>O [11], and trans-1,3-butadiene [12,13]. In addition, a number of

high-lying electronic states of the methyl radical have been characterized by Hudgens and co-workers using this optical technique [14–17]. In that work the CH<sub>3</sub> radicals were produced in either a pyrolysis oven or in a fast flow reactor. Methyl radicals have also been probed in photofragmentation [18–20], pyrolysis [21], and surface decomposition [22] experiments using multiphoton ionization.

This paper reports the first flame observation of methyl radicals with multiphoton ionization; transitions have been detected between the ground electronic state and the  $3p^2A_2''$  Rydberg state [17]. Profile measurements are also presented, and methyl radical concentrations are estimated.

### 2. Experimental apparatus

Methane/air diffusion flames were burned at atmospheric pressure on an open Wolfhard–Parker slot burner [23], shown in fig. 1. Fuel flows through an 8 mm X 41 mm center slot and oxidant (air) through two 16 mm X 41 mm slots, thus creating two flame fronts. A rectangular, wire screen chimney with gulls was used to stabilize the flame at a height of 45 mm above the burner. The methyl radical profiles were obtained by moving the burner in the lateral direction (along the *x*-axis in fig. 1) at a series of heights, using

<sup>1</sup> NBS/NRC Postdoctoral Research Associate.

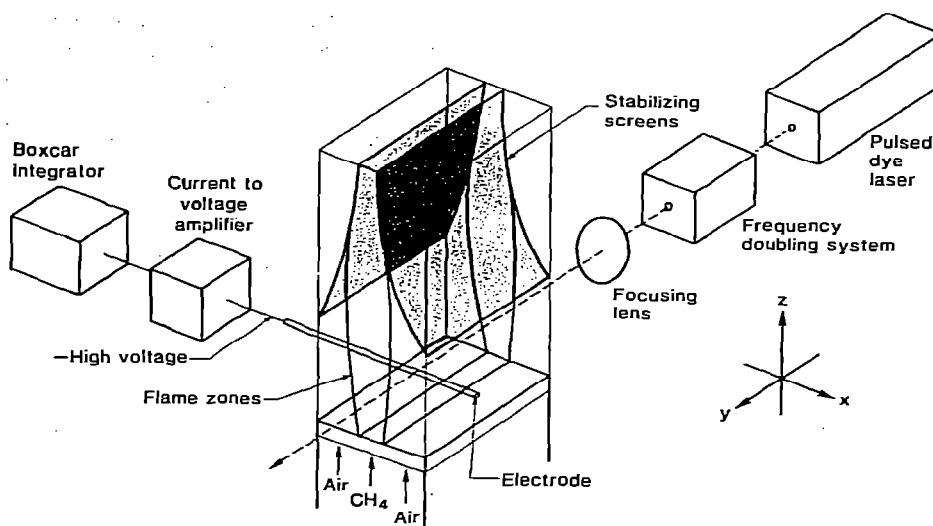


Fig. 1. Schematic diagram of the experimental apparatus. The incoming ultraviolet light is focused with a 100 mm focal length lens at a position 1–2 mm below the detection electrode. This electrode is biased at  $-700$  V, with the burner body providing the ground return.

a programmable micrometer stage; the laser and detection electrode remained fixed. The cold flow velocity of the air was twice that of the methane, typical values being 19.4 and 9.7 cm/s. Chemically pure ( $\geq 99$  mole %) methane was used in all measurements. For these flame conditions extensive temperature, velocity, and species profiles have been obtained in an earlier investigation [23].

Ionization signals were produced by irradiation with a Nd:YAG-pumped tunable dye laser, whose output beam was frequency doubled using an autotracking frequency doubler. A combination of DCM and LDS 698 dyes (Exciton Chemical Company) yielded ultraviolet light in the 330–350 nm wavelength region with a bandwidth of  $1\text{--}2\text{ cm}^{-1}$ . The near-UV beam was isolated from the visible fundamental beam with a colored glass filter and was then directed into the flame parallel to the burner slot; beam energies were 100–500  $\mu\text{J}/\text{pulse}$ . For detecting laser-induced ionization a 1 mm diameter tungsten electrode was inserted into the flame perpendicular to the laser beam and 1–2 mm above it. This electrode was biased at  $-700$  V, and the burner body provided the ground return. Using a current-to-voltage amplifier ( $10^5$  V/A), the signal was amplified and then processed by a boxcar averager; the laser

energy was simultaneously recorded with a pyrometer. Laser-induced fluorescence measurements of OH profiles are not affected by the presence of the tungsten electrode, indicating that the flame is not significantly perturbed at the location of the laser beam [23].

The wavelength of the UV beam was calibrated by monitoring the laser-enhanced ionization signal following excitation of the  $3s \rightarrow 4p$  sodium transitions at 330.24 and 330.30 nm. Sodium was aspirated into a premixed acetylene/air flame for this measurement. The polarization dependence of the multiphoton ionization signals was determined by using an air-spaced calcite polarizer to ensure highly polarized incident radiation and a Soleil–Babinet compensator as a quarter-wave retardation plate to produce circularly polarized light.

