

**Measurements of Methyl Radicals and Temperatures by using
Coherent Microwave Rayleigh Scattering from
Resonance Enhanced Multiphoton Ionization**

**A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville**

**Yue Wu
August 2015**

ACKNOWLEDGMENTS

During my years in University of Tennessee, I have been fortunate to find support, guidance and generous encouragement from many people. Without them, this thesis would not be possible. It is my pleasure here to express my gratitude to all those who helped me during this process.

First I would like to express my most sincere thanks to my advisor Professor Zhili Zhang. Since he gave me an offer and a studying opportunity in USA on April 2010, I have been studying and pursue my Ph.D. degree for almost five year. When I first time walked into the lab, he gave me a tour and start to teach me how to use laser and conduct experiments. He gave me lots of support and guidance including how to write a technical paper, how to give a good presentation and how to response the comments back from paper reviewers. He spent countless hours with me sharing his deep insights and bold ideas, and discussing various aspects of physical modeling and experimental results. His deep understanding of physics, contagious enthusiasm and excellent personality set up an ideal figure for me.

Second I want to thank Dr. Rao V. Arimilli. He did not only teach and share the deep understandings and insights on fluid mechanics in the class, but also gave me great encourage on academic research and daily live.

I also want to thanks Mr. Dennis Higdon. He gave me many supports on solving the engineering issues. Some of them seem not big problems. However, without his help and advice, my experiment schedule could not go smoothly.

Finally I want to thank my mother Yinfen Su. She gives me my life, endless support, and boundless love.

ABSTRACT

This thesis includes two main parts: (I) The CH_3 [methyl radical] detection in methane/air flames and (II) the rotational temperature measurement of O_2 [molecular oxygen] in a variety of environments by using coherent microwave Rayleigh scattering from resonance enhanced multiphoton ionization (Radar REMPI).

In first the part, from Chapter I to Chapter III, the methyl radical detection and quantitative measurements have been conducted in hydrocarbon flame with one-dimensional and two-dimensional spatial-resolved concentration distribution. Due to the proximity of the argon resonance state (4+1 REMPI by 332.5 nm) with the CH_3 state (2+1 REMPI by 333.6 nm), *in situ* calibration with argon was performed to quantify the absolute concentration of CH_3 . The numerical simulations performed using the detailed kinetic mechanism of GRI-3.0 were also provided in the comparison between experimental results and numerical calculations. The details of experimental results and discussions have been reported in Chapter I, II, and III.

In the second part, the O_2 rotational temperature has been measured using Radar REMPI. The Rydberg state $\text{C}^3\Pi[\text{C}3\Pi]$ has been selected as the intermediate state of O_2 in the 2+1 REMPI process, the rotational-resolved spectra from two-photon $\text{C}^3\Pi \leftarrow \leftarrow \text{X}^3\Sigma[\text{X}3\Sigma]$ transition have been obtained in a variety of conditions from room temperature (294K) to flame temperature (1658 K). The temperature extraction based on the Boltzmann plots has been used in Chapter IV~VI. In Chapter VII, measurements of rotational temperatures of molecular oxygen have been demonstrated based on the empirical analyses of the O_2 spectra without the requirement of highly resolved rotational features using (1) linewidth fitting, (2) linear fitting, and (3) area fitting methods. In the last chapter, the O_2 REMPI spectral model has been built up to accomplish the simulation calculations. The temperature information has been determined based on the comparison between experimental results and REMPI spectral simulations. The O_2 REMPI spectral model has been first reported in the community as a demonstration for the rotational temperature measurement of molecular oxygen with a wide temperature measuring range.

TABLE OF CONTENTS

INTRODUCTION	1
References	7
CHAPTER I Direct Measurement of Methyl Radicals in a Methane/air Flame at Atmospheric Pressure by Radar REMPI	11
Abstract	12
Introduction	12
Experimental set-up	14
Results and discussion	15
Conclusion	17
Acknowledgments	17
References	18
Appendix	21
CHAPTER II Quantitative Radar REMPI Measurements of Methyl Radicals in Flames at Atmospheric Pressure	25
Abstract	26
Introduction	26
Experimental setup	27
Estimation of REMPI cross sections of argon and CH ₃	28
Argon	29
Methyl radical (CH ₃)	30
Quantitative determination of CH ₃ concentration in the flames	32
Conclusions	33
Acknowledgments	34
References	35
Appendix	37
CHAPTER III Two Dimensional Quantitative Measurements of Methyl Radicals in Methane/Air Flame	41
Abstract	42
Introduction	42
Experimental setup	43
Results and Discussion	44
1D and 2D Quantitative Measurements	45
Comparison of 2D CH ₃ Numerical Calculations and Experimental Measurements	46
Conclusion	48
Acknowledgements	49
References	50
Appendix	52
CHAPTER IV O ₂ Rotational Temperature Measurements by Coherent Microwave Scattering from REMPI	57
Abstract	58
Introduction	58

Structure of molecular oxygen.....	59
Experimental results and discussions	61
Conclusions.....	63
Acknowledgments	63
References.....	64
Appendix	65
CHAPTER V Flame Temperature Measurements by Radar Resonance-Enhanced Multiphoton Ionization of Molecular Oxygen	68
Abstract.....	69
Introduction	69
Molecular oxygen REMPI structure	70
Experimental setup.....	73
Results and Discussion	74
Conclusions.....	75
Acknowledgments	75
References.....	76
Appendix	78
CHAPTER VI O ₂ Rotational Temperature Measurements in an Atmospheric Air Microdischarge by Radar Resonance-Enhanced Multiphoton Ionization	82
Abstract.....	83
Introduction	83
Molecular oxygen structure and REMPI scheme.....	85
Experimental setup.....	87
Results and Discussion	88
Conclusions.....	89
Acknowledgements	89
References.....	90
Appendix	92
CHAPTER VII O ₂ Rotational Temperature Determination by Empirical Analyses of C ³ Π(v' = 2) ← X ³ Σ(v'' = 0) Transitions	99
Abstract.....	100
Introduction	100
Experimental Setup.....	102
Results and Discussions	103
Linewidth Fitting Method.....	104
Linear Fitting Method	104
Area Fitting Method	105
Conclusion	106
Acknowledgements	107
References.....	108
Appendix	110
CHAPTER VIII Rotational Temperature Measurements in O ₂ by Radar REMPI	115
Abstract.....	116

Introduction	116
Experimental setup.....	119
O ₂ Structure and REMPI Scheme	120
Experimental Results and Discussion	122
Conclusion	124
Acknowledgements	125
References.....	126
Appendix	129
CONCLUSION	136
VITA.....	137

LIST OF TABLES

Table 1. Parameters used in the calculation of the cross section of CH_3 .	40
Table 2. Adopted Constants for $C^3\Pi(v=2)$ of Molecular Oxygen	80
Table 3. Selected Rotational Lines of S_{21} for Low Temperature Measurements.	80
Table 4. Selected Rotational Lines for Elevated Temperature Measurements	80
Table 5. Referenced and Measured Temperatures in Pure Oxygen, Room Air, and H_2 / Air Flame	81
Table 6. Adopted constants for $C^3\Pi(v=2)$ of molecular oxygen	98
Table 7. Selected rotational lines for temperature measurements in the microdischarge.	98
Table 8. Percent errors of temperature calculated using the linewidth fitting method in O_2 and ambient air	114
Table 9. Percent errors of temperature using linear fitting method in O_2 and ambient air	114
Table 10. Adopted constants for $\text{O}_2(C^3\Pi_g(v'=2))$	135
Table 11. The comparison between experimental temperatures and O_2 REMPI model simulation results.	135

LIST OF FIGURES

Figure 1. Plot of the temperature and CH ₃ profile from a simulated laminar, adiabatic, one-dimensional, freely-propagating methane/air flame at an equivalence ratio of 1.22 at atmospheric pressure	21
Figure 2. Schematics and pictures of the experimental setup of Radar REMPI for methyl radical measurements. M1 and M2 are highly reflective mirrors for the UV laser beam.	21
Figure 3. Microwave signal from REMPI of CH ₃ in the flame at atmospheric pressure. The laser beam was set at 333.7 nm and the power was approximately 6 mJ/pulse. The measurement was conducted at 1.45 mm above the burner surface, which corresponded to the maximum concentration of CH ₃ . The lifetime of the REMPI electrons in the flame was about 84 ns, which shows promise for measurements at lower or higher pressures.	22
Figure 4. REMPI spectrum of methyl radical (CH ₃) in a methane/air flame at atmospheric pressure. The measurement was conducted at 1.45 mm above the burner surface, which corresponded to the maximum concentration of the CH ₃	22
Figure 5. Two-dimensional spatial distribution of methyl radicals (CH ₃) across two flamelets given by UNICORN using GRI-3.0 in a methane/air flame produced by the Hencken burner at atmospheric pressure.	23
Figure 6. Spatial distribution of methyl radicals (CH ₃) in a methane/air flame produced by the Hencken burner at atmospheric pressure. (a) comparison of experimental and calculated CH ₃ concentration profiles with each simulation number corresponding to different locations of the 2.4 mm averaging across the two flamelets, (b) comparison of experimental and calculated CH ₃ concentration profiles with the uncertainty of ± 0.4 mm for the laser focal length.....	24
Figure 7. Experimental setup for the CH ₃ measurements in the Hencken burner by Radar REMPI. SM step motor, Mx mixer, SI splitter, CI circulator, Pa Preamplifier, M1 and M2 are mirrors	37
Figure 8. REMPI spectra of free flowing argon (Ar) through the burner and methyl radical [20] 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 $5.7 \times 10^{15} / \text{cm}^3$	37
Figure 9. Original microwave signals obtained by scanning the laser focus above the burner surface at various conditions.	38
Figure 10. Quantitative spatial distribution of methyl radicals (CH ₃) in a CH ₄ /air (1.15:10.2slpm) flame produced by the Hencken burner at atmospheric pressure. (a) Chemiluminescence image, (b) UNICORN result and (c) comparison of experimental and computational results. The red box in (a) indicates the position of the measurement. The burner surface is marked with a white line and the wrinkles in the flame are shown. The computational	

CH ₃ profile by UNICORN has been moved downstream of 2.0 mm to match the experimental results.....	38
Figure 11. Quantitative comparison of methyl radicals (CH ₃) in a H ₂ diluted CH ₄ /air flame (0.22:1.1:11 slpm). The computational CH ₃ profile by UNICORN has been moved downstream of 2.0 mm to match the experimental results.....	39
Figure 12. (Color online) The experimental setup for 2D CH ₃ measurements using Radar REMPI. MDS is microwave detection system with the schematic diagram shown in the subplot; M1 and M2 are high-reflective mirrors; SM1 and SM2 are stepper motors.....	52
Figure 13. (Color online) A chemiluminescence image of the Hencken-burner flame with the equivalence ratio of 1.07 (CH ₄ :air = 1.15:10.20) at atmospheric pressure. Flamelets are generated and shown in the image..	52
Figure 14. (Color online) A single scanning result of the 2D CH ₃ concentration distribution.	53
Figure 15. (Color online) The processed 2D CH ₃ distribution with lateral-interpolation operation compared to the original averaged results.....	53
Figure 16. (Color online) The relative spatial distribution of CH ₃ and the instrument function of the microwave detection system. The instrument function was used for calibration of the microwave detection system.....	54
Figure 17. (Color online) The calibrated CH ₃ distribution in the Hencken-burner flame.....	54
Figure 18. (Color online) The simulation results of the 2D CH ₃ concentration distribution at the center of one flamelet. Unit: molecules·cm ⁻³	55
Figure 19. (Color online) The laser-intensity distribution along the axis of propagating light (red line). 2+1 REMPI efficiency distribution (integration results of cubic laser intensity and its cross section) (black line).	55
Figure 20. (Color online) The simulated 3D CH ₃ concentration distribution within a single flamelet.	56
Figure 21. (Color online) The numerical calculation of CH ₃ concentration distribution with line-integral effect (left) compared to experimental results (right). Unit: molecules·cm ⁻³	56
Figure 22. Experimental setup for coherent microwave scattering from the REMPI of molecular oxygen and room air at different temperatures. M ₁ is a partially reflective mirror.....	65
Figure 23. Typical normalized microwave scattering of the REMPI in the pure oxygen. (a) at room temperature and 60 Torr, (b) at 250 °C, 500 °C and 600 Torr. Laser wavelength is fixed at 287.5 nm and power is ~3.0 mJ/pulse...	65
Figure 24. Comparison of experimental REMPI spectra of air (blue) and pure oxygen (red) at room temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).....	66
Figure 25. Comparisons of experimental REMPI spectra of the pure oxygen and air at different temperatures. (a) pure oxygen, (b) room air.	66

Figure 26. Boltzmann plots for oxygen temperature determination by rotational lines of S5–S25. (a) in pure oxygen and (b) in room air. The temperatures in parentheses are the furnace temperature values.....	67
Figure 27. (Color online) Experimental setup for coherent microwave scattering from the REMPI of molecular oxygen, in flames.	78
Figure 28. (Color online) (a) REMPI spectrum of molecular oxygen in room air and (b) temperature determination by the Boltzmann plot.	78
Figure 29. (Color online) REMPI spectrum of room air (green) compared to H ₂ / air flame mixtures (blue2 : 14 and red3 : 14) with temperature determination by Boltzmann plot fit.	79
Figure 30. (Color online) Boltzmann plots, where T is the adiabatic flame temperature in the Hencken burner and in parentheses is the oxygen rotational temperature in the flames determine by the fit.	79
Figure 31. Spectra of molecular oxygen in atmospheric air (300 K) and air microdischarge (1200 K).....	92
Figure 32. Experimental setup, the microdischarge was generated by two pin electrodes, microwave detection system (MDS) was used to collect the REMPI signal in the microdischarge.	92
Figure 33. The first eight sequential photographs show the different scanning positions between the two electrodes without the microdischarge; the ninth and tenth photographs show the microdischarge (glow discharge) with and without camera light, respectively.	93
Figure 34. Spectrum of molecular oxygen in an atmospheric microdischarge. ...	93
Figure 35(a)-(d). Boltzmann plots at different positions in the atmospheric microdischarges.....	94
Figure 36. The temperature distribution in the microdischarge was determined by eight points between anode and cathode at equal intervals of 0.10 mm.	97
Figure 37. (Color online) The experimental setup for molecular oxygen temperature measurements within (1) O ₂ and ambient air in quartz cell, respectively; and (2) CH ₄ /air and H ₂ /air flames generated by the Hencken burner, respectively.	110
Figure 38. (Color online) The schematic diagram of the microwave homodyne transceiver detection system.	110
Figure 39. (Color online) The O ₂ 2+1 REMPI spectra obtained in O ₂ at 773 K and 1 atm. The black line is the original experimental spectrum and the red line is smoothed by moving-averaging 500 points from the original data.	111
Figure 40. O ₂ rotational temperature determination by empirical equations for O ₂ and ambient air, respectively, with temperature range varying from 294 K ~ 773 K.	111
Figure 41. (Color online) O ₂ rotational temperature empirical equation obtained for O ₂ and ambient air, respectively, using spectral slope linear fitting method. The range of temperature is 294 K ~ 773 K.	112
Figure 42. (Color online) Selected O ₂ rotational spectra used in the area fitting method.....	112

Figure 43. The empirical equation obtained with a wider temperature range (~300 K to ~1700 K) from the area fitting method within O ₂ , ambient air, H ₂ /air and CH ₄ /air flames.....	113
Figure 44. The experimental setup for temperature measurements of target gas species (i.e. pure O ₂ , air-like gas and ambient air) in a quartz cell heating by a pair of cylindrical furnace.	129
Figure 45. The potential energy of molecular oxygen for each state including (1) the ground state O ₂ (X ³ Σ _g ⁻), (2) the intermediate Rydberg state O ₂ (C ³ Π _g), and (3) the O ₂ ⁺ (X ² Π _g) state above the ionization level (12.07 eV). The 2+1 REMPI process is schematically expressed in the plot.....	130
Figure 46. The rotational spectra of the (3sσ)C ³ Π _g (v' = 2) ←← X ³ Σ _g ⁻ (v'' = 0) the transition. The upper spectrum was obtained in a supersonic beam with rotational temperature ~5K. The lower spectrum was simulation results based on the O ₂ RMEPI model.....	131
Figure 47. The O ₂ REMPI spectra at room temperature (294 K). Four different conditions were explored in order to confirm that there is no effect on the pressure and other gas species.....	131
Figure 48(a)-(h). The spectral comparison between experimental results and simulation calculations.....	132

INTRODUCTION

Combustion is commonly known as the rapid oxidation generating heat, or both light and heat. It is essential for existence and evolution of human beings in this planet including the heat and electricity usage in people's daily life, transportation system, industrial processes and waste disposal. Also combustion gives rise to the downside issues on the environment pollution, global warming effect and *et al.* As one of the most complicated phenomena of the world, combustion has been extensively studied by scientist and engineers with strong practical motivations and intellectual stimulations in that it integrates thermochemistry, molecular transport of mass and heat, chemical kinetics and fluid mechanics. The rapid oxidation of combustion emphasizes the intrinsic importance of chemical reactions to combustion process transforming energy stored in chemical bonds to heat formation, i.e. a given chemical reaction is the change in energy or heat constant associated with the reaction at some specific temperature. Hence the gaseous species and temperature associated to the chemical reactions are playing the key roles in the chemical thermodynamics. It is desirable to be able to conveniently determine the flame temperature and concentration of chemical species of any fuel with oxidizer at any equivalence ratio[1, 2].

With the introduction and rapid development on laser system with its increasing availability, power energy and higher reliability, laser spectroscopy is now playing an expanding role in the diagnostic probing of combustion processes. In general, such methods are important for the combustion researcher because they offer the strong capability for remote, non-intrusive, spatially and temporally precise measurements of temperature and concentration profiles for a variety of species in many flames of practical interest. Laser techniques offer a number of advantages over the physical probing methods which have been traditionally employed to investigate and characterize combustion phenomena.

Obviously, the combustion processes and fundamental flame behaviors can be easily perturbed and altered thermally or catalytically due to the intrusion of the physical probes which can act as the flame holder locally changing the flame structure. Meanwhile the physical probing methods are also generally limited in both the spatial resolution and the temporal response which actually are not in situ measurements and need to be "corrected." A thermocouple, for example, measures its own temperature not the gas temperature. The radiation, convection and conduction corrections have to be made depending on the special environment of the measurement. Gas sampling probes generally measure chemical composition far removed from the sampling location. Great care must be taken during the design and experiments to avoid chemical reactions at the sampling orifice and downstream to the detection equipment. On the other side, laser optical techniques are remote and non-intrusive without disturbing the flame structure and combustion processes. Such techniques are

performed in situ measurements at local position with high spatial and temporal resolution. The temperature and species concentrations are directly measured without the requirement for elaborate and often uncertain “corrections.”

Almost all the laser diagnostic techniques can be categorized into four regions including (1) elastic scattering processes (i.e., Rayleigh and Mie), (2) inelastic scattering processes (i.e., Spontaneous Raman scattering and Laser-induced fluorescence), (3) absorption processes and (4) nonlinear optical processes (i.e., Coherent anti-Stokes Raman scattering and degenerate four-wave mixing). In the recent decades, the Coherent anti-Stokes Raman scattering (CARS) spectroscopy, as a single-shot, single-spot tool, has been widely used for measuring the temperature and concentration of major species in reaction flows [2], counter-flow flames[3-5], practical conditions such as coal furnaces[2, 6-9] , propulsion systems [10-12] and internal combustion engines [13-16]. On the other hand, the Laser-induced fluorescence (LIF) and Planar Laser-induced fluorescence (PLIF) are playing their roles in the detection of selective species (i.e., OH, CO), temperature measurements, and flow imaging and visualization measurements. The rest of the laser diagnostics will not be introduced here, in fact, all the most widely used techniques have strengths and weaknesses.

The temperature measurements using N_2 CARS in practical combustors have the advantage that N_2 is present almost everywhere at high concentrations [17]. Compared to the N_2 CARS temperature measurement, a lesser extent applications of the technique has been used for the simultaneous measurement of major species including O_2 - N_2 [18, 19], CO_2 - N_2 [17, 20, 21], H_2 - N_2 [22], CH_4 - N_2 [23], O_2 - H_2 - N_2 [24], CO_2 - O_2 - N_2 [25]. Obviously such technique with great advantages must have strong supports from well-calibrated spectroscopic models and complicated experimental setups with more than one laser system. While applying the N_2 CARS to the temperature and concentration measurements in practical testing environments is always challenging, three laser beams pump, Stokes and probe must have excellent alignment with great effects. Meanwhile the following issues must also be considered and well solved: (1) interference from high luminous environments, (2) steering of the laser beams due to the temperature and density gradients, and (3) absorption and scattering of the CARS signal by gas species and high pressures. Obviously, CARS shows the strong capability in the temperature and concentration measurements as a single-shot laser diagnostic tool. However, compared to the concentration measurement of stable major species, such technique has a lesser extent on the direct measurement of intermediate species which play the important roles in the combustion chemistry especially at the initial stage of reaction involving chain-branching and propagation processes.

