2D Methyl Radical Measurement in a Methane/Air Flame at Atmospheric Pressure

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Abstract

2D measurements of methyl radicals (CH$_3$) in CH$_4$/air flames at atmospheric pressure have been achieved using coherent microwave Rayleigh scattering from Resonance Enhanced Multi-Photon Ionization, Radar REMPI. Relative direct measurements of the methyl radicals were conducted by Radar REMPI via the two-photon resonance of the intermediate state and subsequent one-photon ionization. Because of the proximity of the argon resonance state of $2s^22p^54f$ [7/2, $J=4$] (4+1 REMPI by 332.5nm) with the CH$_3$ state (2+1 REMPI by 333.6nm), in situ calibration with argon was performed to quantify the absolute concentration of CH$_3$. The REMPI cross sections of CH$_3$ and argon were calculated based on time-dependent quantum perturbation theory. The Radar REMPI method has shown great flexibility for spatial scanning, large signal to noise ratio for measurements at atmospheric pressures, and significant potential to be generalized in a straightforward manner for quantitative measurements of other radicals and intermediate species in practical and relevant combustion environments.
1. Introduction

The methyl radicals is one of key intermediates in the combustion. In combustion, ignition and flame propagation reactions (via hydrogen abstraction by H atoms and hydroxyl radicals (OH)) is controlled by the CH$_3$ radical \[1\]. The formation of polycyclic aromatic hydrocarbons (PAH) and soot is also highly dependent on this radical \[2\]. An important aspect of the chemical kinetics of methane combustion concerns the production and removal of methyl radicals (CH$_3$).

Due to the strong predissociation and low concentration in flame front, many optical methods based on laser are not applicable to detect CH$_3$ in methane/air flames at atmospheric pressure. The conventional REMPI technique was first used to obtain the relative spatial distribution of methyl radicals in the methane/air diffusion flame by Smyth and Tyler in 1985\[3\]. The electrical probes were applied in the experiments to detect the signal of plasma generated by multiphoton ionization. The probe interference and measurement accuracy must be carefully considered due to the introduction of probes\[4\]. In this paper, the non-intrusive measurement was conducted by Radar REMPI technique, which has already proven its capabilities to detect methyl radical in flames with high spatial resolution and non-intrusive characteristics \[5, 6\].

The study of the two-dimensional spatial distribution of methyl radicals in methane/air flame was conducted with the similar methods in this paper. The difference between this research and the previous ones is that a two dimensional transition stage was introduced to accomplish the two-dimensional scanning in the experiments. The two-dimensional distribution of methyl radicals was obtained by 24 discrete vertical scanning results. The interpolation method was used here to improve the quality of the two-dimensional image of methyl radicals. The distribution of methyl radicals was calibrated and quantified by argon and the absolute concentration distribution was given.

2. Experimental Setup

REMPI laser system, microwave homodyne transceiver detection system and 2-D transition stage with Hencken burner were involved in the experiment exploiting the two-dimensional distribution of methyl radicals in flames at atmospheric pressure. In the REMPI laser system, Surelite I10 Nd:YAG laser was employed as a source to pump ND6000 dye laser. The output of the dye laser was frequency doubled by a UVT tracking system and the 10Hz pulsed UV light was generated and used to detect methyl radicals in the Hencken flames. The energy of the Surelite laser output was about 200mJ, The Rhodamine 6G was used here as the dye in ND6000. The energy of the UV light was about 10 mJ/pulse (pulse width: 4-6 nm, linewidth: 1 cm$^{-1}$, Beam Diameter: 6 mm). The 2-D transition stage was introduced in the experimental to fulfill two-dimensional methyl radical scanning task. Two step motors were used in the experiments shown in Fig.1. The Step Motor One (SM1) was used to change the laser beam vertically, and the Step Motor (SM2) was applied to move the Hencken burner horizontally. Using such transition stage with step motors, the two-dimensional spatial scanning could then be achieved. A focal lens with
500 mm local length was assembled in the transition stage, which was used to focus the laser beam and increase the intensity at the focal point ionizing the methyl radicals in flames by 2+1 REMPI at 333.6 nm. The relative long focal length of the lens could increase the strength of signal and help to avoid the avalanche ionization due to the high power of laser as well.

Microwave detection system was successfully used in our previous experiments. The best advantages compared to the conventional REMPI, this system could fulfill the non-intrusive measurements without disturbing the flames and combustion process as the conventional method did by using thermocouple or any other sample probes. The microwave homodyne transceiver detection system was used to detect the REMPI plasma. A 10 dBm tunable microwave source (HP 8350B sweep oscillator, set at ~10GHz) was first split into two channels. One was used to illuminate the ionization point through a microwave horn (WR75, 15dB gain). Microwave scattering from the plasma was collected by the same microwave horn. The received microwave passed through a microwave circulator and was amplified 30 dB by one preamplifier at approximately 10 GHz. After the frequency was down converted in the mixer, two other amplifiers with bandwidth of 2.5 kHz to 1.0 GHz amplified the signal by another factor of 60 dB. From the geometry of dipole radiation, the polarization of the microwave was chosen to be along the propagation direction of the laser to maximize the scattering signal. The microwave scattering signal was monitored by an oscilloscope and recorded in an automatic data acquisition system.