### 3. Results and discussion

#### 3.1. Multiphoton ionization spectrum

Fig. 2 presents the multiphoton ionization spectrum obtained in the methane/air diffusion flame. The ionization signals exhibit a localized spatial de-

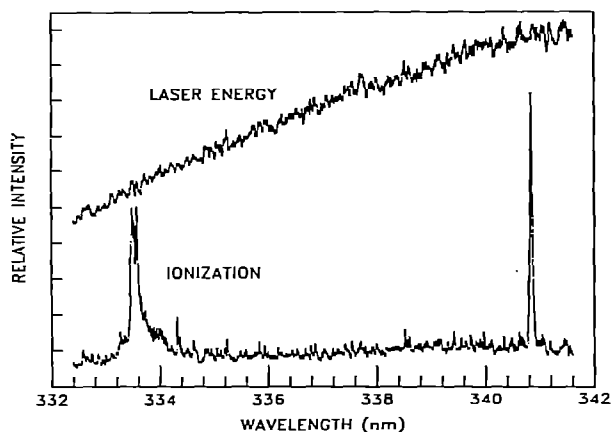


Fig. 2. Multiphoton ionization spectrum obtained at a position 2 mm above the burner and 4.6 mm from the burner centerline. The features at 333.5 nm and 340.8 nm are assigned to the multiphoton ionization of methyl radicals and carbon atoms (see text). Also shown is the relative dye laser energy as a function of wavelength; the ionization spectrum has not been corrected for the variation in laser intensity.

pendence (see next section), and their maximum values occur at a temperature of approximately 1700 K [23]. The peak at 333.5 nm corresponds to the strong Q branch of the origin band for the two-photon transition between the ground electronic state of the methyl radical  $\tilde{X}^2A_2''$  and the  $3p^2A_2''$  Rydberg state [17]. A third photon of the same energy ionizes the methyl radicals following two-photon excitation of this Rydberg state (a "2 + 1" ionization process).

The polarization dependence of the origin band was investigated and gave a ratio of the peak ionization signal using circular polarization to that with linear polarization of  $\approx 0.7$ . This value is consistent with the results of Hudgens et al. [17]. In the flame measurements the spectral width of this band is found to be  $15 \text{ cm}^{-1}$  at half maximum, which is close to the width observed by Chou at 1375 K ( $12\text{--}14 \text{ cm}^{-1}$ ) [21].

The  $3p^2A_2''$  Rydberg state of the methyl radical exhibits vibrational activity in the  $\nu_2$  out-of-plane bending mode, with a number of transitions reported at wavelengths shorter than the origin band [17]. However, these bands are much weaker than the origin band and were not observed in the methane/air diffusion flame. On the other hand, fig. 2 shows a second feature at 340.8 nm which may arise from  $\nu_2$  activity.

The ionization signal at 340.8 nm has the same spatial dependence low in the flame as the origin band at 333.5 nm and shows a similar polarization dependence (circular/linear peak intensity ratio of  $\approx 0.8$ ). These results suggest that the multiphoton ionization of methyl radical also yields the peak at 340.8 nm. This band was not reported previously (see table 2 of ref. [17]).

For  $D_{3h}$  structural symmetry the allowed transitions involving the  $\nu_2$  vibrational mode occur for only  $\Delta\nu_2 = 0, \pm 2$  [17]. This mode also exhibits pronounced negative anharmonicity in the ground electronic state [24–27]. Assuming two-photon excitation, the energy separation between the band centers in fig. 2 is  $1280 \text{ cm}^{-1}$ , which is very close to the value of  $1288.1 \text{ cm}^{-1}$  measured for the ground state  $\nu_2 = 0$  to  $\nu_2 = 2$  separation [26]. Thus, the observed feature at 340.8 nm exhibits an energy separation appropriate for the  $2\nu_2$  hot band in the  $3p^2A_2'' - \tilde{X}^2A_2''$  electronic transition. This methyl radical band has also been observed in pump-probe photodissociation experiments in a low-pressure beam environment [20].

The 340.8 nm feature is quite sharp, with a full width at half maximum of  $\approx 5 \text{ cm}^{-1}$ , or only one third the width of the origin band. Chen has pointed out to us that the two-photon  $2p^1D_2 \rightarrow 3p^1P_1$  transition of neutral carbon occurs at 340.83 nm [28] and that multiphoton ionization of carbon atoms is readily detected in photofragmentation studies [20]. Additional two-photon transitions from the same excited electronic state of the carbon atom occur at 320.33 nm ( $2p^1D_2 \rightarrow 3p^1D_2$ ) and 313.48 nm ( $2p^1D_2 \rightarrow 3p^1S_0$ ). Both of these transitions have also been observed in our flame measurements using multiphoton ionization. Thus, it is likely that three-photon ionization of carbon atoms is being detected at 340.8 nm, as well as ionization due to methyl radicals. If the atomic contribution were dominant, this would account for the narrow peak shape.