Laser-induced fluorescence is another spectroscopic diagnostic tool which has been widely used in the minor species detection and temperature measurements. Commonly, the target species with large cross section are excited by a laser from ground state, the fluorescence photons then emit through

de-excite process after a few nanoseconds to microseconds. As the fluorescence signal is usually isotropic, the two-dimensional/three-dimensional imaging technique can be performed by PLIF. Combined with particle image velocimetry (PIV), this allows for the simultaneous measurement of a fluid velocity field and species concentration. However, as a sensitive diagnostic tool, LIF/PLIF suffers from collisional quenching at the high pressures found in flames, and is often masked by background or other species (i.e., hydrocarbons) in high luminous flame systems. The temperature measurements typically required two laser sources. Such technique is highly dependent on the selected species with large cross section such as OH and CO. LIF and PLIF techniques are limited on the detection of species with weak and no fluorescence effect (i.e., methyl radical, CH₃).

Resonance-enhanced multiphoton ionization (REMPI) technique has been widely used in the detection of atoms and small molecules. Typically, the nonlinear optical process with the resonance enhanced effect is approached by a resonant single or multiple photon absorption to an electrically excited intermediate state. The weakly ionized plasma with electron and ion pairs is afterwards generated by the absorption of another single or multi photon. The REMPI process provides spectroscopic information with detailed structures of atoms or molecules. For example rotational structure of molecular oxygen is easily detected by such technique. Since 1980s the conventional REMPI technique has been widely used in the species detection in a variety of environments including CH₃ [26-28], H[29-31], NO[32-34], PO[35], O[31, 36], the Rydberg states of 1,3-Trans-Butadiene[37, 38], CH[39, 40], CO[41, 42], C₂O[41], HCO[43, 44], C[40], and O₂[40]. It has been successfully proved to detect small intermediate species in flame environments with good spatial resolution [27-31, 36, 40, 41] and quantitative results[34]. Generally, a tunable laser is focused by a focal lens and the target species are ionized at the focal region. The physical probing techniques have been developed starting with the nickel wires to the platinum ionization probe and later widely usage of the time-of-flight mass spectrometer (TOF-MS). Obviously, conventional REMPI has to use physical probing methods to detect species in the experiments which the disadvantages have been already explained. The combustion processes are easily disturbed and the flame structures are markedly changed with the intrusive physical probes. Hence, the coherent microwave Rayleigh scattering from resonance enhanced multiphoton ionization has been developed in recent years [45].

Coherent microwave Rayleigh scattering (Radar) from resonance-enhanced multiphoton ionization (REMPI) has recently been demonstrated to have the capability to achieve high spatial and temporal resolution measurements, which allow highly sensitive, nonintrusive, and spatially resolved diagnostics, and accurate determinations of concentration profiles without the use of physical probes or electrodes. Radar REMPI has been applied to the optical detection of argon [45], xenon, nitric oxide [46], carbon monoxide [47], oxygen atom [48], methyl radicals (CH₃) [49], singlet oxygen O₂(a¹Δ_g) [50], and

1,4-diazobicyclooctane (DABCO) [51] in the gas cell, open air, weakly ionized plasma, and atmospheric pressure flames.

In this thesis, the detection of methyl radicals in flames and the rotational temperature measurements in a variety of environments have been studied from chapter I to chapter VIII. The whole thesis is mainly including such two parts. In the first three chapters, the methyl radical detection has been introduced in details, and in the rest chapters (from chapter IV to chapter VIII) the temperature measurements associated with the rotational structures of molecular oxygen have been conducted in a variety of environments including pure O₂, air-like gas, ambient air, microdischarges and flames. Several strategies have been introduced to extract the rotational temperature information from the spectroscopic data based on the thermal distribution and Boltzmann effect.

In the chapter I, the methyl radicals (CH₃) in methane/air flame was successfully detected by using coherent microwave Rayleigh scattering from resonance enhanced multiphoton ionization. A tunable dye laser was used to selectively induce the (2+1) REMPI ionization process of methyl radicals in a near adiabatic and premixed laminar methane/air flame that was generated by a typical Hencken burner. The REMPI spectrum of the CH₃ radical was obtained and a one-dimensional (1D) spatial distribution of the radicals limited by focused laser beam geometry was determined. To the author's knowledge, these experiments represent the first directly-measured spatial-resolved CH₃ in a flame at atmospheric pressure.

In the chapter II, the quantitative measurements of methyl radicals were demonstrated in methane/air flame at atmospheric pressure. Due to the proximity of the argon resonance state $2s^22p^54f$ [$7/2, J=4$] (4+1 REMPI process at 332.5 nm) with the CH₃ state of $3p^2A_2''0_0$ (2+1 REMPI process at 333.6 nm), in situ calibration with argon was performed to quantify the absolute concentration of methyl radicals. The REMPI cross sections of CH₃ and argon were calculated based on time-dependent quantum perturbation theory. The measured CH₃ concentration in CH₄/air flames was in good agreement with numerical simulations performed using detailed chemical kinetics.

Based on the experience and accomplishment in chapter I and II, the two dimensional quantitative measurements of methyl radicals in methane/air flame was conducted and the 2D spatial results were reported in the chapter III. Since unique flamelets were generated by the Hencken burner, Radar REMPI was performed to investigate such structure of the flamelet that was close to the burner surface. The line-integral effect was taken account during the comparison between experimental results and numerical calculations based on the detailed chemical kinetics with a moderate uncertainty.

In these three chapters, Radar REMPI shows its capability in the measurement of the intermediate species – methyl radical (CH₃). The 1D and 2D distribution of methyl radicals in the Hencken flame have been obtained with high-spatial resolution. With the help of argon, the simultaneous calibration can be conducted directly in the flame and the concentration of CH₃ was obtained as

a demonstration for the quantitative measurement of intermediate species in flame environment by using Radar REMPI. The second part of this thesis mainly introduced the demonstration of rotational temperature measurements of molecules in a variety of environments from chapter IV to VIII.

In the chapter IV, the non-intrusive local rotational temperature measurements of molecular oxygen have been reported. Radar REMPI technique was used to obtain the spectra of molecular oxygen ($C^3\Pi(v'=2) \leftarrow X^3\Sigma(v''=0)$) in air and pure oxygen at different temperatures with subsequent analysis of the rotational state distribution. Rotational temperatures have been determined from the Boltzmann plots of a single S transition branch in a variety of experiments. The overall measurements have an accuracy of $\sim 60^\circ\text{C}$ in the pure oxygen and $\sim 50^\circ\text{C}$ in the room air, with experiments conducted up to 500°C . After the first demonstration of rotational temperature measurement in pure oxygen and air, the flame temperature measurements by Radar REMPI have also been conducted in the combustion environment. The details are given in the chapter V. Rotationally resolved 2+1 REMPI spectra of the molecular oxygen $C^3\Pi(v'=2) \leftarrow X^3\Sigma(v''=0)$ transition at different temperatures were obtained experimentally by radar REMPI. The rotational temperatures have been determined from the resulting Boltzmann plots. The measurements in general had an accuracy of $\pm 60\text{ K}$ in the hydrogen/air flames at different equivalence ratios. Discussions about the decreased accuracy for the temperature measurement at elevated temperatures have been presented in this chapter. In the chapter VI, the non-intrusive spatially resolved rotational temperature measurements in an atmospheric air microdischarge have been presented. The open air DC microdischarge source operated in a stable “normal-glow” mode and pin-to-pin electrodes spaced 1.3 mm apart. Coherent microwave Rayleigh scattering was used to collect the two-photon rotational spectra of O_2 at $C^3\Pi(v'=2) \leftarrow X^3\Sigma(v''=0)$ transitions. The Boltzmann plots from analyses of the O_2 rotational lines determined local rotational temperatures at various axial locations between the electrodes. The molecular oxygen rotational temperature varied from 1150 K to 1350 K within the discharge area. The measurements had an accuracy of around $\pm 50\text{ K}$.

In the laser three chapters, the Boltzmann plots have been applied in the temperature measurements in a variety of environments including pure oxygen, ambient air, H_2/air flame and microdischarges. The two-photon transition branches have been selectively chosen and used in the Boltzmann plots. In fact, experience and great effort have been required on such procedure to select right branches to extract the temperature information from the rotational structure of O_2 spectrum. Hence, in the chapter VII, measurements of rotational temperatures of molecular oxygen have been demonstrated based on the empirical analyses of the O_2 spectra without the requirement of highly resolved rotational features. Three methods, including (1) linewidth fitting, (2) linear fitting, and (3) area fitting have been investigated for temperature measurements within pure oxygen, ambient air, and H_2/air and CH_4/air flame environments. The first

two methods were applied in a moderately low temperature environment with measurement uncertainties less than 11% and 26%, respectively. The area fitting method covered a wider temperature range, from room temperature (~ 300 K) to flame temperature (~ 1700 K), with minimal dependence on the fine structures of the O_2 spectra. Less elaborate than Boltzmann plot analyses of ultrafine rotational lines from congested upper rotational energy levels in $O_2(C^3\Pi(v'=2))$, these empirical analyses are predictably sensitive to the thermal distribution of molecular oxygen, and have been successfully demonstrated as simple and quick methods for remote gas-phase temperature measurement.

The Boltzmann plot analyses and the empirical analyses of the O_2 spectra have been introduced and applied in the O_2 rotational temperature measurements in the chapter IV to VII. One of them has critical requirements on the experience for the transition branch selection and the other one is based on the overall shape of the O_2 spectra with empirical analyses. In the last chapter, The O_2 REMPI spectral model has been built up to simulate the experimental data which is dependent on the temperature. The model has been calibrated at an ideal temperature condition (~ 5 K) and then accomplished the temperature measurements with the overall error percentage less than $\pm 10\%$. The O_2 REMPI spectral model has been first reported in the community as a demonstration for the rotational temperature measurement with a wide temperature testing range. Further fine tunes of the model will be accomplished based on more experimental data in both low temperature (<300 K) and high temperature ranges (>1300 K).

References

1. Turns, S. R., *An introduction to combustion : concepts and applications*, The McGraw-Hill Companies, Inc., 2000.
2. Eckbreth, A. C., *Laser diagnostics for combustion temperature and species*. Vol. 3. CRC Press, 1996.
3. Magre, P., et al., "Temperature and Concentration Measurements by Cars in Counterflow Laminar Diffusion Flames." *Experiments in Fluids*, Vol. 18, No. 5, 1995, pp. 376-382.
4. Brackmann, C., et al., "Quantitative measurements of species and temperature in a DME-air counterflow diffusion flame using laser diagnostic methods." *Combustion Science and Technology*, Vol. 178, No. 6, 2006, pp. 1165-1184.
5. Diessel, E., et al., "Cars Measurements and Numerical-Simulation Results for Methane Air Counterflow Flames." *Berichte Der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics*, Vol. 96, No. 4, 1992, pp. 579-585.
6. Eckbreth, A. C., "Cars Thermometry in Practical Combustors." *Combustion and Flame*, Vol. 39, No. 2, 1980, pp. 133-147.
7. Greenhalgh, D. A., Porter, F. M., and England, W. A., "The Application of Coherent Anti-Stokes Raman-Scattering to Turbulent Combustion Thermometry." *Combustion and Flame*, Vol. 49, No. 1-3, 1983, pp. 171-181.
8. Alden, M. and Wallin, S., "Cars Experiments in a Full-Scale (10 X 10 M) Industrial Coal Furnace." *Applied Optics*, Vol. 24, No. 21, 1985, pp. 3434-3437.
9. Braeuer, A., et al., "Investigation of the combustion process in an auxiliary heating system using dual-pump CARS." *Journal of Raman Spectroscopy*, Vol. 37, No. 6, 2006, pp. 633-640.
10. Eckbreth, A. C., et al., "Cars Temperature and Species Measurements in Augmented Jet Engine Exhausts." *Applied Optics*, Vol. 23, No. 9, 1984, pp. 1328-1339.
11. Eckbreth, A. C., Anderson, T. J., and Dobbs, G. M., "Multi-Color Cars for Hydrogen-Fueled Scramjet Applications." *Applied Physics B-Photophysics and Laser Chemistry*, Vol. 45, No. 4, 1988, pp. 215-223.
12. Klimenko, D. N., et al., "CARS temperature mapping in a cryogenic LOX-H₂ rocket combustion chamber under supercritical conditions." *Journal of Raman Spectroscopy*, Vol. 33, No. 11-12, 2002, pp. 900-905.
13. Bengtsson, P.-E., et al., "Dual-broadband rotational cars measurements in an IC engine." *Symposium (International) on Combustion*, Vol. 25, No. 1, 1994, pp. 1735-1742.
14. Lebel, M. and Cottureau, M. J., "Study of the Effect of the Residual Gas Fraction on Combustion in a S.I. Engine Using Simultaneous CARS

- Measurements of Temperature and CO₂ Concentration." SAE Technical Paper 922388, 1992.
15. Bood, J., et al., "Knock in Spark-Ignition Engines: End-Gas Temperature Measurements Using Rotational CARS and Detailed Kinetic Calculations of the Autoignition Process." SAE Technical Paper 971669, 1997.
 16. Ball, D., et al., "Coherent Anti-Stokes-Raman Spectroscopy Temperature-Measurements in an Internal-Combustion Engine." Optical Engineering, Vol. 33, No. 9, 1994, pp. 2870-2874.
 17. Roy, S., et al., "Temperature and CO₂ concentration measurements in the exhaust stream of a liquid-fueled combustor using dual-pump coherent anti-Stokes Raman scattering (CARS) spectroscopy." Combustion and Flame, Vol. 138, No. 3, 2004, pp. 273-284.
 18. Lucht, R. P., "3-Laser Coherent Anti-Stokes Raman-Scattering Measurements of 2 Species." Optics Letters, Vol. 12, No. 2, 1987, pp. 78-80.
 19. Hancock, R. D., et al., "Dual-pump coherent anti-Stokes Raman scattering measurements of nitrogen and oxygen in a laminar jet diffusion flame." Applied Optics, Vol. 36, No. 15, 1997, pp. 3217-3226.
 20. Bruggemann, D., et al., "Cars Spectroscopy for Temperature and Concentration Measurements in a Spark-Ignition Engine." Combusting Flow Diagnostics, Vol. 207, 1992, pp. 495-511.
 21. Lucht, R. P., et al., "Dual-pump coherent anti-Stokes Raman scattering temperature and CO(2) concentration measurements." Aiaa Journal, Vol. 41, No. 4, 2003, pp. 679-686.
 22. Schauer, F. R., Ph.D. thesis, University of Illinois at Urbana-Champaign, Urbana, IL, 1998.
 23. Green, S. M., et al., "Annular phase-matched dual-pump coherent anti-Stokes Raman spectroscopy system for the simultaneous detection of nitrogen and methane." Applied Optics, Vol. 37, No. 9, 1998, pp. 1690-1701.
 24. O'Byrne, S., Danehy, P. M., and Cutler, A. D., "Dual-pump CARS thermometry and species concentration measurements in a supersonic combustor." AIAA Paper, Vol. 710, 2004, pp. 5-8.
 25. Meyer, T. R., et al., "Dual-pump dual-broadband CARS for exhaust-gas temperature and CO₂-O₂-N₂ mole-fraction measurements in model gas-turbine combustors." Combustion and Flame, Vol. 142, No. 1-2, 2005, pp. 52-61.
 26. Diggiuseppe, T. G., Hudgens, J. W., and Lin, M. C., "Multi-Photon Ionization of CH₃ Radicals in the Gas-Phase." Journal of Physical Chemistry, Vol. 86, No. 1, 1982, pp. 36-41.
 27. Smyth, K. C. and Taylor, P. H., "Detection of the Methyl Radical in a Methane Air Diffusion Flame by Multiphoton Ionization Spectroscopy." Chemical Physics Letters, Vol. 122, No. 5, 1985, pp. 518-522.

28. Meier, U. and Kohsehoinghaus, K., "Rempi Detection of CH_3 in Low-Pressure Flames." *Chemical Physics Letters*, Vol. 142, No. 6, 1987, pp. 498-502.
29. Goldsmith, J. E. M., "Resonant Multi-Photon Optogalvanic Detection of Atomic-Hydrogen in Flames." *Optics Letters*, Vol. 7, No. 9, 1982, pp. 437-439.
30. Tjossem, P. J. H. and Cool, T. A., "Detection of Atomic-Hydrogen in Flames by Resonance 4-Photon Ionization at 365 Nm." *Chemical Physics Letters*, Vol. 100, No. 6, 1983, pp. 479-483.
31. Goldsmith, J. E. M., "Flame studies of atomic hydrogen and oxygen using resonant multiphoton optogalvanic spectroscopy." *Symposium (International) on Combustion*, Vol. 20, No. 1, 1985, pp. 1331-1337.
32. Mallard, W. G., Miller, J. H., and Smyth, K. C., "Resonantly Enhanced 2-Photon Photo-Ionization of No in an Atmospheric Flame." *Journal of Chemical Physics*, Vol. 76, No. 7, 1982, pp. 3483-3492.
33. Rockney, B. H., Cool, T. A., and Grant, E. R., "Detection of Nascent No in a Methane Air Flame by Multi-Photon Ionization." *Chemical Physics Letters*, Vol. 87, No. 2, 1982, pp. 141-144.
34. Cool, T. A., "Quantitative Measurement of No Density by Resonance 3-Photon Ionization." *Applied Optics*, Vol. 23, No. 10, 1984, pp. 1559-1572.
35. Smyth, K. C. and Mallard, W. G., "2-Photon Ionization Processes of Po in a C_2H_2 Air Flame." *Journal of Chemical Physics*, Vol. 77, No. 4, 1982, pp. 1779-1787.
36. Goldsmith, J. E. M., "Resonant Multiphoton Optogalvanic Detection of Atomic Oxygen in Flames." *Journal of Chemical Physics*, Vol. 78, No. 3, 1983, pp. 1610-1611.
37. Mallard, W. G., Miller, J. H., and Smyth, K. C., "The Ns Rydberg Series of 1,3-Trans-Butadiene Observed Using Multiphoton Ionization." *Journal of Chemical Physics*, Vol. 79, No. 12, 1983, pp. 5900-5905.
38. Taylor, P. H., Mallard, W. G., and Smyth, K. C., "Multiphoton Ionization Spectra of Trans-1,3-Butadiene - Reassignment of a Rydberg Series." *Journal of Chemical Physics*, Vol. 84, No. 2, 1986, pp. 1053-1055.
39. Chen, P., Chupka, W. A., and Colson, S. D., "Multiphoton Spectroscopy and Analysis of the $\text{E}^2\text{-Pi}^- \text{X}^2\text{-Pi-R}$ Band of Ch." *Chemical Physics Letters*, Vol. 121, No. 4-5, 1985, pp. 405-407.
40. Tjossem, P. J. H. and Smyth, K. C., "Multiphoton Ionization Detection of Ch, Carbon-Atoms, and O_2 in Premixed Hydrocarbon Flames." *Chemical Physics Letters*, Vol. 144, No. 1, 1988, pp. 51-57.
41. Tjossem, P. J. H. and Cool, T. A., "Species density measurements with the rempi method; The detection of CO and C_2O in a methane/oxygen flame." *Symposium (International) on Combustion*, Vol. 20, No. 1, 1985, pp. 1321-1329.

42. Tjossem, P. J. H. and Smyth, K. C., "Multiphoton Excitation Spectroscopy of the B1sigma+ and C1sigma+ Rydberg States of Co." *Journal of Chemical Physics*, Vol. 91, No. 4, 1989, pp. 2041-2048.
43. Tjossem, P. J. H., Goodwin, P. M., and Cool, T. A., "2-Photon Resonance Remp Detection of the Formyl Radical." *Journal of Chemical Physics*, Vol. 84, No. 10, 1986, pp. 5334-5343.
44. Tjossem, P. J. H., et al., "Spectroscopy of the 3p 2ii Rydberg State of Hco by Resonance-Enhanced Multiphoton Ionization." *Journal of Chemical Physics*, Vol. 88, No. 2, 1988, pp. 617-626.
45. Zhang, Z. L., Shneider, M. N., and Miles, R. B., "Coherent microwave rayleigh scattering from resonance-enhanced multiphoton ionization in argon." *Physical Review Letters*, Vol. 98, No. 26, 2007.
46. Miles, R. B., et al., "Microwave scattering from laser ionized molecules: A new approach to nonintrusive diagnostics." *Aiaa Journal*, Vol. 45, No. 3, 2007, pp. 513-515.
47. Dogariu, A. and Miles, R. B., "Detecting localized trace species in air using radar resonance-enhanced multi-photon ionization." *Applied Optics*, Vol. 50, No. 4, 2011, pp. A68-A73.
48. Dogariu, A., et al., "High-Gain Backward Lasing in Air." *Science*, Vol. 331, No. 6016, 2011, pp. 442-445.
49. Wu, Y., et al., "Direct measurement of methyl radicals in a methane/air flame at atmospheric pressure by radar REMPI." *Optics Express*, Vol. 19, No. 24, 2011, pp. 23997-24004.
50. Wu, Y., Zhang, Z. L., and Ombrello, T. M., "Spatially resolved measurement of singlet delta oxygen by radar resonance-enhanced multiphoton ionization." *Optics Letters*, Vol. 38, No. 13, 2013, pp. 2286-2288.
51. Rudakov, F. and Zhang, Z. L., "Standoff detection of large organic molecules using Rydberg fingerprint spectroscopy and microwave Rayleigh scattering." *Optics Letters*, Vol. 37, No. 2, 2012, pp. 145-147.