![Figure 1 The experimental setup of two-dimensional methyl radical distribution measurements](image)

3. Quantitative Calibration of CH₃ with Argon

The principle technique for the quantitative calibration of CH₃ concentration in the flame with argon is shown in Figure 1. In this approach, due to the proximity of argon resonance state 2s²2p⁵4f [7/2, J=4] (4+1 REMPI by 332.5nm) with the state 3p²4s⁰(4+1 REMPI by 333.6nm), Radar REMPI measurements of freely flowing argon and methyl radicals in the flame were performed with the same configurations. Thus there was no need to modify the optical setup, burner positions, microwave horn positions, or microwave frequency. Since the freely flowing argon number density could be determined accurately, the number density of methyl radicals could be inferred from the relation.
\[ N(CH_3) = \frac{S(CH_3)}{S(Ar)} \cdot \left( \frac{\sigma^{(4+1)}(Ar)}{\sigma^{(2+1)}(CH_3)} \right) \cdot \frac{I^2}{I_0^2} \cdot N(Ar) \] 

where \( N \) is the number density, \( S \) is the observed signal, \( \sigma \) is the REMPI cross section and \( I \) is the laser intensity. The corresponding quantities for CH\(_3\) or argon are represented in brackets.

The key components for the quantitative calibration of Radar REMPI signals were the identification of the absolute baselines and determination of REMPI cross sections for different radical species. For CH\(_3\) measurement, the resonance state \( 2s^22p^54f \) \([7/2, J=4]\) of argon was in close proximity of the resonance state \( 3p^2A_2^0\) of CH\(_3\), as shown in Figure 1. The absolute collection efficiency could thus be established. Since there were no well-established values for the cross sections in the references, the cross sections of argon and CH\(_3\) were calculated based on time-dependent quantum perturbation theory.

**Figure 2.** REMPI spectra of free flowing argon (Ar) through the burner and methyl radical \([7]\) in a CH\(_4\)/air flame at atmospheric pressure. The measurement was conducted at the same location above the burner surface and the corresponding CH\(_3\) concentration was approximately \( 5.7 \times 10^{15} / \text{cm}^3 \).

Detailed computation of REMPI cross sections of argon and CH\(_3\) can be found in our recent publications. Basically time dependent perturbation theory was used to compute the multiphoton absorption of argon and CH\(_3\). Argon is resonantly populated by four photons at 332.5nm and ionized by one more photon from the resonance state. The 4+1 REMPI ionization cross section of argon has been calculated following the references. The 2+1 REMPI ionization cross section of methyl radical has been estimated based on time dependent quantum perturbation theory and will be experimentally determined \([8-11]\). The quantum theory uses the absorption coefficients to
calculate the first order dipole moments. The multiphoton absorption coefficient can be estimated by multiplying the dipole moments weighted by quantum defects.

4. Experimental Results and Discussion

The two-dimensional spatial distribution of methyl radicals in flame was obtained and the false color image was provided in Fig. 3(a). The whole image was composed by 24 discrete vertical scannings of methyl radicals above the burner surface. The distance between each separate scanning position is 100 µm. The total scanning width perpendicular to the laser propagating direction was 2.3 mm. Hence, 24 discrete vertical scanning gave the two-dimensional scanning results. In Fig. 3(a) the left and right side had certain signals from the adjacent flamelets. The signals were stronger at left side than that of the right side because the ionization point was much closer to the microwave detector. Hence the noble gas Argon was used in the experiments to calibrate the characterization of the detection system and used to quantify the absolute concentration of methyl radicals in the flames.

![Figure 3](image)

Figure 3. (a) The original two-dimensional data of methyl radicals in the flame front. (b) The 2D distribution of methyl radicals after the image processing.

In order to get better image and boost the deeper understanding the distribution of methyl radical in flames, the interpolation method and polynomial fitting were used in the data processing. Fig.3(b) shows the methyl radical 2D spatial distribution after the data processing.

5. Conclusions

In conclusion, 2D measurements of methyl radicals (CH₃) in CH₄/air flames at atmospheric pressure have been achieved using coherent microwave Rayleigh scattering from Resonance Enhanced Multi-Photon Ionization, Radar REMPI. Relative direct measurements of the methyl radicals were conducted by Radar REMPI via the two-photon resonance of the intermediate state
and subsequent one-photon ionization. Because of the proximity of the argon resonance state of $2s^22p^54f [7/2, J=4]$ (4+1 REMPI by 332.5nm) with the CH$_3$ state (2+1 REMPI by 333.6nm), in situ calibration with argon was performed to quantify the absolute concentration of CH$_3$.

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7. References