### 3.2. Profile measurements

Fig. 3 presents methyl radical profiles along the x-direction (fig. 1) at two heights above the burner. Data were obtained at 2 mm height increments from 1 to 19 mm. For these measurements the origin band at 333.5 nm was monitored. In addition, profiles were obtained off-resonance at 335.0 nm, since numerous

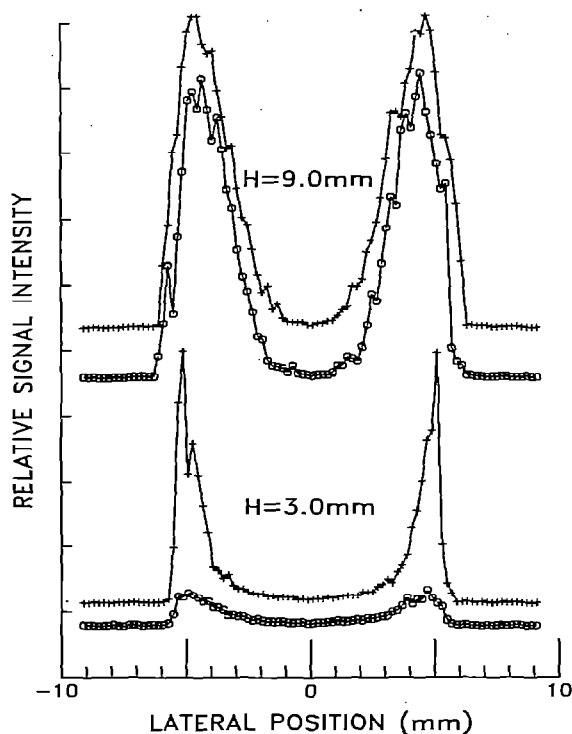


Fig. 3. Methyl radical profile measurements obtained at two heights above the burner and at two wavelengths: on-resonance (333.5 nm, crosses) and off-resonance (335.0 nm, open circles). The zero positions have been offset for clarity. Maximum temperatures occur in this flame at  $\pm 5.9$  mm for  $H = 3.0$  mm and at  $\pm 6.6$  mm for  $H = 9.0$  mm [23].

intermediate hydrocarbons are produced in a methane/air diffusion flame [23] and these may also undergo multiphoton ionization.

Low in the flame the methyl radical profile exhibits sharp peaks, and the off-resonance background ionization signal is small. At higher positions the background signal grows rapidly and overwhelms the methyl radical signal by a height of 9.0 mm, where the on-resonance and off-resonance profiles are indistinguishable. These profiles remain identical at each height for higher flame positions. Thus, methyl radicals can be detected free from interferences only low in this methane/air diffusion flame using multiphoton ionization.

Profile measurements were also made at a wavelength of 340.8 nm. Low in the flame this profile is identical to that obtained for the methyl radical origin

band (333.5 nm). To the degree that carbon atom ionization contributes to the signal at 340.8 nm, this result suggests that carbon atoms are produced from the photolysis of methyl radicals (perhaps via  $\text{CH}_2$  [29] and/or  $\text{CH}$  [30]). Higher in the flame the profile broadens toward the burner centerline, due to non-resonant ionization of hydrocarbons as well as carbon atom ionization following photolysis of these species.

The multiphoton ionization spectrum and the profile measurements shown in figs. 2 and 3 are attributed to nascent  $\text{CH}_3$  radicals in the methane/air diffusion flame, as opposed to laser-produced methyl radicals. The profile measurements support this assignment: the observed spatial dependence for the methyl radical signals is very different from that of methane and ethane, which are the two most logical photolysis precursors. These stable species have been probed using mass spectrometric methods [23]. The methane profile shows a single peak at the burner centerline [23], and the ethane profile exhibits peaks which are much broader than the methyl peaks and extend significantly closer to the burner centerline [31].

The peak methyl radical concentrations can be estimated from the measured ethane concentrations, if one assumes that the methyl radical recombination reaction (1) is equilibrated. At the peak of the methyl radical ionization signal the ethane mole fraction is  $\approx 2.0 \times 10^{-4}$  ( $\pm 50\%$ ) [31]. Using tabulated free energies at a temperature of 1700 K [32,33], the maximum methyl radical mole fraction is found to be  $\approx 5.5 \times 10^{-4}$ . Since steep temperature gradients ( $\approx 250$  K/mm) and concentration variations occur in the methane/air diffusion flame [23], the ionization detection efficiency may not be constant across an entire profile measurement. Therefore, in order to determine concentration profile from the signal profiles shown in fig. 3, the detection efficiency as a function of flame position must be measured.

#### Acknowledgement

We are pleased to acknowledge stimulating discussions with Mau-Song Chou and Tony Dean (Exxon), Peter Chen (Yale), and Jeffrey Hudgens, Houston Miller and Gary Mallard (NBS). Special thanks are due to Peter Chen for sending us his results prior to publication and for pointing out the importance of photo-

lytically produced carbon atoms in multiphoton ionization measurements.

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