CHAPTER I
DIRECT MEASUREMENT OF METHYL RADICALS IN A
METHANE/AIR FLAME AT ATMOSPHERIC PRESSURE BY
RADAR REMPI

This article, "Direct measurement of methyl radicals in a methane/air flame at atmospheric pressure by radar REMPI", was received on 22 Aug 2011; revised on 10 Oct 2011; accepted on 12 Oct 2011; published on 10 Nov 2011.

Author affiliations:

Yue Wu,¹ Andrew Bottom,¹ Zhili Zhang,^{1,*} Timothy M. Ombrello,² and Viswanath R. Katta³

¹*Mechanical, Aerospace and Biomedical Engineering, University of Tennessee of Tennessee, Knoxville TN 37996, USA*

²*Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB, Dayton OH 45433, USA*

³*Innovative Scientific Solutions Incorporated, Dayton OH 45440, USA*

*Corresponding author: zzhang24@utk.edu

Optics Express, Vol. 19, Issue 24, pp. 23997-24004 (2011)
<http://dx.doi.org/10.1364/OE.19.023997>

Abstract

We report the direct measurements of methyl radicals (CH_3) in methane/air flames at atmospheric pressure by using coherent microwave Rayleigh scattering (Radar) from Resonance Enhanced Multi-Photon Ionization (REMPI), also known as the Radar REMPI technique. A tunable dye laser was used to selectively induce the (2+1) REMPI ionization of methyl radicals (CH_3 , $3p^2A_2''0_0^0$ band) in a near adiabatic and premixed laminar methane/air flame, generated by a Hencken burner. *In situ* measurements of the REMPI electrons were made by non-intrusively using a microwave homodyne transceiver detection system. The REMPI spectrum of the CH_3 radical was obtained and a spatial distribution of the radicals limited by focused laser beam geometry, approximately 20 μm normal to the flame front and 2.4 mm parallel to the flame, was determined. The measured CH_3 was in good agreement with numerical simulations performed using the detailed kinetic mechanism of GRI-3.0. To the authors' knowledge, these experiments represent the first directly-measured spatially-resolved CH_3 in a flame at atmospheric pressure.

Introduction

Radical species are key reaction components in combustion, but the spatially-resolved quantitative measurements of many radicals are still unsatisfactory, especially at elevated pressure. One of the most prevailing radicals and chain carriers in hydrocarbon flames, the methyl radicals (CH_3) is involved in ignition and flame propagation reactions (via hydrogen abstraction by H atoms and

hydroxyl radicals (OH)) [1]. However, detection of CH₃ is a significant challenge. The methyl radical is characterized by a strong predissociation of its electronically excited states, preventing fluorescence detection. For this reason, direct measurements of CH₃ have mostly been conducted using absorption-based methods [2-4], conventional REMPI [5,6] and degenerate four wave mixing (DFWM) [7,8]. Absorption-based methods, either direct absorption of CH₃ or cavity ring-down spectroscopy, have the limitation of path integration, leading to limited spatial resolution. Conventional REMPI has a low signal-to-noise ratio for measurement of the CH₃ distribution in flames at atmospheric pressure [9] but a physical probe or electrodes required for the collection of electrons or ions may introduce irrelevant disturbances in the reacting flows. DFWM utilizes third order optics effects, which may have a low signal to noise ratio for applications at low pressures. Indirect measurements have been conducted by photolysis of CH₃ into the methylidyne radical (CH) and its subsequent laser induced fluorescence [10-12], which inherently complicates the detection scheme and requires care for the interpretation of the experimental data.

Coherent microwave Rayleigh scattering (Radar) from Resonance Enhanced Multi-Photon Ionization (REMPI) has been demonstrated recently to have the capability to achieve high spatial and temporal resolution measurements, which allow for sensitive nonintrusive diagnostics and accurate determinations of concentration profiles without the use of physical probes and electrodes. It has been applied for the optical detection of species such as argon [13], xenon, nitric oxide [14], carbon monoxide [15] and atomic oxygen [16] both within enclosed cells and open air. For the first time, we have demonstrated Radar REMPI to *in situ*, non-intrusively and directly measure the methyl radical in methane/air flames at atmospheric pressure. To the authors' knowledge, this represents the first directly-measured spatially-resolved CH₃ measurement in flames at atmospheric pressure.

Compared to other techniques, the Radar REMPI technique is easy to set-up, robust to perturbations, and possible from standoff detection. It uses only one tunable laser, such as a commercial dye laser or OPO laser, as the excitation source. It requires a simple lens to focus the beam and can be spatially scanned easily. Minimal optical alignment is required for the measurement and necessitates only one optical access port. It has a higher spatial resolution compared to line integrated absorption measurements. In contrast to conventional CARS or DFWM, the signal to noise ratio may even be better at lower pressure due to the slow recombination and/or attachment processes in the REMPI plasma. Furthermore, it does not require a dark environment to perform the measurements. It may also be used as a standoff approach, due to the limited radiation background in the microwave range [15].

In this paper, the REMPI spectrum of the methyl radical ($3p^2A_2''0_0^0$ band) was obtained in flames at atmospheric pressure. The spatial distribution of the radical with a resolution of approximately 20 μm was measured through the flame. Good agreement has been achieved between the experimental

measurements and numerical simulations using detailed combustion kinetics. The method has demonstrated excellent spatial resolution for measurements in flames at atmospheric pressure. It has also shown great promise for the key radical measurements at lower or higher pressures, which may significantly improve our understanding of combustion processes at practical engine or combustor conditions.

Experimental set-up

In order to provide a platform for the detection of CH_3 using the Radar REMPI technique, a near adiabatic flat flame at atmospheric pressure with optical access of the detailed structure of the flame would be ideal. An example of such a type of flame is a freely-propagating premixed flame. The structure of a freely-propagating rich methane/air flame at atmospheric pressure is shown in Figure 1. The temperature and CH_3 number density across the flame front was computed using the PREMIX code from the CHEMKIN package [17] and the chemical kinetic mechanism of GRI-3.0 [18]. While significant number densities (on the order of 10^{16} molecules/cm³) of CH_3 can be produced, it is present across a thickness of only 0.5 mm in the flame. Furthermore, in experiments, this type of flame is typically close to the burner surface with significant heat loss, such as with a porous plug flat flame burner [19], complicating the use of detailed optical measurements. Alternatively, a Hencken burner with a 1 inch by 1 inch square exit geometry (Technologies for Research, Model: RT1x1) was used to generate a laminar and near adiabatic methane/air flame with sufficient optical access. This burner has been widely used as a test bed for laser diagnostic techniques [20-26]. The Hencken burner produces a unique, nearly adiabatic flame that is lifted from the burner surface since the fuel and oxidizer streams are separated until the exit of the burner. The fuel tubes have an inner diameter (ID) of approximately 0.54 mm and an outer diameter (OD) of approximately 0.83 mm. The oxidizer honeycomb is a hexagonal pattern with cell size of approximately 0.90 mm. For current experiments, the air flow rate was fixed at 11 slpm (Standard Liters Per Minute) and the methane flow rate was fixed at 1.35 slpm, which produced a flame with an equivalence ratio of 1.22.

The experimental setup of the Radar REMPI measurements of CH_3 is shown in Figure 2. A frequency double Nd: YAG laser (Continuum Surelite SL-10) was used to pump a tunable dye laser (Continuum ND6000, DCM, [2-[2-[4-(dimethylamino)phenyl]ethenyl]-6-methyl-4H-pyran-4-ylidene]-propanedinitrile, $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}$ as the dye).. The output of the dye laser was frequency doubled by an automatic frequency doubling and tracking system (Continuum UVT). The output wavelengths were tunable from 332 to 335 nm, with output power ranging from 6 to 8 mJ/pulse. The laser output was then focused by a lens with a focal length of 50 cm to generate the REMPI plasma in the methane/air flame of a Hencken burner in open air. A lens with a long focal length (50 cm) was used to

avoid gas breakdown or avalanche ionization in the flame. From Gaussian beam geometry, the focal region was about 20 μm in diameter and 2.4 ± 0.4 mm in length. The length of the interrogation region arose from the microwave signal scattering along the laser beam upstream and downstream of the focus. The length and uncertainty was related to the laser intensity and corresponding microwave scattering signal. At 2.8 mm, the laser intensity falls to about 33% and the REMPI efficiency and microwave scattering drop to about 11%, compared to the center of the laser focus. The beam steering mirrors and focusing lens were placed on a translational stage to move the laser focus through the flame front.

A microwave homodyne transceiver detection system was used to detect the REMPI plasma. A 10 dBm tunable microwave source (HP 8350B sweep oscillator, set at ~ 10 GHz) was first split into two channels. One channel 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. It should be noted that the filter after the mixer can effectively block the scattering background from the environment. Therefore Radar REMPI measurements inside an enclosure will not suffer from surface scattering interference. 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.

Results and discussion

The time-accurate microwave scattering signal was monitored by an oscilloscope. Shown in Figure 3, the lifetime (at $1/e$ of the peak) of the REMPI electrons in the flame was about 84 ns, which shows promise for the radical measurements at lower and higher pressures. Since the lifetime of REMPI electrons becomes longer at lower pressures, the signal to noise ratio will be significantly improved. The microwave signal was also input to an automatic gated integrator data acquisition system (gate width = 10 ns), which recorded the REMPI spectrum of the methyl radicals as the laser was tuned. In order to eliminate the perturbations caused by microwave interferences or laser pulse-to-pulse fluctuations, the microwave background and laser pulses were sampled and averaged over 20 times. Subtraction of the microwave background and scaling of the laser pulses were undertaken for the final spectrum.

Figure 4 shows a typical REMPI spectrum of CH_3 in a methane/air flame at atmospheric pressure. The spectrum obtained in the flame was in agreement with previously published spectra [27–29]. The measurement was conducted at 1.45 mm above the burner surface, which corresponded to about the maximum

concentration of CH_3 in the flame. Only transition from the ground state of CH_3 to the state of $3p^2A_2''0_0^0$ was obtained in the flame by Radar REMPI. No clear vibrational structure of the transitions was observed. The wings off the peak at 333.6 nm have different values for the measurement conducted at different locations of the flame, which indicated different rotational temperatures of the CH_3 radicals in the flame.

The one-dimensional reaction zone structure in Figure 1 is not applicable to the flames produced by the Hencken burner because the separated fuel and air streams tend to establish small diffusion flamelets. Therefore, two-dimensional simulations were performed using UNICORN (UNsteady Ignition and COMbustion with ReactionNs) [30] with the detailed chemical kinetics of GRI-3.0 for a single flamelet at atmospheric pressure. Figure 5 shows the calculated two-dimensional spatial distribution of CH_3 across two flamelets. UNICORN is a time-dependent, axisymmetric mathematical model that is used to investigate two-dimensional steady and unsteady reacting flows. It has been tested with experiments designed to predict ignition, extinction, stability limits, and the dynamic and steady-state characteristics of diffusion and premixed flames burning various fuels. Here UNICORN used a detailed chemical kinetics model, GRI-3.0, for methane/air flames at atmospheric pressure. The Hencken burner using methane/air at an equivalence ratio of 1.22 at atmospheric pressure produces a flame front with many flamelets (one flamelet for each fuel tube). This is clearly evident in Figure 5 with two flamelets shown. The Radar REMPI measurement was 20 μm normal to the flame front and 2.4 mm $\pm$ 0.4 mm in length parallel to the top of the burner. Therefore the Radar REMPI measurement crossed through two flamelets (depicted by the black box in Figure 5). Depending upon where the 2.4 mm interrogation area was located across the flamelets, there could be different shaped profiles. Figure 6(a) shows the variation when moving the interrogation area across the two flamelets with each simulation number accounting for a successive translation of 0.25 mm. Simulations 2 – 5 were translated 0.25, 0.5, 0.75 and 1.0 mm from the case of the 2.4 mm length centered over the edge of the flamelets, respectively. The translation produced a significant difference on the upstream side of the CH_3 profile (closer to the burner surface) because of the bell shaped CH_3 distribution. Furthermore, all of the profiles from the simulations were moved in the streamwise direction (closer to the burner) to match the experimental profile. This movement was not unreasonable since past simulations have also predicted higher flame liftoff heights than experiments [21]. Nevertheless, the flame shape and therefore CH_3 profile should remain predominately independent of the changes in flame liftoff height in the current experiment and provide a good means of comparison. Since the REMPI interrogation area covered more than one flamelet, an average of the CH_3 concentration with 2.4 $\pm$ 0.4 mm along the flame front was sampled from the calculation results and is shown in Figure 6(b). There is good agreement between the measured and calculated normalized CH_3 profiles, including the total width and asymmetric structure of the profile. The

relatively low signal to noise ratio from the measurements is most likely due to short time gate, laser fluctuations, and flame instability.

Conclusion

In summary, for the first time, Radar REMPI was demonstrated to *in situ*, non-intrusively and directly measure the methyl radicals in methane/air flames at atmospheric pressure. The REMPI spectrum of the methyl radical ($3p^2A_2''0_0^0$ band) was obtained in the flame. Good agreement has been achieved between the experimental measurements and calculations for the spatial distribution of methyl radicals in methane/air flames.

Acknowledgments

Funding for this research at the University of Tennessee Knoxville was provided by NSF CBET-1032523.

References

1. C. K. Law, *Combustion Physics*, 1st ed. (Cambridge University Press, New York, 2006).
2. N. L. Arthur, "Methyl-radical absorption cross-section at 216.4 nm and rate constant for methyl-radical recombination," *J. Chem. Soc., Faraday Trans. 2*, **82**, 331-336 (1986).
3. J. J. Scherer, K. W. Aniolek, N. P. Cernansky, and D. J. Rakestraw, "Determination of methyl radical concentrations in a methane/air flame by infrared cavity ringdown laser absorption spectroscopy," *J. Chem. Phys.* **107**(16), 6196-6203 (1997).
4. P. Zalicki and R. N. Zare, "Cavity ring-down spectroscopy for quantitative absorption measurements," *J. Chem. Phys.* **102**(7), 2708-2717 (1995).
5. K. C. Smyth and D. R. Crosley, "Detection of Minor Species with Laser Techniques," in *Applied Combustion Diagnostics*, K. Kohse-Höinghaus and J.B. Jeffries, eds. (Taylor & Francis, New York, 2002).
6. T. A. Cool, "Quantitative measurement of NO density by resonance three-photon ionization," *Appl. Opt.* **23**(10), 1559 (1984).
7. V. Sick, M. N. Bui-Pham, and R. L. Farrow, "Detection of methyl radicals in a flat flame by degenerate four-wave mixing," *Opt. Lett.* **20**(19), 2036-2038 (1995).
8. J. Kiefer and P. Ewart, "Laser diagnostics and minor species detection in combustion using resonant four-wave mixing," *Pror. Energy Combust. Sci.* **37**(5), 525-564 (2011).
9. K. Kohse-Höinghaus, "Laser techniques for the quantitative detection of reactive intermediates in combustion systems," *Proc. Energy Combust. Sci.* **20**(3), 203-279 (1994).
10. C. Kassner, P. Heinrich, F. Stuhl, S. Couris, and S. Haritakis, "Fragments in the UV photolysis of the CH₃ and CH₃O₂ radicals," *Chem. Phys. Lett.* **208**(1-2), 27-31 (1993).
11. S. W. North, D. A. Blank, P. M. Chu, and Y. T. Lee, "Photodissociation dynamics of the methyl radical 3s Rydberg state," *J. Chem. Phys.* **102**(2), 792-798 (1995).
12. C. Kassner and F. Stuhl, "The VUV photodissociation CH₃→ CH(A²Δ) and B²Σ⁺ + H₂," *Chem. Phys. Lett.* **222**(5), 425-430 (1994).
13. Z. Zhang, M. N. Shneider, and R. B. Miles, "Coherent microwave rayleigh scattering from resonance-enhanced multiphoton ionization in argon," *Phys. Rev. Lett.* **98**(26), 265005 (2007).
14. R. B. Miles, Z. Zhang, S. H. Zaidi, and M. N. Shneider, "Microwave scattering from laser ionized molecules: A new approach to nonintrusive diagnostics," *AIAA J.* **45**(3), 513-515 (2007).
15. A. Dogariu and R. B. Miles, "Detecting localized trace species in air using radar resonance-enhanced multiphoton ionization," *Appl. Opt.* **50**(4), A68-

- A73 (2011).
16. A. Dogariu, J. B. Michael, M. O. Scully, and R. B. Miles, "High-gain backward lasing in air," *Science* **331**(6016), 442–445 (2011).
 17. R. Design, PREMIX FROM CHEMKIN, Reaction Design, 6440 Lusk Boulevard, Suite D-205, San Diego CA 92121, 2010.
 18. G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, J. W. C. Gardiner, V.V. Lissianski, and Z. Qin, "GRI-Mech 3.0" (2011), retrieved http://www.me.berkeley.edu/gri_mech/.
 19. M. A. C. Stuart, W. T. S. Huck, J. Genzer, M. Muller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, and S. Minko, "Emerging applications of stimuli-responsive polymer materials," *Nat. Mater.* **9**(2), 101–113 (2010).
 20. R. S. Barlow, R. W. Dibble, J. Y. Chen, and R. P. Lucht, "Effect of Damkohler number on superequilibrium OH concentration in turbulent nonpremixed jet flames," *Combust. Flame* **82**(3-4), 235–251 (1990).
 21. F. Takahashi, W. John Schmoll, and V. R. Katta, "Attachment mechanisms of diffusion flames," *Symposium (International) on Combustion* **27**, 675–684 (1998).
 22. J. Sakakibara and R. J. Adrian, "Whole field measurement of temperature in water using two-color laser induced fluorescence," *Exp. Fluids* **26**(1-2), 7–15 (1999).
 23. J. Guasto and K. Breuer, "Simultaneous, ensemble-averaged measurement of near-wall temperature and velocity in steady micro-flows using single quantum dot tracking," *Exp. Fluids* **45**(1), 157–166 (2008).
 24. X. Perpiñà, X. Jordà, M. Vellvehi, and J. Altet, "Hot spot analysis in integrated circuit substrates by laser mirage effect," *Appl. Phys. Lett.*, **98**, 164104 (2011).
 25. W. D. Kulatilaka, R. P. Lucht, S. F. Hanna, and V. R. Katta, "Two-color, two-photon laser-induced polarization spectroscopy (LIPS) measurements of atomic hydrogen in near-adiabatic, atmospheric pressure hydrogen/air flames," *Combust. Flame* **137**(4), 523–537 (2004).
 26. S. Roy, T. R. Meyer, M. S. Brown, V. N. Velur, R. P. Lucht, and J. R. Gord, "Triple-pump coherent anti-Stokes Raman scattering (CARS): temperature and multiple-species concentration measurements in reacting flows," *Opt. Commun.* **224**(1-3), 131–137 (2003).
 27. J. W. Hudgens, T. G. DiGiuseppe, and M. C. Lin, "Two photon resonance enhanced multiphoton ionization spectroscopy and state assignments of the methyl radical," *J. Chem. Phys.* **79**(2), 571–582 (1983).
 28. J. F. Black and I. Powis, "Rotational Structure and Predissociation Dynamics of the Methyl 4pz(V=O) Rydberg State Investigated by Resonance Enhanced Multiphoton Ionization Spectroscopy," *J. Chem. Phys.* **89**(7), 3986–3992 (1988).
 29. K. C. Smyth and P. H. Taylor, "Detection of the methyl radical in a

- methane/air diffusion flame by multiphoton ionization spectroscopy,” Chem. Phys. Lett. **122**(5), 518–522 (1985).
30. W. M. Roquemore and V. R. Katta, “Role of Flow Visualization in the Development of UNICORN,” J. Vis. **2**(3-4), 257–272 (1999).

Appendix

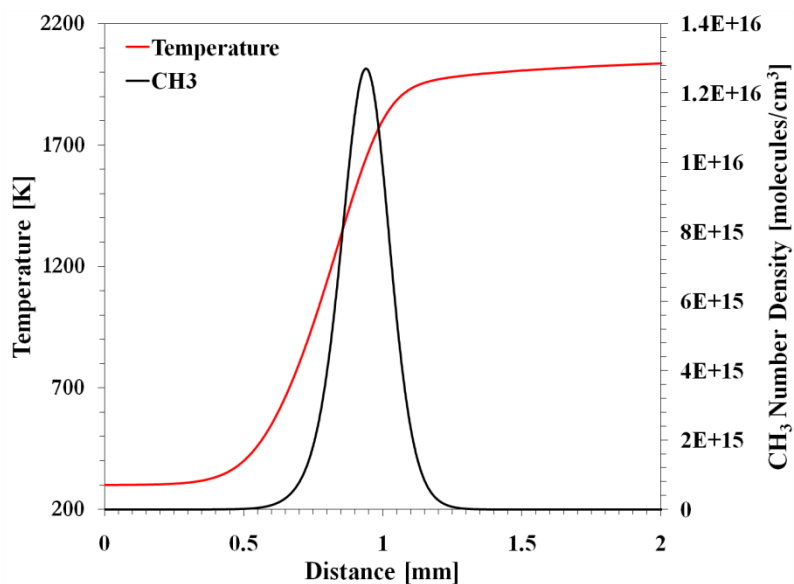


Figure 1. Plot of the temperature and CH₃ profile from a simulated laminar, adiabatic, one-dimensional, freely-propagating methane/air flame at an equivalence ratio of 1.22 at atmospheric pressure

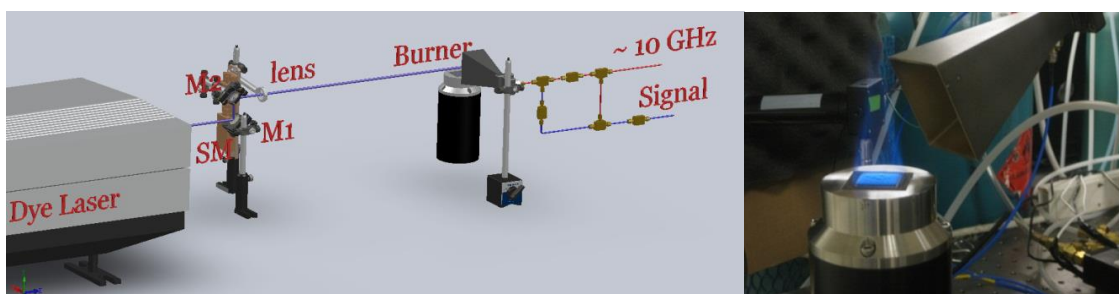


Figure 2. Schematics and pictures of the experimental setup of Radar REMPI for methyl radical measurements. M1 and M2 are highly reflective mirrors for the UV laser beam.

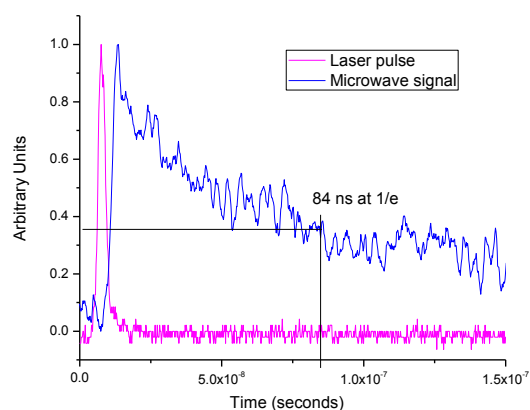


Figure 3. Microwave signal from REMPI of CH_3 in the flame at atmospheric pressure. The laser beam was set at 333.7 nm and the power was approximately 6 mJ/pulse. The measurement was conducted at 1.45 mm above the burner surface, which corresponded to the maximum concentration of CH_3 . The lifetime of the REMPI electrons in the flame was about 84 ns, which shows promise for measurements at lower or higher pressures.

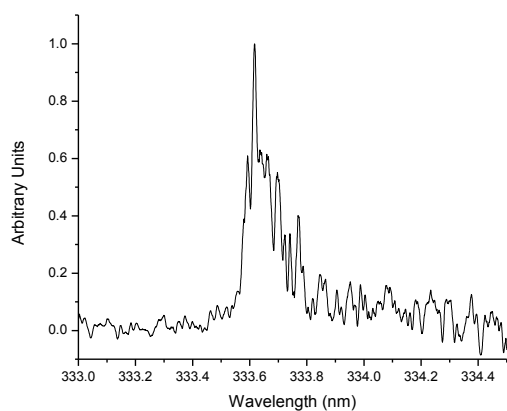


Figure 4. REMPI spectrum of methyl radical (CH_3) in a methane/air flame at atmospheric pressure. The measurement was conducted at 1.45 mm above the burner surface, which corresponded to the maximum concentration of the CH_3 .

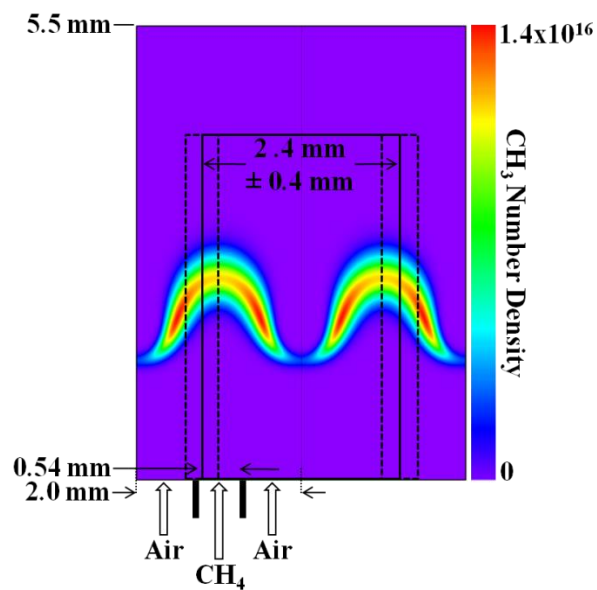


Figure 5. Two-dimensional spatial distribution of methyl radicals (CH_3) across two flamelets given by UNICORN using GRI-3.0 in a methane/air flame produced by the Hencken burner at atmospheric pressure.

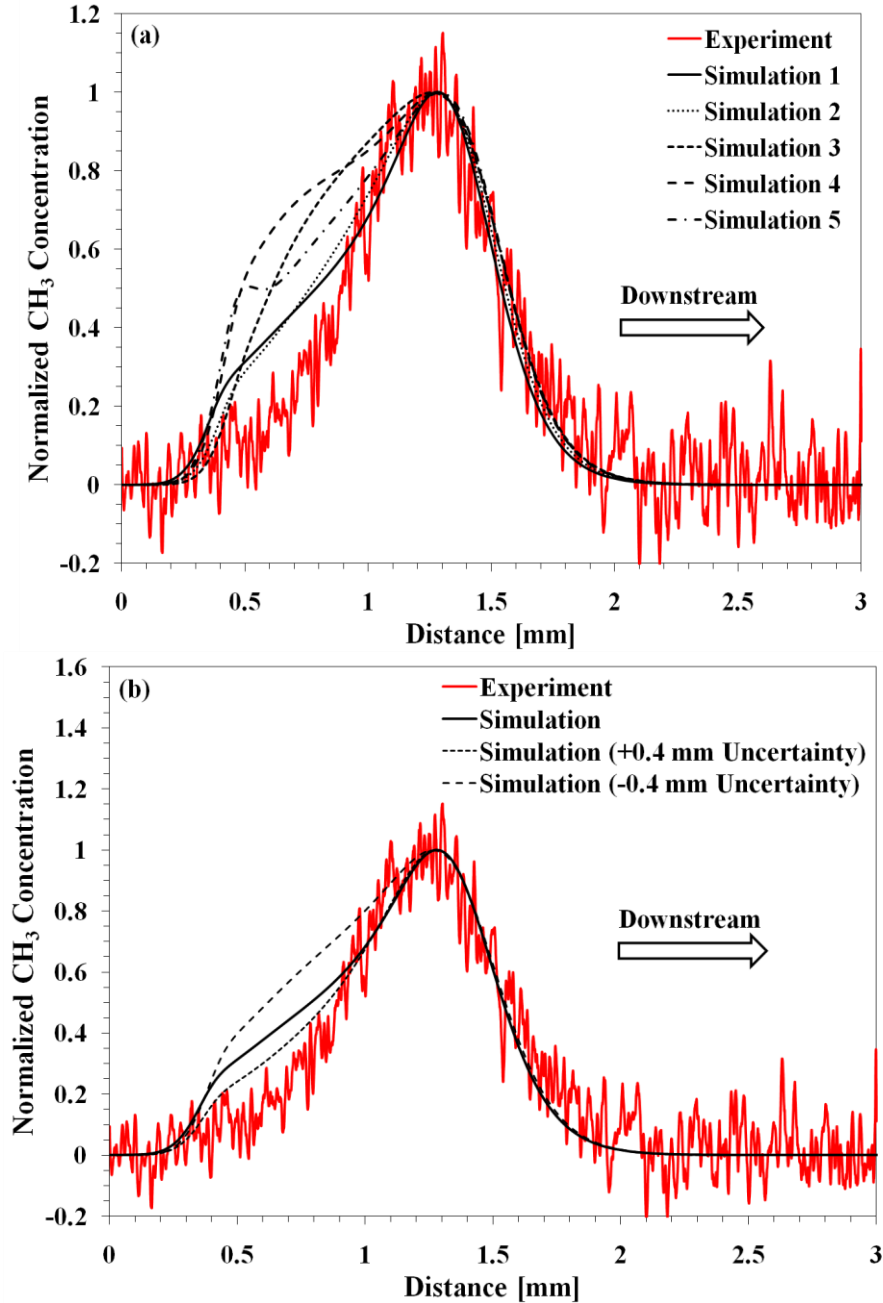


Figure 6. Spatial distribution of methyl radicals (CH_3) in a methane/air flame produced by the Hencken burner at atmospheric pressure. (a) comparison of experimental and calculated CH_3 concentration profiles with each simulation number corresponding to different locations of the 2.4 mm averaging across the two flamelets, (b) comparison of experimental and calculated CH_3 concentration profiles with the uncertainty of ± 0.4 mm for the laser focal length.

CHAPTER II
QUANTITATIVE RADAR REMPI MEASUREMENTS OF METHYL
RADICALS IN FLAMES AT ATMOSPHERIC PRESSURE

This article, “Quantitative Radar REMPI measurements of methyl radicals in flames at atmospheric pressure”, was received on 20 August 2012; accepted on 16 January 2013; published on 31 January 2013.

Author affiliations:

Yue Wu,¹ Zhili Zhang,^{1,*} Timothy M. Ombrello,² and Viswanath R. Katta³

¹*Mechanical, Aerospace and Biomedical Engineering, University of Tennessee of Tennessee, Knoxville TN 37996, USA*

²*Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB, Dayton OH 45433, USA*

³*Innovative Scientific Solutions Incorporated, Dayton OH 45440, USA*

*Corresponding author: zzhang24@utk.edu

Applied Physics B, Vol. 111, Issue 3, pp. 391-397 (2011)

DOI: 10.1007/s00340-013-5345-1

Abstract

Spatially resolved quantitative 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 $3p^2A_2''0_0^0$ state and subsequent one-photon ionization. Due to the proximity of the argon resonance state of $2s^22p^54f [7/2, J = 4]$ (4+1 REMPI by 332.5 nm) with the CH_3 state of $3p^2A_2''0_0^0$ (2+1 REMPI by 333.6 nm), *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 measured CH_3 concentration in CH_4 /air flames was in good agreement with numerical simulations performed using detailed chemical kinetics. 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 straightforwardly generalized for the quantitative measurements of other radicals and intermediate species in practical and relevant combustion environments.

Introduction

The methyl radical (CH_3) is one of the most important species in combustion [1], atmospheric chemistry [2], chemical vapor deposition [3], and ultrafast kinetics [4, 5]. In combustion, ignition and flame propagation reactions [via hydrogen

abstraction by H atoms and hydroxyl radicals (OH)] is controlled by the CH₃ radical [1]. The formation of polycyclic aromatic hydrocarbons (PAH) and soot is also highly dependent on this radical [6]. However, quantitative measurements of CH₃ are very challenging, especially at elevated pressures. The methyl radical is characterized by a strong predissociation of its electronically excited states, preventing fluorescence detection. For this reason, direct measurements of CH₃ have mostly been conducted using absorption-based methods [3, 7-9], conventional REMPI [10-12] and degenerate four wave mixing (DFWM) [13, 14]. Absorption-based methods, either direct absorption of CH₃ or cavity ring-down spectroscopy, have the limitation of path integration, leading to limited spatial resolution. Conventional REMPI has a low signal-to-noise ratio for measurement of the CH₃ distribution in flames at atmospheric pressure [15]. Additionally, a physical probe or electrodes required for the collection of electrons or ions may introduce some disturbances in the reacting flows. DFWM utilizes third order nonlinear optics effects, which can have low signal-to-noise ratios for applications at low pressures. Indirect measurements have been conducted by photolysis of CH₃ into the methylidyne radical (CH) and its subsequent laser-induced fluorescence [16–19], which inherently complicates the detection scheme and requires care for the interpretation of the experimental data.

Relative direct measurements of CH₃ were conducted in our previous study [20]. A tunable dye laser was used to selectively induce the (2+1) REMPI ionization of methyl radicals (CH₃, $3p^2A_2''0_0^0$ band) in a near adiabatic and premixed laminar CH₄/air flame at atmospheric pressure. *In situ* measurements of the REMPI electrons were made by non-intrusively using a microwave homodyne transceiver detection system. The REMPI spectrum of the CH₃ radical was obtained and a spatial distribution of the radicals with a resolution of approximately 20 μm was determined across the flame front. There was good agreement between the normalized measured and calculated CH₃ profiles, including the total width and asymmetric structure.

The focus of the present investigation was to performing *situ* calibration to quantitatively measure the absolute concentration of CH₃ in a flame. The calibration was achieved through a multi-part process that included: (1) time-dependent quantum perturbation theory calculations of the REMPI cross sections of CH₃ and argon, (2) quantitative measurements of CH₃ in CH₄/air flames at atmospheric pressure, and (3) comparisons with the calculated CH₃ profiles using the detailed kinetic mechanism of GRI-3.0.

Experimental setup

The experimental setup was described in our previous publications [20, 21] and therefore a brief summary is only provided here. The excitation wavelength for the Radar REMPI measurement was created using a frequency doubled Nd:YAG laser (Continuum Surelite SI-10) that was used to pump a tunable dye laser

(Continuum ND6000, DCM, $C_{19}H_{17}N_3O$ as the dye) is shown in Figure 7. The output of the dye laser was frequency doubled by an automatic frequency doubling and tracking system (Continuum UVT). The output wavelengths were automatically tunable from 332 to 335 nm, with output power ranging from 6 to 8 mJ/pulse. The laser output was then focused with a 50 cm focal length lens to generate the REMPI plasma in the flame of a Hencken burner. The Hencken burner with 1 in. by 1 in. square exit geometry (Technologies for Research, Modal: RT1x1) was employed to generate a near-adiabatic, flat flame. Each fuel stream, flowing through a tube, is individually surrounded by six oxidizing gas stream tubes. Therefore, a combustible mixture exists only above the burner surface. The fuel tubes have an inner diameter (ID) of approximately 0.54 mm and an outer diameter (OD) of approximately 0.90 mm. The combined fuel and air flow rate must be high enough to keep the flame slightly lifted from the burner surface in order to reduce heat loss to the burner. The relatively long focal length lens (50 cm) was used to avoid gas breakdown or avalanche ionization in the flames and also allowed for the focal point to be close to the burner surface. From ideal Gaussian beam geometry, the focal region was roughly 20 μm in diameter and 2.4 ± 0.4 mm in length. The length of the interrogation region arose from the microwave signal scattering along the laser beam upstream and downstream of the focus. The focal region length and uncertainty was related to the laser intensity and corresponding microwave scattering signal. At a 2.8 mm length, the laser intensity falls to about 33 % and the REMPI efficiency and microwave scattering drop to approximately 11 %, compared to the center of the laser focus. The beam steering mirrors and focusing lens were placed on a translational stage to move the laser focus to different heights above the burner and therefore through the flame front.

A microwave homodyne transceiver detection system was used to detect the REMPI plasma. A 10-mW tunable microwave source (HP 8350B sweep oscillator set at ~ 10 GHz) was first split into two channels. One channel was used to illuminate the ionization point through a microwave horn (WR75, 15 dB gain), while the 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 bandwidths of 2.5 kHz-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.

Estimation of REMPI cross sections of argon and CH_3

The principle technique for the quantitative calibration of CH_3 concentration in the flame with argon is shown in Figure 8. In this approach, due to the proximity of

argon resonance state $2s^22p^54f$ [$7/2, J = 4$] (4+1 REMPI by 332.5 nm) with the state $3p^2A_2''0_0^0$ of CH_3 (2+1 REMPI by 333.6 nm), Radar REMPI measurements of freely flowing argon and methyl radicals in the flame were performed with the same configurations. Since the laser beam properties can be assumed constant within such a short wavelength range, 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.

$$N(CH_3) = \frac{S(CH_3)}{S(Ar)} \cdot \left(\frac{\sigma^{(4+1)}(Ar)}{\sigma^{(2+1)}(CH_3)} \right) \cdot \frac{I^5}{I^3} \cdot N(Ar) \quad (1)$$

where N is the number density, S is the observed signal, σ 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 the radical species (CH_3) and inert gas (argon). Baselines for the microwave measurement were established by not alternating the experimental setup to vary the microwave reflections. For CH_3 measurement, the resonance state $2s^22p^54f$ [$7/2, J = 4$] of argon was in close proximity to the resonance state $3p^2A_2''0_0^0$ of CH_3 , as shown in Figure 8. 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.

Argon

Argon is resonantly populated to the $2s^22p^54f$ [$7/2, J = 4$] by four photons at 332.5 nm and ionized by one more photon from the resonance state. The four-photon absorption cross section of argon has been calculated following the references [22–24]. The four-photon absorption process for argon can be described as:

$$W_{f,g}^{(4)} = (2\pi)(2\pi\alpha)^4 F(r,t)^4 \omega_L^4 \times \left| \sum_1 \frac{\langle f|r|3\rangle \langle 3|r|2\rangle \langle 1|r|i\rangle}{(\omega_{fg} - 3\omega_L)(\omega_{fg} - 2\omega_L)(\omega_{fg} - \omega_L)} \right|^2 G(\omega_L) \quad (2)$$

where g and f denote the ground ($3p^61S$) and the intermediate state ($2s^22p^54f$ [$7/2, J = 4$]) of the argon atom, respectively, ω_{fg} is the frequency difference between the two state of $|f\rangle$ and $|g\rangle$, α is the fine-structure constant ($1/137.036$), $F(r,t) = I(r,t)/\hbar\omega_L$ is the total photon flux measured in the number of photons per cm^2 per second, where the laser intensity has a Gaussian profile ($I(r,t) = I_0(t)\exp(-r^2/r_b^2)$, with r_b the radius of laser focus), $G(\omega_L)$ is lineshape

function where a Voigt function for convoluting the laser Gaussian profile and natural broadening was used, ω_L is the angular frequency of the exciting incident laser, $\langle r |$ are the dipole transition matrix elements connecting the ground state, virtual states and final state $|g\rangle$, $|1\rangle$, $|2\rangle$, $|3\rangle$ and $|f\rangle$. The general four-photon excitation cross section $\sigma_{(4)}$ is defined as:

$$W^{(4)} = \sigma_{(4)} F^4 \quad (3)$$

To calculate the dipole transition matrix elements, the relation between the Einstein coefficients and the matrix elements was used [24, 25].

$$|\langle \alpha L S J M_J | r | \alpha' L' S' J' M_{J'} \rangle|^2 = (2J'+1) \begin{pmatrix} J & 1 & J' \\ -M_J & 0 & M_{J'} \end{pmatrix}^2 \frac{A}{0.66702\sigma^2} \frac{3a_0^2}{\Delta E} \quad (4)$$

where J and J' are total angular momentum of the initial and final states, M_J and $M_{J'}$ are z components of the total angular momentum, A is the Einstein coefficient of the final state, ΔE is the energy gap between two states in units of Rydbergs, σ is the transition wavelength in cm^{-1} and a_0 is the Bohr radius, 5.2918×10^{-11} m. The four-photon transition can be conceptually decomposed to four one-photon transitions. Therefore, the four-photon selection rules will be $\Delta L = 0, \pm 4$, $\Delta J = 0, \pm 1, \pm 1, \pm 1$ and ± 1 without $J = 0 \rightarrow J = 0$ for the single photon transition. Since the ground state is at $|p\rangle$ and final state is at $|f\rangle$ there are a few dominant routes for the four-photon transitions: $3p-4s-4p-3d-4f$, $3p-5s-4p-3d-4f$, $3p-3d-4p-3d-4f$, $3p-3d-4f-3d-4f$, and $3p-3d-4f-5g-4f$. From the principle of multi-photon transition, the transition probability is inversely proportional to the energy gap between virtual states and photon energy. Based on the above calculation and current experimental conditions, the four-photon transition rate was calculated to be approximately $1.06 \times 10^{-133} \text{ cm}^8 \text{ s}^4$ for the laser linewidth of 0.01 at 332.5 nm.

The one-photon ionization from the excited bound state of an atom can be approximated as [24],

$$\sigma_{pi} = \frac{8 \times 10^{-22}}{Z(U_I / R)^{1/2} (\hbar \omega_L / U_I)^3} [m^2] \quad (5)$$

where Z is the net charge on the ion, U_I is the ionization potential for the atom in the excited state, R is the Rydberg constant and $\hbar \omega_L$ is the photon energy. The formula is exact for hydrogenic atoms and within the uncertainties of experimental measurements for excited inert gas atoms [26, 27].

Methyl radical (CH₃)

Similar to argon, the two-photon absorption cross section of CH₃ was estimated based on time-dependent quantum perturbation theory. The two-photon absorption coefficient was found by multiplying the dipole moments weighted by quantum defects. The two-photon absorption process for CH₃ is described as:

$$W_{f,g}^{(2)} = (2\pi)(2\pi\alpha)^2 F(r,t)^2 \omega_L^2 \times \left| \sum_1 \frac{\langle f | r | 1 \rangle \langle 1 | r | i \rangle}{\sqrt{(\omega_{fg} - \omega_L)^2 + \gamma^2 / 4}} \right|^2 \times FC \times G(\omega_L) \quad (6)$$

where FC is the Franck-Condon factor for the excited state, which was taken as 0.91 [28].

Instead of using Einstein coefficients to calculate the dipole moments as was done for argon, the absorption coefficients or oscillator strengths were used to calculate the first-order dipole moments of various transitions for CH_3 . The dipole moments of CH_3 were calculated from the oscillator strengths and absorption coefficients from [29].

$$f(a \rightarrow b) = \frac{2}{3} \frac{m_e}{\hbar e^2} (E_b - E_a) Q(a \rightarrow b) |R_{ab}|^2 \quad (7)$$

where m_e and e are the electron mass and charge, respectively, $\hbar$ is Plank constant $h/2\pi$, $Q(a \rightarrow b)$ is the angular factors resulting from the angular integration [29], and the radial transition moment integral is defined as:

$$R_{ab} = \langle R_a(r) | r | R_b(r) \rangle \quad (8)$$

For CH_3 , the absorption coefficient and oscillator strength were found in references [30, 31]. The transitions from the virtual state to the excited state were from Ref. [29]. The predissociation fraction of the excited state $3p^2A_2''0_0$ was set as 54% [32]. The parameters used in the calculations are summarized in Table 1.

In summary, the two-photon absorption cross section for CH_3 was found to be $3.1 \times 10^{-47} \text{ cm}^4 \text{ s}^2$ for the laser linewidth of 0.01 nm at 333.6 nm, which is of the same order as the estimation of $1.9 \times 10^{-47} \text{ cm}^4 \text{ s}^2$ in Ref. [32]. The difference could be due to the difference of laser linewidths. The one-photon ionization cross section of the excited state of CH_3 was calculated using Eq. (5). Therefore, the corresponding CH_3 concentration was found to be approximately $5.7 \times 10^{15} / \text{cm}^3$ in Figure 8.

It should be noted that the cross sections for both argon and CH_3 resonance enhanced absorption and ionization were calculated from time-dependent quantum perturbation theory. The uncertainty of REMPI cross section is hard to quantify. It is estimated to be around 50 %. The accuracy was based on the methodology limitations of incomplete summation of intermediate states and the indetermination of directions of dipole moments in the calculations. The experimental determination of cross sections of absolute multiphoton absorption and ionization is highly desired as in references [33–36]. Regardless, any measurements of CH_3 can still be accurately calibrated by inert argon such that the relative measurements in other flames can be compared to the well-established CH_4/air flame measurement and model.

Quantitative determination of CH₃ concentration in the flames

Calibration of the microwave detection system was conducted for freely flowing argon and molecular oxygen in room air. Argon was flowed through the Hencken burner at two standard liters per minute (slpm). Argon was resonantly populated to $2s^2 2p^5 4f [7/2, J=4]$ by four photons at 332.5 nm and ionized by one more photon from the resonance state. Molecular oxygen in room air was also detected by Radar REMPI via 2 photon resonance of $C\leftarrow X$ and 1 photon ionization near 286.5 nm [21] as a second validation and confirmation for the calibration. Figure 9(a) shows the normalized spatial distribution profiles of argon and molecular oxygen. Great repeatability for measurements of both argon and molecular oxygen was achieved. A numerical fitting of the experimental data yielded $y = 0.02727 + 0.07865x^{1.5189}$ with $R^2 = 99.3\%$. Since argon and molecular oxygen were evenly distributed above the burner surface, the curves could be considered as the instrument function for the microwave system and were used to calibrate all other measurements on the burner. Any undesired microwave reflection and interference from the metallic burner and/or equipment in the laboratory were thus eliminated. The monotonic increase in the Radar REMPI signal was due to blocking of the microwave scattering by the burner surface. Above a certain height, the microwave signal becomes periodic according to the microwave wavelength, which was approximately 3 cm and therefore beyond the interrogation region for the current experiments. Figure 9(b) shows two separate uncalibrated spatially resolved measurements of methyl radicals in the CH₄ : air (1.15:10.2 slpm) flame at atmospheric pressure.

The Radar REMPI measurements shown in Figure 10(b) were performed on a Hencken burner that is comprised of a matrix of fuel tubes set within a honeycomb where the oxidizer is flowing. The design allows for a separation between the fuel and oxidizer until exiting the burner in order to produce a flame that does not flashback and is near adiabatic. Under the conditions used in the current experiments, the result is a flame that is composed of many small flamelets, each centered on a fuel tube. In order to validate the quantitative measurements of CH₃, two-dimensional simulations were performed using UNsteady Ignition and COMbustion with ReactionNs (UNICORN) [37–41] with the detailed chemical kinetics of GRI-3.0. Figure 10 shows the results of the simulations for two flamelets at atmospheric pressure with the calibrated quantitative experimental result, as well as a chemiluminescence image of the CH₄ : air (1.15:10.2 slpm) flame. UNICORN is a time-dependent, axisymmetric mathematical model that is used to investigate two-dimensional steady and unsteady reacting flows. It has been validated with experiments designed to predict ignition, extinction, stability limits, and the dynamic and steady-state characteristics of diffusion and premixed flames burning various fuels. Here, UNICORN used a detailed chemical kinetics model, GRI-3.0, for the CH₄/air flames at atmospheric pressure with the geometry of the Hencken burner. While Figure 10(a) shows a chemiluminescence image of a side view of the entire

flame with multiple flamelets, Figure 10(b) shows the computational results of the two-dimensional distribution of CH_3 across two flamelets given by UNICORN. The calibrated quantitative experimental results, Figure 10(c), were obtained by two steps. Dividing Figure 9(b) by Figure 9(a) gives a calibrated relative profile of CH_3 in the flame. Due to the monotonic increase of the instrument function, the noise near the burner surface was significantly amplified by the division compared to the consistent noise level in Figure 9(b). Calibration of the relative concentration of CH_3 to argon was then conducted to give a quantitative value, i.e. Figure 10(c). The Radar REMPI measurement had a spatial resolution of approximately $20\mu\text{m}$ normal to the flame front and $2.4\pm 0.4\text{ mm}$ in length parallel to the top of the burner. Therefore, the Radar REMPI measurement crossed through two flamelets (depicted by the red box in Figure 10(a) and white box in b). Depending upon where the 2.4 mm interrogation area was located across the flamelets, there could be different shaped profiles and peak CH_3 number densities. To mitigate any discrepancies with regard to the interrogation area, a parametric study was performed by averaging different 2.4 mm areas, plotting the average CH_3 profiles, and then comparing to the experimental results. This procedure was successfully applied in our previous study when comparing the normalized CH_3 profiles [20]. Additionally, all of the profiles from the simulations were moved in the stream wise direction (closer to the burner) to match the experimental profile. This movement was not unreasonable since past simulations have also predicted higher flame liftoff heights than experiments [42]. The agreement between the experiment and simulations was very good by capturing both the width and height of the CH_3 profile through the flame. Similar measurements were performed for other equivalence ratio CH_4/air Hencken flames, as well with H_2 dilution. An example of the comparison between experiments and simulations for a H_2 diluted CH_4/air flame (0.22:1.1:11 slpm) is shown in Figure 11. Again, the agreement is good within the experimental uncertainties, and the Radar REMPI measurement captured the slightly smaller peak CH_3 number density, narrower width, and higher liftoff height compared to the result shown in Figure 10(c) without H_2 dilution.

Conclusions

Spatially resolved and quantitative measurements of methyl radicals in CH_4/air flames at atmospheric pressure were performed for the first time using the Radar REMPI technique. The proximity of resonances of argon and CH_3 allowed for the CH_3 profiles to be calibrated based on theoretical estimations of the cross sections of both argon and CH_3 . The quantitative determination of CH_3 was compared with numerical simulations using detailed kinetics and good agreement was achieved. Since the Radar REMPI method utilizes microwaves to detect electrons generated by the laser in situ, sensitively and non-intrusively, it has great potential to be straightforwardly generalized for quantitative measurements

of other radicals and intermediate species in practical and relevant combustion environments with elevated temperatures and pressures.

Acknowledgments

The work at the University of Tennessee Knoxville was supported by NSF CBET-1032523. We also thank Dr. James R. Gord, Dr. Sukesh Roy and Dr. Hans Stauffer at the Air Force Research Laboratory for insightful discussions with regard to multiphoton ionization.

References

1. C. K. Law, *Combustion Physics*, 1st ed. (Cambridge University Press, New York, 2006)
2. R. P. Wayne, *Chemistry of atmospheres: an introduction to the chemistry of the atmospheres of earth, the planets, and their satellites* (Oxford University Press, Oxford, 2000)
3. P. Zalicki, R. N. Zare, *J. Chem. Phys.* **102**(7), 2708–2717 (1995)
4. F. Wang, J.-S. Lin, K. Liu, *Science* **331**(6019), 900–903 (2011)
5. W. Zhang, H. Kawamata, K. Liu, *Science* **325**(5938), 303–306 (2009)
6. M. Frenklach, *Phys. Chem. Chem. Phys.* **4**(11), 2028–2037 (2002)
7. N. L. Arthur, *J. Chem. Soc. Faraday Trans. 2 mol. Chem. Phys.* **82**(3), 331–336 (1986)
8. J. J. Scherer, K. W. Aniolek, N. P. Cernansky, D. J. Rakestraw, *J. Chem. Phys.* **107**(16), 6196–6203 (1997)
9. P. Zalicki, Y. Ma, R. N. Zare, E. H. Wahl, J. R. Dadamio, T. G. Owano, C. H. Kruger, *Chem. Phys. Lett.* **234**(4–6), 269–274 (1995)
10. K. C. Smyth, D. R. Crosley, in *Applied Combustion Diagnostics*, ed. by K. Kohse-Hoinghaus, J. B. Jeffries (Taylor & Francis, New York, 2002)
11. K. C. Smyth, P. J. H. Tjossem, *Appl. Opt.* **29**(33), 4891–4898 (1990)
12. T. A. Cool, *Appl. Opt.* **23**, 10 (1984)
13. V. Sick, M. N. Bui-Pham, R. L. Farrow, *Opt. Lett.* **20**(19), 2036–2038 (1995)
14. J. Kiefer, P. Ewart, *Prog. Energy Combust. Sci.* **37**(5), 525–564 (2011)
15. K. Kohse-Hoinghaus, *Prog. Energy Combust. Sci.* **20**(3), 203–279 (1994)
16. C. Kassner, P. Heinrich, F. Stuhl, S. Couris, S. Haritakis, *Chem. Phys. Lett.* **208**(1–2), 27–31 (1993)
17. S. W. North, D. A. Blank, P. M. Chu, Y. T. Lee, *J. Chem. Phys.* **102**(2), 792–798 (1995)
18. C. Kassner, F. Stuhl, *Chem. Phys. Lett.* **222**(5), 425–430 (1994)
19. P. Desgroux, L. Gasnot, B. Crunelle, J. F. Pauwels, *Symposium (International) on Combustion* **26**(1), 967–974 (1996)
20. Y. Wu, A. Bottom, Z. Zhang, T. M. Ombrello, V. R. Katta, *Opt. Express* **19**(24), 23997–24004 (2011)
21. Y. Wu, Z. Zhang, S. F. Adams, *Chem. Phys. Lett.* **513**(4–6), 191–194 (2011)
22. Z. Zhang, (Princeton University, Princeton, NJ, 2008)
23. Z. Zhang, M. Shneider, R. Miles, *Phys. Rev. Lett.* **98**(26), 265005 (2007)
24. N. M. Khambatta, L. J. Radziemski, S. N. Dixit, *Phys. Rev. A* **39**(8), 3842–3845 (1989)
25. R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Los Angeles, 1981)
26. A. Siegel, J. Ganz, W. Bussert, H. Hotop, *J. Phys. B At. Mol. Phys.* **16**(16), 2945 (1983)

27. M. D. Perry, O. L. Landen, Phys. Rev. A **38**(6), 2815–2829 (1988)
28. A. M. Mebel, S.-H. Lin, Chem. Phys. **215**(3), 329–341 (1997)
29. A. M. Velasco, I. Martin, C. Lavi'n, Chem. Phys. Lett. **264**(6), 579–583 (1997)
30. M. A. Childs, K. L. Menningen, L. W. Anderson, J. E. Lawler, Chem. Phys. Lett. **246**(6), 567–570 (1995)
31. M. J. Pilling, A. M. Bass, W. Braun, Chem. Phys. Lett. **9**(2), 147–148 (1971)
32. J. Zhou, J. J. Lin, W. Shiu, S.-C. Pu, K. Liu, J. Chem. Phys. **119**(5), 2538–2544 (2003)
33. V. A. Shubert, S. T. Pratt, J. Phys. Chem. A **114**(42), 11238–11243 (2010)
34. C. A. Taatjes, D. L. Osborn, T. M. Selby, G. Meloni, H. Fan, S. T. Pratt, J. Phys. Chem. A **112**(39), 9336–9343 (2008)
35. B. R. Gans, G. A. Garcia, S. V. Boye'-Pe ´ronne, J.-C. Loison, S. P. Douin, F. O. Gaie-Levrel, D. Gauyacq, J. Phys. Chem. A **115**(21), 5387–5396 (2011)
36. J.-C. Loison, J. Phys. Chem. A **114**(23), 6515–6520 (2010)
37. W. M. Roquemore, V. R. Katta, J. Vis. **2**(3,4), 257–272 (1999)
38. W. M. Roquemore, V. R. Katta, J. Vis. **2**, 257–272 (2000)
39. V. R. Katta, L. P. Goss, W. M. Roquemore, Combust. Flame **96**(1–2), 60–74 (1994)
40. V. R. Katta, L. P. Goss, W. M. Roquemore, Aiaa J. **32**(1), 84–94 (1994)
41. V. R. Katta, L. P. Goss, W. M. Roquemore, Int. J. Numer. Methods Heat Fluid Flow **4**(5), 413–424 (1994)
42. F. Takahashi, W. John Schmoll, V. R. Katta, Symp. (International) Combust. **27**(1), 675–684 (1998)

Appendix

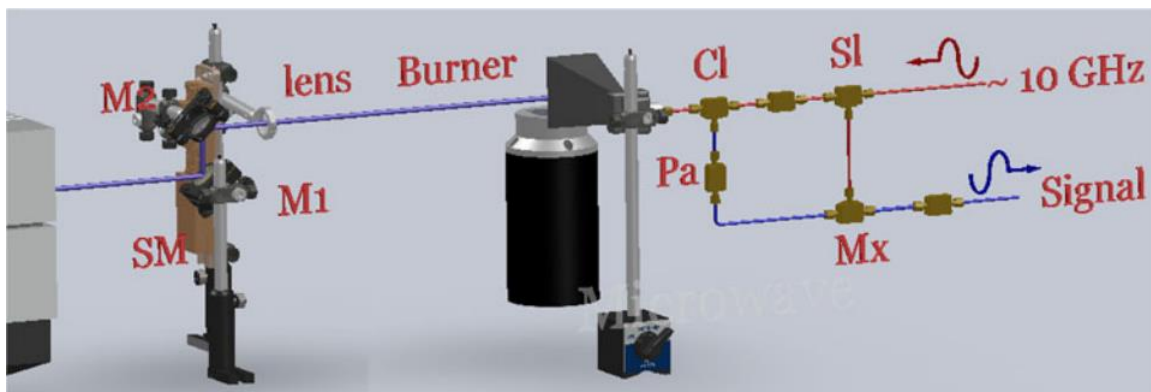


Figure 7. Experimental setup for the CH_3 measurements in the Hencken burner by Radar REMPI. SM step motor, Mx mixer, Sl splitter, Cl circulator, Pa Preamplifier, M1 and M2 are mirrors

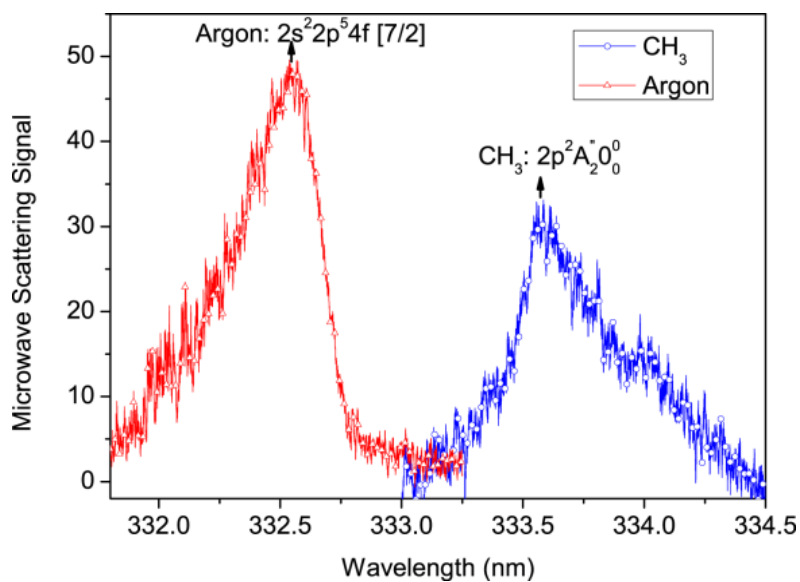


Figure 8. REMPI spectra of free flowing argon (Ar) through the burner and methyl radical [20] in a CH_4 /air flame at atmospheric pressure. The measurement was conducted at the same location above the burner surface and the corresponding CH_3 concentration was approximately $5.7 \times 10^{15} / \text{cm}^3$.

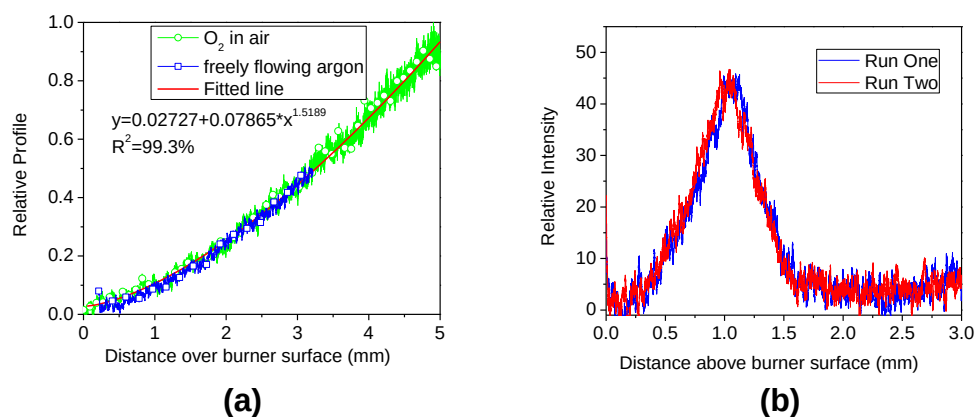


Figure 9. Original microwave signals obtained by scanning the laser focus above the burner surface at various conditions.

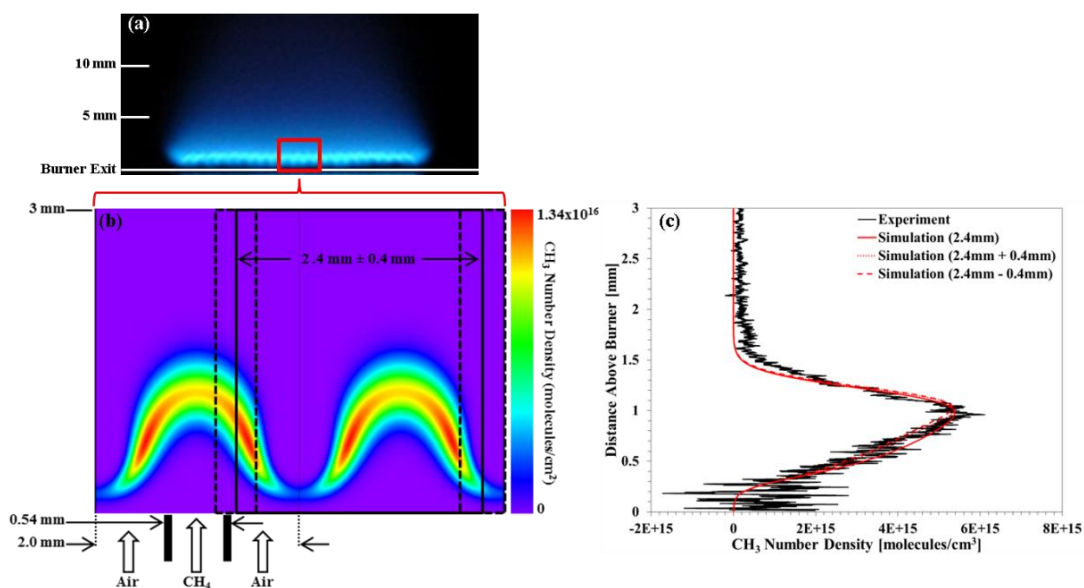


Figure 10. Quantitative spatial distribution of methyl radicals (CH_3) in a CH_4 /air (1.15:10.2slpm) flame produced by the Hencken burner at atmospheric pressure. (a) Chemiluminescence image, (b) UNICORN result and (c) comparison of experimental and computational results. The red box in (a) indicates the position of the measurement. The burner surface is marked with a white line and the wrinkles in the flame are shown. The computational CH_3 profile by UNICORN has been moved downstream of 2.0 mm to match the experimental results

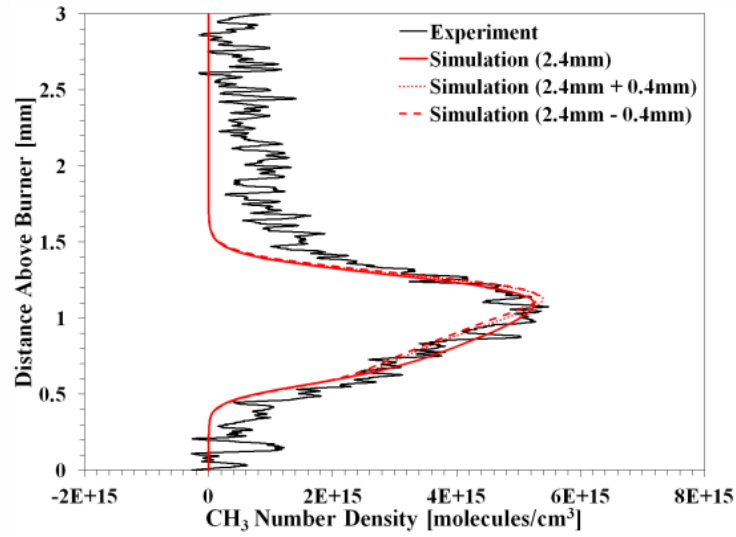


Figure 11. Quantitative comparison of methyl radicals (CH_3) in a H_2 diluted CH_4/air flame (0.22:1.1:11 slpm). The computational CH_3 profile by UNICORN has been moved downstream of 2.0 mm to match the experimental results.

Table 1. Parameters used in the calculation of the cross section of CH₃.

Parameters used in the calculation of the cross section of CH ₃	
Transition between the ground state and intermediate states (IS)	
IS : $3s^2A'_1$	$3s^2A'_1 - X$
IS : $3d^2E$	$3d^2E'' - X$
IS : $3d^2A'_1$	$3d^2A'_1 - X$
Transition between the intermediate states (IS) and the excited state of $3p^2A''_20_0$	
IS : $3s^2A'_1$	$3p^2A^2 - 3s^2A'_1$, wavelength = 728 nm, $Q = 1/3$, $f = 2 \times 10^{-5}$
IS : $3d^2E$	$3p^2A^2 - 3d^2E''$, wavelength = 1,520 nm, $Q = 0.4$, $f = 0.03$
IS : $3d^2A'_1$	$3p^2A^2 - 3d^2A'_1$, wavelength = 1,461 nm, $Q = 4/15$, $f = 0.021$

CHAPTER III
TWO DIMENSIONAL QUANTITATIVE MEASUREMENTS OF
METHYL RADICALS IN METHANE/AIR FLAME

This article, "Two Dimensional Quantitative Measurements of Methyl Radicals in Methane/Air Flame", was received on 9 September 2014; revised on 20 October 2014, accepted on 19 November 2014; published on 7 January 2015.

Author affiliations:

Yue Wu and Zhili Zhang*

Mechanical, Aerospace and Biomedical Engineering, University of Tennessee of Tennessee, Knoxville TN 37996, USA

*Corresponding author: zzhang24@utk.edu

Applied Optics, Vol. 54, Issue 2, pp. 157-162 (2015)

DOI: 10.1364/AO.54.000157

Abstract

Two-dimensional (2D) quantitative measurements of methyl (CH_3) radicals in a methane/air Hencken flame at atmospheric pressure are performed using coherent microwave Rayleigh scattering (Radar) from Resonance Enhanced Multi-Photon Ionization (REMPI) technique. The 2D scanning and subsequent quantification are employed for Radar REMPI. The 2D quantitative results were used to verify the numerical calculations. The line-integral effect was involved in the calculation due to the real experimental configuration. A 25% difference existed between the experimental results and numerical calculation while the overall concentration distributions between experiment and modeling of single flamelet have fairly good agreement with each other. © 2014 Optical Society of America

OCIS codes: (170.0110) Imaging systems; (170.3010) Image reconstruction techniques; (170.3660) Light propagation in tissues.

<http://dx.doi.org/10.1364/AO.54.000157>

Introduction

Multi-dimensional, *in-situ* quantitative diagnostics of combustion radicals and intermediate species are in demand because of the intricacy of the flow and chemistry coupling in many practical combustion environments. Many factors affect the overall reaction pathways in the combustion environment. The sharp temperature gradient across the flame front, numerous radical species, and even more chemical reactions are a few of these factors. Multi-dimensional *in-situ* characterization can automatically take those factors into account. Quantitative measurements can provide not only calibration data for modelers to fine-tune combustion kinetic mechanisms but also insight into local reactions that may be

used to identify and track key rate-controlling reaction pathways in the combustion environment.

In combustion, ignition and flame propagation reactions [via hydrogen abstraction by H atoms and hydroxyl radicals (OH)] are controlled by the CH₃ radical [1]. However, only a few direct measurements of CH₃ in flames have been reported because the strong predissociation of the electronically excited states of CH₃ prevents fluorescence detection [2]. Most direct measurements of CH₃ have been performed using absorption-based methods [3-6], conventional resonance-enhanced multi-photon ionization (REMPI) [7-10], and degenerate four-wave mixing (DFWM) [11, 12]; these methods are limited either in spatial resolution or in low signal-to-noise ratios for applications at low pressures. Multi-dimensional diagnostic measurements including those of CH₃ are even rarer.

In the present work, two-dimensional (2D) quantitative measurements of CH₃ in a well-calibrated Hencken CH₄/air flame were performed utilizing an *in-situ* laser diagnostic technique: coherent microwave Rayleigh scattering from Resonance Enhanced Multi-Photon Ionization (REMPI) for CH₃. The absolute and quantitative concentration of CH₃ radicals was measured using Radar REMPI. This technique has recently been demonstrated to have the capability to provide high-spatial- and -temporal-resolution measurements and accurate determinations of concentration profiles without the use of physical probes or electrodes. The quantitative measurement of CH₃ radicals was first performed in flames at atmospheric pressure [2]; the flame-temperature distribution of molecular oxygen in a near-adiabatic flat flame was also measured recently [13]. Moreover, Radar REMPI has also been applied to the optical detection of argon [14], nitric oxide [15], carbon monoxide [16], the oxygen atom [17], and 1,4-diazobicyclooctane (DABCO) [18] in gas cells, open air, flames, and weakly ionized plasma. Because of the high-spatial resolution of Radar REMPI, two-dimensional quantitative measurements of CH₃ may be helpful to evaluate the combustion model and analyze the processes of generation and consumption of CH₃ in atmospheric flames.

Experimental setup

The experimental setup used for conducting 2D CH₃ radical measurements, shown in Figure 12, is similar to that used for one dimensional (1D) CH₃ radical detection in our previous work [19]. Briefly, a Hencken burner was used to produce a unique and near-adiabatic flame that is lifted from the burner surface because the fuel and oxidizer streams are separated until they reach the burner exit. The fuel tubes have an inner diameter (ID) of ~0.54 mm and an outer diameter (OD) of ~0.83 mm. The oxidizer honeycomb is a hexagonal pattern with the cell size of ~0.9 mm. For the current experiment, the air flow rate was 10.20 slpm (standard liters per minute), and the CH₄ flow rate was set at 1.15 slpm, which produced a flame with an equivalence ratio of 1.07. A frequency-

double Nd: YAG laser (Continuum Surelite I-10) was used to pump a tunable dye laser (Continuum ND 6000). The output of the dye laser was frequency doubled by an automatic frequency-doubling-and-tracking system (Continuum UVT-1). The output wavelengths were automatically tuned from 332 to 335 nm, with the output power ranging from 6 to 8 mJ/pulse. The laser output was then focused with a 500-mm-focal-length lens to generate the REMPI plasma in the Hencken flame. For the Gaussian beam geometry, the beam waist w_0 of the focal point was $\sim 18 \mu\text{m}$, and the Rayleigh range z_R was $\sim 2.9 \text{ mm}$. The length of the interrogation region was determined by the microwave signal scattering along the laser beam upstream and downstream of the focus. The focal-region length and the uncertainty were related to the laser intensity and the corresponding microwave scattering signal. At a 2.9 mm from the beam waist, the laser intensity decreased to 50%, and the REMPI efficiency and the microwave scattering decreased to 25%, as compared to those at the center of the laser focus. Two linear translation stages were employed to perform 2D CH_3 radical measurements. The partial assembly, including one beam-steering mirror (M2) and one 500-mm-focal-length lens, was mounted on the vertical translation stage that was controlled by the stepper motor 1 (SM1). In the horizontal translation stage, the second stepper motor (SM2) was connected with the Hencken burner through a rigid coupling that was mounted on four roller bearings.

A microwave-homodyne-transceiver detection system (MDS) was designed to detect REMPI plasma. A 10-dBm tunable microwave source (HP 8350B sweep oscillator, set at $\sim 10 \text{ GHz}$) was first split into two channels, one of which 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 $\sim 10 \text{ GHz}$. After the frequency was down-converted with the original source of the second channel in the mixer, two other amplifiers with a bandwidth of $2.5 \text{ kHz} - 1.0 \text{ GHz}$ amplified the signal by an additional factor of 60 dB. From the geometry of the dipole radiation, the polarization of the microwave was chosen to be along the propagation direction of the laser for maximizing the scattering signal. The microwave scattering was monitored by an oscilloscope and recorded with an automatic data-acquisition system.

Results and Discussion

The experiments were conducted in a flat and slightly fuel-rich flame produced by a Hencken burner at atmospheric pressure. The flow rate of CH_4 and air were 1.15 slpm and 10.20 slpm, respectively. In order to obtain the CH_3 radical spatial distribution and analyze CH_3 generation and consumption in the flame front, the 2D quantitative measurements of CH_3 were conducted at atmospheric pressure using the well-calibrated Hencken burner. Figure 13 displays a

chemiluminescence image of the CH₄/air flame produced by the Hencken burner that comprised a matrix of fuel tubes set within a honeycomb where the oxidizer was flowing. The flame was lifted above the burner surface, and the near-adiabatic feature of the flame was thus preserved. Because of the unique configuration of the burner, the matrix of flamelets was generated within the diffusion flame. The two-dimensional profiles of both fluid and chemistry components were well developed in each single flamelet. Therefore, it is necessary and desirable to conduct 2D measurements within such a unique flame.

1D and 2D Quantitative Measurements

The 2D measurements of CH₃ in the CH₄/air flame at atmospheric pressure were performed with the aid of two vertical/horizontal translation stages. The vertical scan was controlled by SM1 of the vertical translation stage with a scanning speed of 0.005 mm/sec. After each vertical scan accomplished, the lateral movement of the Hencken burner was activated at regular intervals of 0.1 mm that were controlled by SM2 of the horizontal translation stage. Three sets of 21-vertical scan were made in the 2D CH₃ measurement (-1.0 mm - 1.0 mm). The original CH₃ concentration data of one individual experimental scanning set is shown in Figure 14 with a relatively low resolution in the x-axis direction. To increase the resolution and obtain a better 2D CH₃ image, the piecewise cubic Hermite interpolation (“pchip” in MATLAB) was applied to process the original data with the assumption of the symmetry of the 2D CH₃ distribution. The processed 2D CH₃ concentration distribution compared with the original averaged data set is shown in Figure 15.

To quantify the 2D CH₃ concentration distribution, the 1D calibration experiment was followed, and the beam position was set at both ± 0.2 mm from the flamelet center because of the optimum signal-to-noise ratios (SNR) at these two positions with the highest CH₃ concentration. The results of uncalibrated spatially resolved measurements of CH₃ in the CH₄/air (1.15:10.20 slpm) flame at atmospheric pressure are shown in Figure 16 as well as an instrument function for the calibration of the microwave detection system. Spatially resolved measurements of CH₃ were obtained by Radar REMPI via the two-photon resonance of the $3p^2A_2''0_0^0$ state (2+1 REMPI by 333.6 nm). To provide a means of correcting for undesired microwave reflection and blockage of the signal by the surface of the metallic burner, the instrument function was obtained by flowing argon and molecular oxygen into room air through the Hencken burner. Since the concentration of the argon and oxygen gases can be assumed to be constant within 3 mm of the burner surface, the microwave-signal variation must arise from the microwave detection system. These variations defined the instrument function. Details concerning the calibration of the microwave detection system can be found in our previous paper [19]. The instrument function here yielded

$y = 0.02727 + 0.07865x^{1.5189}$ ($0 \leq x \leq 5$ mm, $R^2 = 99.3\%$) for the microwave system, which was used to calibrate all of the other measurements on the Hencken burner.

The 1D quantitative CH_3 concentration in the Hencken flame at atmospheric pressure is shown in Figure 17. Two steps were taken: 1) conversion from relative to quantitative concentration based on *in-situ* argon and 2) oxygen calibration and deconvolution by the microwave instrument function. First, *in-situ* calibration was performed with argon to quantify the absolute concentration of CH_3 because of the proximity of the argon resonance state of $2s^2 2p^5 4f$ [$7/2, J=4$] ($4+1$ REMPI by 332.5 nm) and the CH_3 state of $3p^2 A_2'' 0_0$ ($2+1$ REMPI by 333.6 nm). The REMPI cross sections of CH_3 and argon were calculated based on the time-dependent quantum-perturbation theory.[19] Since the argon and oxygen concentrations were known, the relative CH_3 concentration was made quantitative based on the relative signal strengths of CH_3 and argon/oxygen. Second, the deconvolution by the instrument function was conducted to eliminate the possible systematic error from the microwave detection system. The corrected 1D CH_3 concentration in CH_4/air flames was in good agreement with numerical simulations that were performed using detailed chemical kinetics. The accuracy of the CH_3 measurement is about $\pm 25\%$ due to the uncertainty of the cross section calculation based on the time-dependent quantum-perturbation theory. [19]

Comparison of 2D CH_3 Numerical Calculations and Experimental Measurements

With the calibration conducted in the 1D CH_3 experiments with argon, the 2D CH_3 concentration distributions with quantitative results were accordingly obtained. To verify the CH_3 spatial distribution with quantitative concentration, the 2D CH_3 numerical calculations were performed using the UNICORN (UNsteady Ignition and COMbustion with ReactionNs) [20] with the detailed chemical kinetics of GRI 3.0 for a single flamelet at atmospheric pressure. The simulation results shown in Figure 18 are the 2D CH_3 concentration distribution at the center of single flamelet. The experimental results and the simulation calculation could not be directly compared until the line-integral effect was considered in the simulation calculation because of the use of the long-focal-length lens and the line-integral effect within the REMPI plasma that existed in the experiments. Specifically, the incident light with diameter of ~ 6 mm was focused through the 500-mm-focal-length lens. Therefore, the beam waist was $\sim 18 \mu\text{m}$ at the focal point, and the Rayleigh range was 2.9 mm, inferred from Eq. (1). The radius $\omega(z)$ of the focused beam was determined by the axial distance z from the beam waist shown in Eq. (2). Therefore, the laser intensity was well described by the Rayleigh distribution [Eq. (3)].

$$\omega_0 = \left(\frac{2\lambda}{\pi} \right) \left(\frac{F}{D} \right), z_R = \frac{\pi \omega_0^2}{\lambda} \quad (1)$$

$$\omega(z) = \omega_0 \sqrt{1 + \left(\frac{z}{z_R} \right)^2} \quad (2)$$

$$I(r, z) = I_0 \left(\frac{\omega_0}{\omega(z)} \right)^2 \exp \left(\frac{-2r^2}{\omega^2(z)} \right) \quad (3)$$

Along the axis of the laser beam, the laser-intensity distribution is shown in Figure 19. The CH_3 radical was theoretically ionized by three subsequent photons at the focal point (2+1 REMPI by 333.6 nm). In fact, the real REMPI efficiency distribution shown in Figure 19 was the result of the flux integration of I^3 along the axis of the incident laser beam. The Full Width at Half Maximum (FWHM) of the REMPI efficiency distribution is 3.8 mm, while the distance between the two flamelets is 2.3 mm. Hence, the line-integral effect must be involved in the numerical calculations that simulate the real situations occurring in the experiments. The 3D concentration-distribution profiles of CH_3 shown in Figure 20 were employed to be weight averaged by the REMPI efficiency distribution, and the final simulation results with the line-integral effect are shown in Figure 21 and compared to the quantitative experimental results of CH_3 in the CH_4/air flame at atmospheric pressure. The overall shapes of the 2D CH_3 concentration distribution are well agreed with each other with respect to the height and width of the “bell-shape” concentration distribution. The generation and occurrence of CH_3 located at ~ 0.4 mm above the burner surface is consistent between the numerical calculation and experimental results. However, there exists a concentration difference at the bottom part of the 2D “bell-shape” distribution between calculation and experimental results mainly due to the comprehensive results of the low CH_3 concentration and the line-integral effect in the experiments. (II) The maximum concentration of CH_3 is located at ~ 1.0 mm above the burner surface in the experimental results while that is ~ 0.8 mm in the numerical calculations. Overall, the experimental results are about 25% higher than the numerical calculations.

Quantitative multi-dimensional measurements can provide not only calibration data for modelers to fine-tune combustion kinetic mechanism but also more insight into local reactions, which may be used to identify and track key radicals and the rate-controlling reaction pathways in the combustion environment. One of the most important aspects of the chemical kinetics of methane combustion involves the production and removal of CH_3 radicals, which are the first and second steps in the methane-oxidation path, respectively [1, 21]. It is generally thought that at the first step, CH_3 is produced by either unimolecular or bimolecular reactions of CH_4 in the flame. The identification of the primary reaction pathways for CH_3 consumption at the second step of flame reactions is important not only for ignition and flame propagation reactions of CH_4

but also for Polycyclic Aromatic Hydrocarbons (PAH) and soot formations. [22] Two main competing mechanisms of CH_3 consumption control the overall reaction pathways in the flame. CH_3 can be directly oxidized by the main oxidation reactants of molecular oxygen (O_2), oxygen (O) atoms and OH, leading to methoxy radicals (CH_3O), formaldehyde (CH_2O), and formyl radicals (HCO). This reaction pathway of CH_3 consumption is preferable since the subsequent chain reactions further oxidize the hydrocarbons. The other main reaction pathway of CH_3 consumption is the radical recombination reaction ($\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2$ hydrocarbon) [23], followed by the hydrogen-abstraction sequence leading to ethyl (C_2H_5), ethane (C_2H_6), ethenyl (C_2H_3), and acetylene (C_2H_2). The pathway has been confirmed as the dominant route for the production of C_2 and higher level hydrocarbon species, leading to PAH and soot generation in the flame [24]. This is especially true since one of the dehydrogenation products, C_2H_2 , plays a most important role of contributor as a soot precursor to the formation and growth of soot in CH_4/air flames at fuel-rich conditions [25-27]. Hence, the 2D concentration distribution of CH_3 at the initial stage of fuel-rich methane/air combustion may be used as a starting point for a rough estimate of the chain reactions. Because of the unique configuration of the Hencken burner, each flamelet is surrounding by a large amount of oxidation reactants. In such a diffusion-flame environment, the CH_3 radicals mainly exist at 1.0-1.5 mm above the burner surface. The temperature is ~ 1650 - 2025 K in this range, as calculated by ChemKIN with GRI 3.0.

Two important features of this demonstration of multi-dimensional diagnostic methods for quantifying the 2D CH_3 concentration in the flame at atmospheric pressure are: 1) measurements in the flame are the most relevant to the combustion chemistry; quantitative *in-situ* measurements at realistic flame conditions and known temperatures are desirable and 2) the 2D CH_3 concentration map may be used as an indicator for pathway identification and tracking of PAH and soot generation.

Conclusion

The two-dimensional *in-situ* quantitative measurements of CH_3 in a CH_4/air Hencken flame at atmospheric pressure have been demonstrated by Radar REMPI. 2D scanning and subsequent quantification were used for Radar REMPI. The 2D numerical calculations were compared to the experimental results with the line-integral effect considered within the REMPI. A 25% difference existed between the experimental results and numerical calculation with fairly good agreement of overall 2D concentration distribution.

Acknowledgements

Efforts at the University of Tennessee Knoxville were supported by NSF CBET-1032523 and CBET-1346944. Zhili Zhang was partially supported by an ASEE Air Force Summer Faculty Fellowship. Experimental support by Drs. Naibo Jiang, Sukesh Roy and James Gord is greatly appreciated.

References

1. C. K. Law, *Combustion Physics*, 1st ed. (Cambridge University Press, New York, 2006)
2. Y. Wu, A. Bottom, Z. Zhang, T. M. Ombrello, and V. R. Katta, "Direct measurement of methyl radicals in a methane/air flame at atmospheric pressure by radar REMPI," *Optics Express* **19**, 23997-24004 (2011).
3. N. L. Arthur, "Methyl-radical absorption cross-section at 216.4 nm and rate constant for methyl-radical recombination," *Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics* **82**, 331-336 (1986).
4. J. J. Scherer, K. W. Aniolek, N. P. Cernansky, and D. J. Rakestraw, "Determination of methyl radical concentrations in a methane/air flame by infrared cavity ringdown laser absorption spectroscopy," *The Journal of Chemical Physics* **107**, 6196-6203 (1997).
5. P. Zalicki, Y. Ma, R. N. Zare, E. H. Wahl, J. R. Dadamio, T. G. Owano, and C. H. Kruger, "Methyl radical measurement by cavity ring-down spectroscopy," *Chemical Physics Letters* **234**, 269-274 (1995).
6. P. Zalicki and R. N. Zare, "Cavity ring-down spectroscopy for quantitative absorption measurements," *The Journal of Chemical Physics* **102**, 2708-2717 (1995).
7. K. C. Smyth and D. R. Crosley, "Detection of Minor Species with Laser Techniques," in *Applied Combustion Diagnostics*, K. Kohse-Hoinghaus and J. B. Jeffries, eds. (Taylor & Francis, New York, 2002).
8. K. C. Smyth and P. J. H. Tjossem, "Signal detection efficiency in multiphoton ionization flame measurements," *Applied Optics* **29**, 4891-4898 (1990).
9. T. A. Cool, "Quantitative measurement of NO density by resonance three-photon ionization," *Applied Optics* **23**, 10 (1984).
10. K. C. Smyth and P. H. Taylor, "Detection of the Methyl Radical in a Methane Air Diffusion Flame by Multiphoton Ionization Spectroscopy," *Chem Phys Lett* **122**, 518-522 (1985).
11. V. Sick, M. N. Bui-Pham, and R. L. Farrow, "Detection of methyl radicals in a flat flame by degenerate four-wave mixing," *Optics Letters* **20**, 2036-2038 (1995).
12. J. Kiefer and P. Ewart, "Laser diagnostics and minor species detection in combustion using resonant four-wave mixing," *Progress in Energy and Combustion Science* **37**, 525-564 (2011).
13. Y. Wu, J. Sawyer, Z. Zhang, and S. F. Adams, "Flame Temperature Measurements by Radar Resonance-Enhanced Multiphoton Ionization of Molecular Oxygen," *Applied Optics* **51**, 6864-6869 (2012).
14. Z. Zhang, M. N. Shneider, and R. B. Miles, "Coherent Microwave Rayleigh Scattering from Resonance-Enhanced Multiphoton Ionization in Argon,"

- Physical Review Letters **98**, 265005 (2007).
15. R. B. Miles, Z. Zhang, S. H. Zaidi, and M. N. Shneider, "Microwave scattering from laser ionized molecules: A new approach to nonintrusive diagnostics," AIAA J. **45**, 513-515 (2007).
 16. A. Dogariu and R. B. Miles, "Detecting localized trace species in air using radar resonance-enhanced multi-photon ionization," Applied Optics **50**, A68-A73 (2011).
 17. A. Dogariu, J. B. Michael, M. O. Scully, and R. B. Miles, "High-Gain Backward Lasing in Air," Science **331**, 442-445 (2011).
 18. F. Rudakov and Z. Zhang, "Standoff detection of large organic molecules using Rydberg fingerprint spectroscopy and microwave Rayleigh scattering," Optics Letters **37**, 145-147 (2012).
 19. Y. Wu, Z. L. Zhang, T. M. Ombrello, and V. R. Katta, "Quantitative Radar REMPI measurements of methyl radicals in flames at atmospheric pressure," Appl Phys B-Lasers O **111**, 391-397 (2013).
 20. W. M. Roquemore and V. R. Katta, "Role of Flow Visualization in the Development of UNICORN," J. Vis. **2**, 257-272 (1999).
 21. J. F. Bott and N. Cohen, "A Shock-Tube Study of the Reaction of Methyl Radicals with Hydroxyl Radicals," Int J Chem Kinet **23**, 1017-1033 (1991).
 22. C. K. Westbrook and F. L. Dryer, "Chemical Kinetic Modeling of Hydrocarbon Combustion," Progress in Energy and Combustion Science **10**, 1-57 (1984).
 23. A. F. Wagner and D. M. Wardlaw, "Study of the Recombination Reaction $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$. 2. Theory," J Phys Chem-Us **92**, 2462-2471 (1988).
 24. H. N. Najm, O. M. Knio, P. H. Paul, and P. S. Wyckoff, "A study of flame observables in premixed methane - Air flames," Combust Sci Technol **140**, 369-+ (1998).
 25. A. V. Mokhov, B. A. V. Bennett, H. B. Levinsk, and M. D. Smooke, "Experimental and computational study of C_2H_2 and CO in a laminar axisymmetric methane-air diffusion flame," Proceedings of the Combustion Institute **31**, 997-1004 (2007).
 26. E. W. Kaiser, "Measured and Computer-Simulated Hydrocarbon and OH Radical Profiles in Fuel-Rich Atmospheric-Pressure Flat Flames - Reactions of CH_4 and C_2H_2 ," J Phys Chem-Us **94**, 4493-4499 (1990).
 27. Crittend.Bd and R. Long, "Formation of Polycyclic Aromatics in Rich Premixed Acetylene and Ethylene Flames," Combust Flame **20**, 359-368 (1973).

Appendix

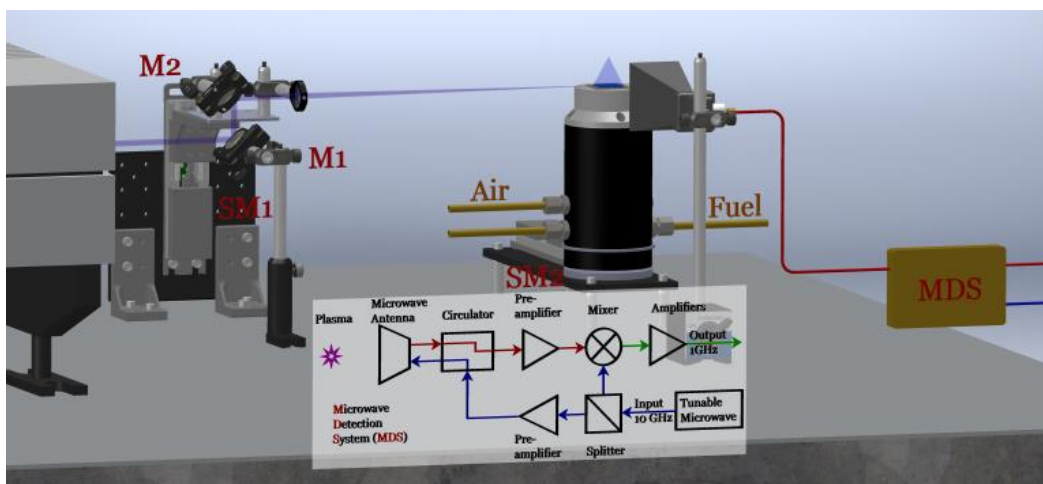


Figure 12. (Color online) The experimental setup for 2D CH_3 measurements using Radar REMPI. MDS is microwave detection system with the schematic diagram shown in the subplot; M1 and M2 are high-reflective mirrors; SM1 and SM2 are stepper motors.

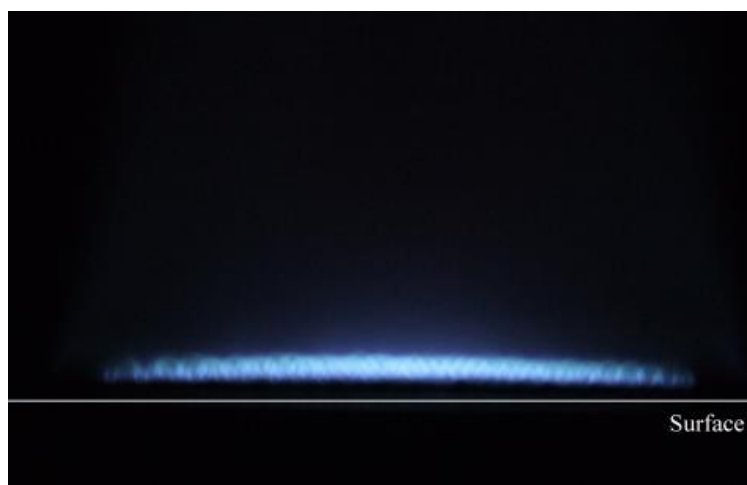


Figure 13. (Color online) A chemiluminescence image of the Hencken-burner flame with the equivalence ratio of 1.07 ($\text{CH}_4:\text{air} = 1.15:10.20$) at atmospheric pressure. Flamelets are generated and shown in the image.

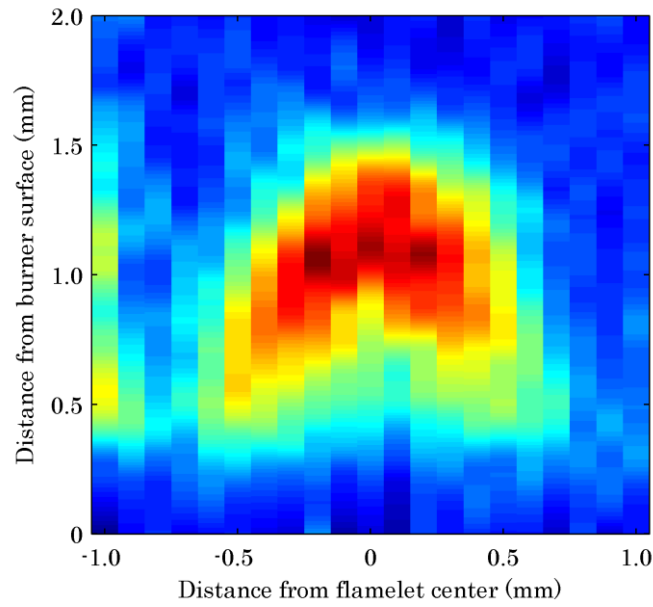


Figure 14. (Color online) A single scanning result of the 2D CH_3 concentration distribution.

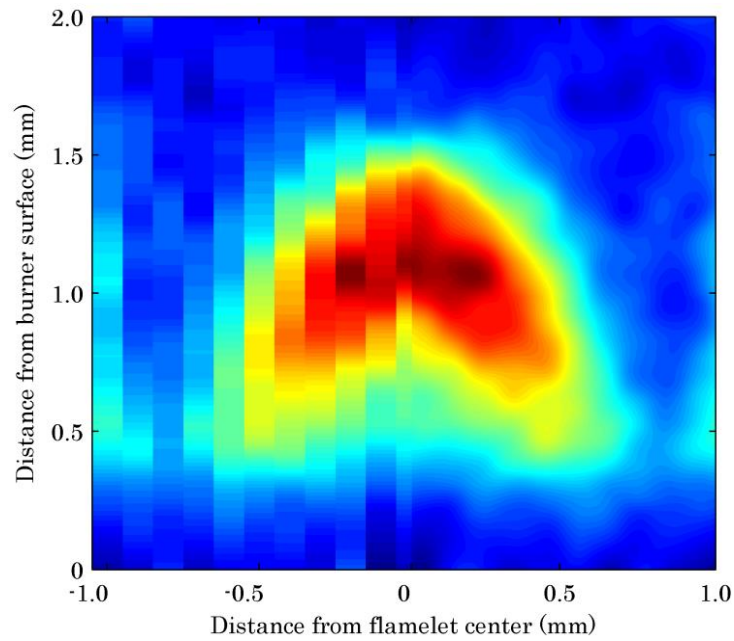


Figure 15. (Color online) The processed 2D CH_3 distribution with lateral-interpolation operation compared to the original averaged results.

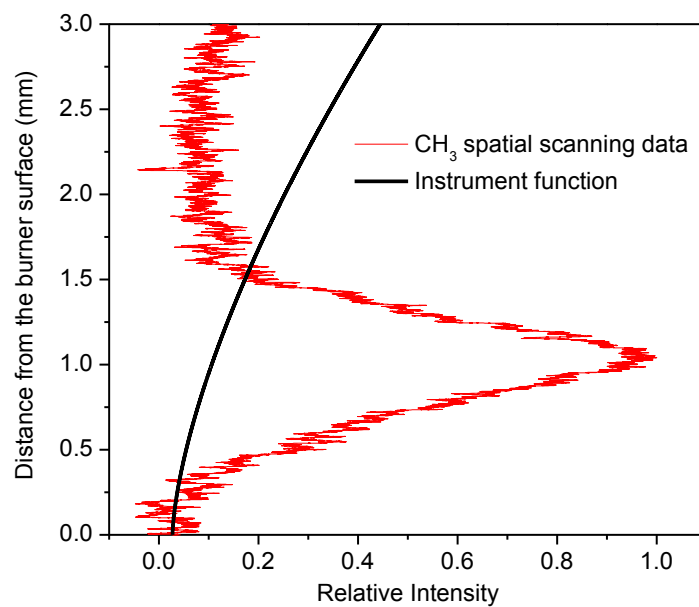


Figure 16. (Color online) The relative spatial distribution of CH_3 and the instrument function of the microwave detection system. The instrument function was used for calibration of the microwave detection system.

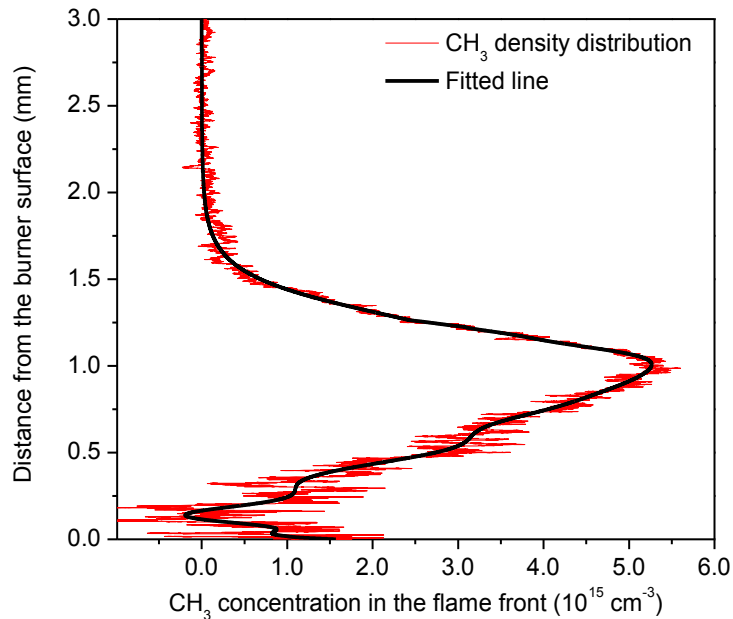


Figure 17. (Color online) The calibrated CH_3 distribution in the Hencken-burner flame.

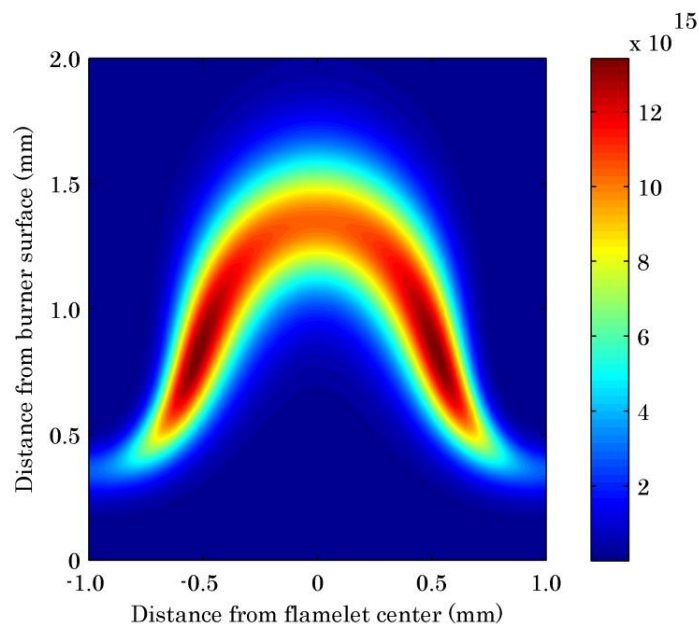


Figure 18. (Color online) The simulation results of the 2D CH_3 concentration distribution at the center of one flamelet. Unit: $\text{molecules}\cdot\text{cm}^{-3}$.

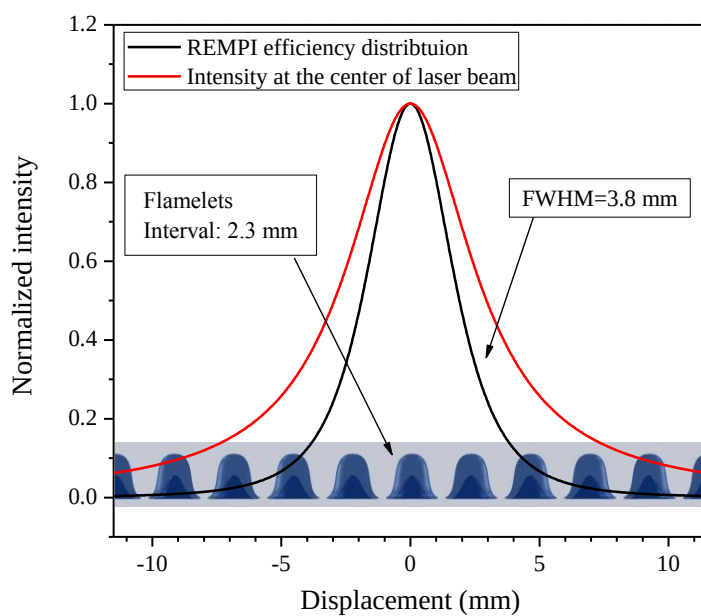


Figure 19. (Color online) The laser-intensity distribution along the axis of propagating light (red line). 2+1 REMPI efficiency distribution (integration results of cubic laser intensity and its cross section) (black line).

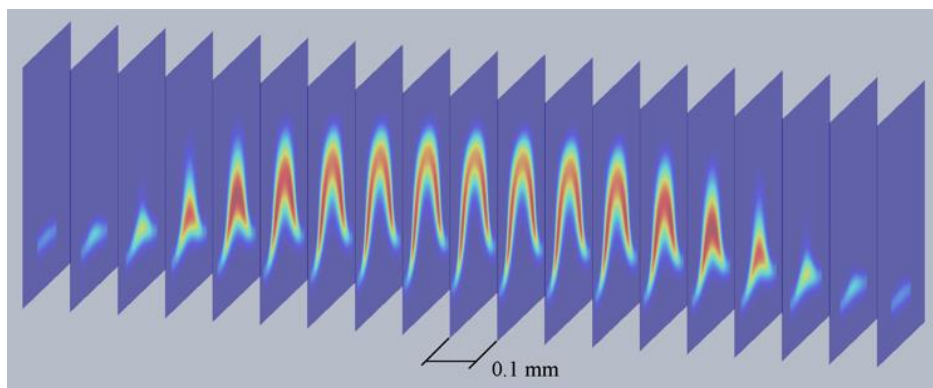


Figure 20. (Color online) The simulated 3D CH_3 concentration distribution within a single flamelet.

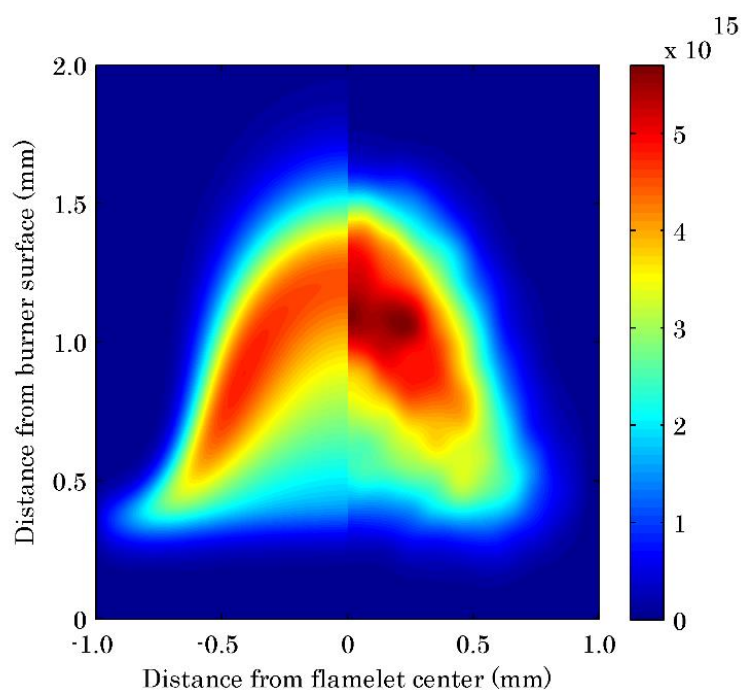


Figure 21. (Color online) The numerical calculation of CH_3 concentration distribution with line-integral effect (left) compared to experimental results (right). Unit: $\text{molecules}\cdot\text{cm}^{-3}$.

CHAPTER IV
O₂ ROTATIONAL TEMPERATURE MEASUREMENTS BY
COHERENT MICROWAVE SCATTERING FROM REMPI

This article, "O₂ rotational temperature measurements by coherent microwave scattering from REMPI", was received on 28 May 2011; accepted on 29 July 2011, available online 31 July 2011.

Author affiliations:

Yue Wu,¹ Zhili Zhang,^{1,*} and Steven F. Adams²

¹*Mechanical, Aerospace and Biomedical Engineering, University of Tennessee of Tennessee, Knoxville TN 37996, USA*

²*Air Force Research Laboratory (AFRL/RZPE), Wright-Patterson AFB, Dayton OH 45433-7919, USA*

*Corresponding author: zzhang24@utk.edu

Chemical Physics Letters, Vol. 513, Issue 4-6, pp. 191-194 (2011)

DOI: 10.1016/j.cplett.2011.07.092

Abstract

This letter reports non-intrusive local rotational temperature measurements of molecular oxygen, based on coherent microwave scattering (Radar) from Resonance Enhanced Multi-Photon Ionization (REMPI) in air and in pure oxygen with subsequent analysis of the rotational state distribution. Rotationally resolved 2+1 REMPI spectra of molecular oxygen ($C^3\Pi(v=2) \leftarrow X^3\Sigma(v'=0)$) at different temperatures have been obtained by Radar REMPI. Rotational temperatures have been determined from the Boltzmann plots of various experiments. The overall measurements have an accuracy of ~60 °C in the pure oxygen and ~50 °C in the room air, with experiments conducted up to 500 °C.

Introduction

Accurate optical measurements of temperature are often required in reacting flows, in which high temperatures or pressures, or highly reactive environments preclude the use of physical probes. The possibility of measuring the vibrational and rotational temperatures of an individual species is also of interest for reacting environments, supersonic flows, surface interactions, and for tracking the evolution of species generated by photo induced fragmentation. Due to its rather easily accessed electronic resonance and its importance in combustion and reacting environments, molecular oxygen is chosen here for the measurement of temperatures.

Coherent microwave Rayleigh scattering (Radar) from Resonance Enhanced Multi-Photon Ionization (REMPI) has recently been demonstrated to have the capability to achieve high spatial and temporal resolution measurements, which allow sensitive nonintrusive diagnostics, and accurate

determinations of concentration profiles without the use of physical probes or electrodes. It has been applied for the optical detection of argon [1], xenon [2], nitric oxide [3], carbon monoxide [4], and oxygen atom [5] etc. both within an enclosed cell and open air. In this Letter, using a frequency tunable laser, rotationally resolved 2+1 REMPI spectra of O₂ have been measured in air and in pure oxygen by Radar REMPI at different temperatures. From the spectra and analysis of the rotational state distribution, the rotational temperatures of molecular oxygen have thus been determined.

Although Radar REMPI is not a single shot measurement compared to the conventional Coherent Anti-stokes Raman Scattering (CARS) [6, 7] and Laser Induced Fluorescence (LIF) [8–10], it is very simple to set up and robust to perturbations. Compared to conventional CARS, it only uses one simple tunable laser, such as a commercial dye laser or OPO laser, as the excitation source. It only requires a simple lens to focus the beam and can be easily spatially scanned. Minimum optical alignment is required for the measurement. It only requires one optical access port. Unlike CARS, the signal to noise may even be better at lower pressure, due to the slow recombination and/or attachment processes in the REMPI plasma. Compared to LIF, a microwave homodyne transceiver system is much cheaper than an intensified CCD camera. It is more robust to perturbation and background radiation due to the separation of generation and detection systems in two spectral regions. It does not require dark environment to perform the measurements. Quenching effect, which is one of key problems in LIF, are physically avoided since the ionization from the excited states can be quicker than the collisional processes. It may even be used as a standoff approach, due to the limited radiation background in the microwave range [4].

Structure of molecular oxygen

The REMPI structure of O₂ can be summarized as the following. The ground state, O₂(X³Σ), can be best described as Hund's case (b), in which the projected component of orbital angular momentum on the molecular axis is $\Lambda' = 0$, the projected component of the spin on the molecular axis, Σ' , can take the values -1, 0, 1 and the projected total angular momentum on the molecular axis, Ω' , is not defined [11]. The splitting due to $\Sigma' = -1, 0$, and 1 leads to the hyperfine structure in the ground state, which has been denoted as F₁, F₂ and F₃, respectively. The excited state of O₂ used in this study, O₂(C³Π) can be best described as Hund's case (a), in which $\Lambda' = 1$ and Σ can take -1, 0, 1, which correspond to Ω taking the values 0, 1, 2, respectively. The Ω values lead to the hyperfine structure in the C state, which has been denoted as S₁, S₂ and S₃, respectively. The 2-photon REMPI spectra obtained in the experiments are convolutions of the hyperfine structures of the molecular oxygen, thermal Doppler

and the laser broadening. The two photon transition line strength $S_{f,g}^2$ between the excited state $C^3\Pi$, Hund's case (a), and the ground state $X^3\Sigma$, case (b), has been modeled by [12]

$$S_{f,g}^2 = \sum_{k=0,2} \frac{|\beta_k^{(2)}|^2}{2k+1} (2J+1)(2J'+1)(2N'+1) \begin{bmatrix} J' & S & N' \\ \Lambda'+\Sigma & -\Sigma & -\Lambda' \end{bmatrix}^2 \begin{bmatrix} J & k & J' \\ \Omega & -\Delta\Lambda & -\Lambda'-\Sigma \end{bmatrix}^2 \quad (1)$$

where [...] is the Wigner 3-j symbol, J is the rotational quantum number, N is total angular momentum except the spin, $\beta_k^{(2)}$ is the polarization coefficient, and primed parameters denote the ground $X^3\Sigma$ state while unprimed parameters denote the excited $C^3\Pi$ state. For linearly polarized light, terms of both $k=0$ and 2 contribute to the final line strength, $\beta_k^{(2)} = \sqrt{10/3}$, while for circularly polarized light, only $k=2$ contributes, giving $\beta_k^{(2)} = \sqrt{5}$.

The microwave scattering signal from the REMPI produced plasma is proportional to the total number of electrons inside the plasma [13], which is proportional to the total number of transitions to the continuum through the resonant two photon transition followed by the single photon ionization. The total number of transitions to the continuum is thus determined by the product of the number of molecules in the ground state and the rate of multiphoton ionization. An expression for the resulting microwave scattering signal can be written as [14]

$$E_{MW} \propto N_e = N_0 \cdot S_{f,g}^{(2)} \cdot I^2 \cdot S_{f,i} \cdot I \cdot \exp(-E_g / k_B T) \quad (2)$$

where E_{MW} is the scattering microwave electric field, N_e is total electron number inside the plasma generated by REMPI, N_0 is the total number of oxygen molecules in the laser focal region, E_g is the energy of the ground state of $X^3\Sigma$, k_B is Boltzmann constant, T is temperature, I is the intensity of the laser beam, and $S_{f,i}$ is the ionization cross section from the excited state to the ionization continuum. It should be noted that the rotational quantum number dependence of $(2J+1)$ for the Boltzmann factor cancels in the Eq. (1), accounting for the rotational degeneracy of ground state J levels.

The variation of the intensity of the rotational lines in an electronic manifold is determined by the thermal population distribution of the rotational levels. The rotational temperature can be extracted from the analysis of the rotational structures revealed in the REMPI spectra. The thermal distribution of the rotational levels is given by a statistically weighted (i.e. quantum degenerated) Boltzmann factor of $(2J+1)\exp(-E_g / k_B T)$, where the rotational level with the maximum population shifts toward higher J values with increasing temperature. If $S_{f,i}$ is assumed to be constant due to limited scanning range and the ground state population N_0 is constant during the scan time, then the Boltzmann plots can be formulated as

$$\frac{\log\left(\frac{E_{MW}}{I^3 S_{f,g}^{(2)}}\right)}{E_g} \propto -\frac{1}{k_B T} \quad (3)$$

When a region of the spectrum including numerous rotational lines is measured, a statistical fit of the Boltzmann plot gives an accurate representation of the rotational populations and thus the rotational temperature, i.e., the slope of the Boltzmann plot as shown in the Eq.(2).

Experimental results and discussions

The experimental setup is shown in the Figure 22. A frequency doubled Nd: YAG laser (Continuum Surelite SI-10) was used to pump a dye laser (Continuum ND6000, Rhodamine 6G as the dye). The output of the dye laser was frequency doubled and scanned by an automatic frequency doubling and tracking system (Continuum UVT-1). The scanning rate is set at 0.01 nm/s. The laser output was then focused by a lens with a focal length of 10 cm to generate the REMPI plasma in the pure oxygen and air at room and elevated temperatures. The gas cell was heated by a furnace, which was heated by a concrete block heater. A K type thermocouple was placed near the cell inside the furnace to control the temperature with an accuracy of ~1 K. Before entering the cell, the laser beam was split by a partially reflected mirror to monitor the laser power. The light scattered by the cell window was collected by a photo diode to trigger the data acquisition system. The positions of the spectra were calibrated according to tabulated nitrogen rotational lines.

A microwave homodyne transceiver system was used to detect the REMPI plasma [15]. A 10 dBm tunable microwave source (HP 8350B sweep oscillator, set at ~10 GHz) was first split into two channels. One was used to illuminate the ionization point through a microwave horn (WR75, 15 dB 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 ~10 GHz. After the frequency was converted down 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 time-accurate microwave scattering signal was monitored by an oscilloscope, shown in the Figure 23 for various conditions. The microwave signal was also input into an automatic data acquisition system, which recorded the rotational spectrum of oxygen as the laser was tuned.

Figure 23 shows the typical microwave scattering temporal signals from REMPI in the pure oxygen at different temperatures and pressures. Microwave scattering signals with similar temporal behavior have been obtained for the

measurements in air. Since microwave scattering is a direct measurement of the total electrons in the microplasma, the generation of the electrons by REMPI corresponds to the rising of the signal. The decay of the microwave signal is due to the loss of the electrons by three body attachment and recombinations. The decay time for pure oxygen at 60 Torr in Figure 23(a) extends to about 100 ns, whereas for 600 Torr in Figure 23(b), the decay time is on the order of 10 ns and is comparable with the laser pulse duration. The observed trend of decreasing decay time with increasing pressure and increase of the temperature is due to the three body attachment of electrons to molecular oxygen and agrees with the values in the Refs.[16,17]. The peak values averaged within 1 ns gates have been recorded to obtain the REMPI spectra, when the laser was scanned.

Figure 24 shows the comparison of REMPI spectra of air and pure oxygen at atmospheric pressure and room temperature. Bands indicating 2+2 and 3+1 REMPI of molecular nitrogen are clearly presented in the air spectrum from 283–286.8 nm [18, 19]. The prominent band representing 2+1 REMPI with the initial 2-photon transition $O_2(C^3\Pi(v=2) \leftarrow X^3\Sigma(v'=0))$ lies between 285 and 289 nm and has a slight overlap with the nitrogen REMPI bands between 283 and 286 nm. It is worth noting that in atmospheric air, the oxygen REMPI ionization with $O_2(C^3\Pi(v=2) \leftarrow X^3\Sigma(v'=0))$ is much larger than any of the nitrogen REMPI bands, which can significantly enhance the signal to noise ratio of REMPI measurements in air. Rotational lines from each branch have been identified through the comparison between the experimental and calculated results from the Eq.(1).

Figure 25 shows the comparisons of the experimental spectra of pure oxygen at (a) 60 Torr and (b) atmospheric pressure air at different temperatures. The pressures of the oxygen and air do not affect the final rotational distribution of the spectra. The spectra have better Signal to Noise Ratio (SNR) at the lower pressures due to longer lifetime of the electrons, which provides stronger integrated signals of the microwave scattering. The REMPI bands of N_2 are noticeable in Figure 25(b) from 283 to 286 nm but are significantly less obvious than the O_2 band, chiefly because N_2 has higher ionization potential than O_2 and requires 4 photons (3+1 or 2+2) to ionize as opposed to three (2+1) [19]. It should be noted that the O_2 rotational spectra have overlaps near the measurement region, especially for the two photon transition, in which all five branches of O, P, Q, R, and S are present. A perfect match of the whole rotational spectrum will involve balance of different branches and introduce large uncertainties. The rotational peaks of the S branch have even levels missing due to degeneracy and less influenced by other branches.

For temperature derivations from the S branches of the REMPI rotational spectra, Boltzmann plots for various experiments in pure oxygen and in room air are given in Figure 26(a) and (b) respectively. Based on Eq.(2), the x-axis of the Boltzmann plot is the energy of the rotational levels at the ground state, E_g from [11], and the y-axis is a log plot of the relative value of peaks in the experimental REMPI spectrum scaled by the rotational line strength, $E_{MW} / S_{f,g}$. Linear fitted

lines are plotted for every measurement by using Microsoft Excel. At room temperature, the slope of the Boltzmann line for pure oxygen gives a rotational temperature of 30 °C with an uncertainty of less than 1% and for room air yields a temperature of 25 °C, with an uncertainty of less than 1%. At elevated temperatures, the Boltzmann plots give 280 °C for a furnace temperature of $T_f = 250$ °C in pure oxygen and 223 °C for $T_f = 200$ °C in room air. The uncertainties are less than 2%. Similar measurements show 436 °C for $T_f = 500$ °C in pure oxygen and 450 °C for $T_f = 500$ °C in room air. The uncertainties for the $T_f = 500$ °C case are around 10%.

The accuracy of the Boltzmann plot temperature determination decreases with increasing temperature, mainly due to the entanglement of many rotational lines in the regions of around 286 nm. The Boltzmann plots in the Figure 26 only show the major rotational lines of S branches from S_5 to S_{25} . As the furnace temperature increases, the rotational level with the maximum population shifts toward higher J values, which lie around 286 nm and coincide with other branches within this region, yielding more uncertainty in these higher temperature derivations.

Conclusions

In conclusion, rotational temperature derivations of molecular oxygen by Radar REMPI have been demonstrated in the pure oxygen and room air. Rotationally resolved 2+1 REMPI spectra of molecular oxygen at different pressures and temperatures have been obtained. Boltzmann plots of various experiments yield good agreements of the spectrally derived temperatures with direct measurements.

Acknowledgments

This work is being supported by NSF CBET-1032523 and Air Force Office of Scientific Research.

References

1. Z. Zhang, M. N. Shneider, R. B. Miles, Phys. Rev. Lett. **98** (2007) 265005.
2. Z. Zhang, M. N. Shneider, S. Zaidi, R. B. Miles, AIAA Meeting, Miami, FL, 2007.
3. R. B. Miles, Z. Zhang, S. H. Zaidi, M. N. Shneider, AIAA J. **45** (2007) 513.
4. A. Dogariu, R. B. Miles, Appl. Opt. **50** (2011) A68.
5. A. Dogariu, J. B. Michael, M. O. Scully, R. B. Miles, Science **331** (2011) 442.
6. N. Chai, S. V. Naik, N. M. Laurendeau, R. P. Lucht, S. Roy, J. R. Gord, Appl. Phys. Lett. **93** (2008) 0911153.
7. R. P. Lucht, Opt. Lett. **12** (1987) 78.
8. J. M. Seitzman, R. K. Hanson, P. A. DeBarber, C. F. Hess, Appl. Opt. **33** (1994) 4000.
9. J. M. Seitzman, G. Kychakoff, R. K. Hanson, Opt. Lett. **10** (1985) 439.
10. S. Cheng, M. Zimmermann, R. B. Miles, Appl. Phys. Lett. **43** (1983) 143.
11. G. Herzberg, Molecular Spectra and Molecular Structure: Spectra of Diatomic Molecules, Krieger Pub Co., New York, 1989.
12. C. Mainos, Phys. Rev. A **33** (1986) 3983.
13. Z. Zhang, Ph.D. Thesis, Princeton University, Princeton, 2008.
14. Z. Zhang, M.N. Shneider, S. Zaidi, R.B. Miles, 46th AIAA Aerospace Sciences Meeting and Exhibit, 2008.
15. Z. Zhang, M. N. Shneider, Phys. Plasmas **17** (2010).
16. A. Dogariu, M. N. Shneider, R. B. Miles, Direct Measurement of Electron Loss Rate in Air, Optical Society of America, 2010, pp. JTuD2.
17. Y. P. Raizer, Gas Discharge Physics, Springer, New York, 1997.
18. S. Adams, J. Williamson, Gas Temperature Measurement in Atmospheric Nitrogen Discharge by Laser REMPI-LIF Technique, 63rd Annual Gaseous Electronics Conference and 7th International Conference on Reactive Plasmas Paris, France, 2010.
19. S. F. Adams, J. C. A. DeJoseph, J. M. Williamson, J. Chem. Phys. **130** (2009) 144316.

Appendix

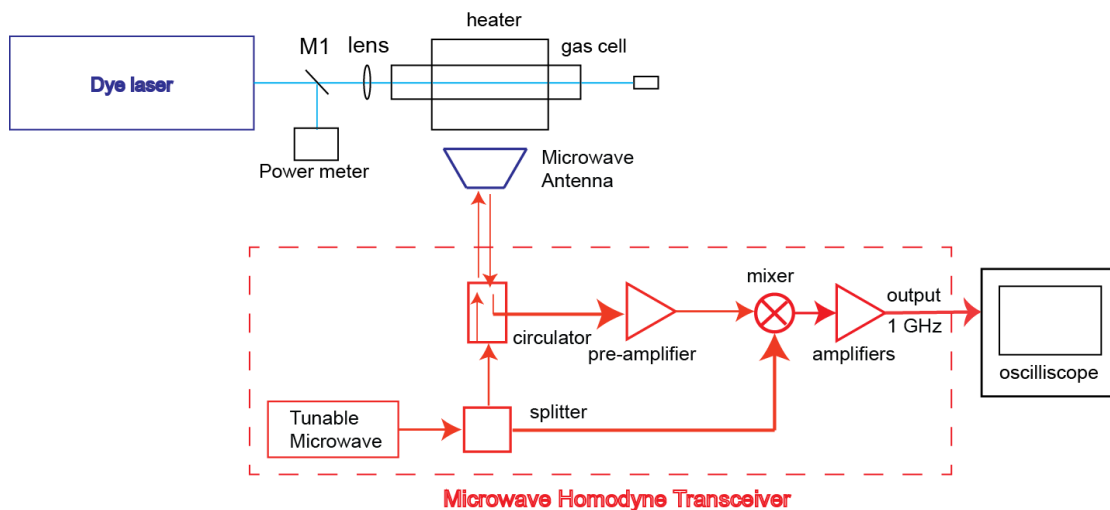


Figure 22. Experimental setup for coherent microwave scattering from the REMPI of molecular oxygen and room air at different temperatures. M_1 is a partially reflective mirror.

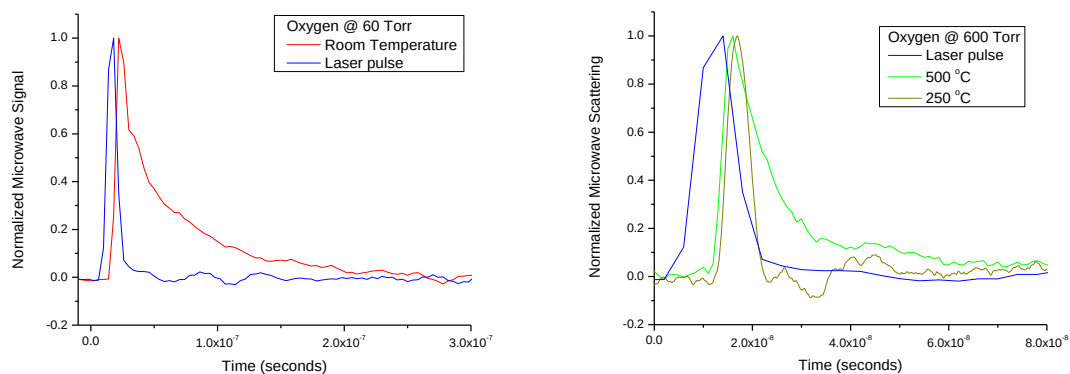


Figure 23. Typical normalized microwave scattering of the REMPI in the pure oxygen. (a) at room temperature and 60 Torr, (b) at 250 °C, 500 °C and 600 Torr. Laser wavelength is fixed at 287.5 nm and power is ~3.0 mJ/pulse.

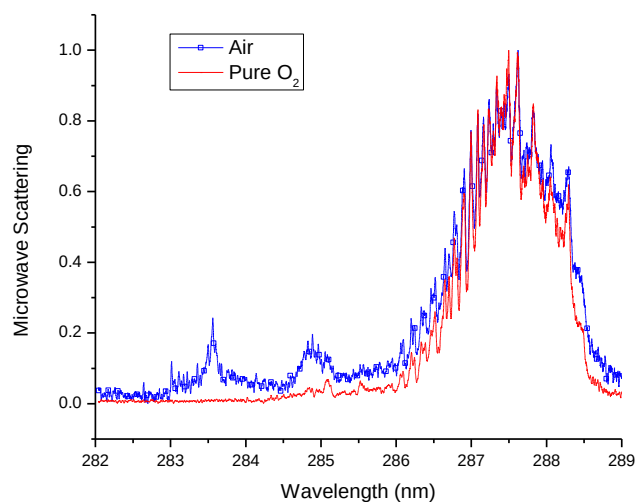


Figure 24. Comparison of experimental REMPI spectra of air (blue) and pure oxygen (red) at room temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

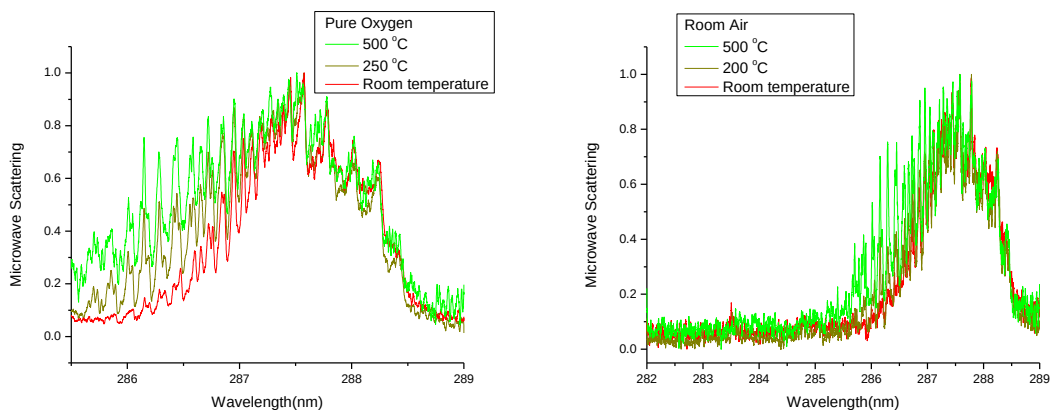


Figure 25. Comparisons of experimental REMPI spectra of the pure oxygen and air at different temperatures. (a) pure oxygen, (b) room air.

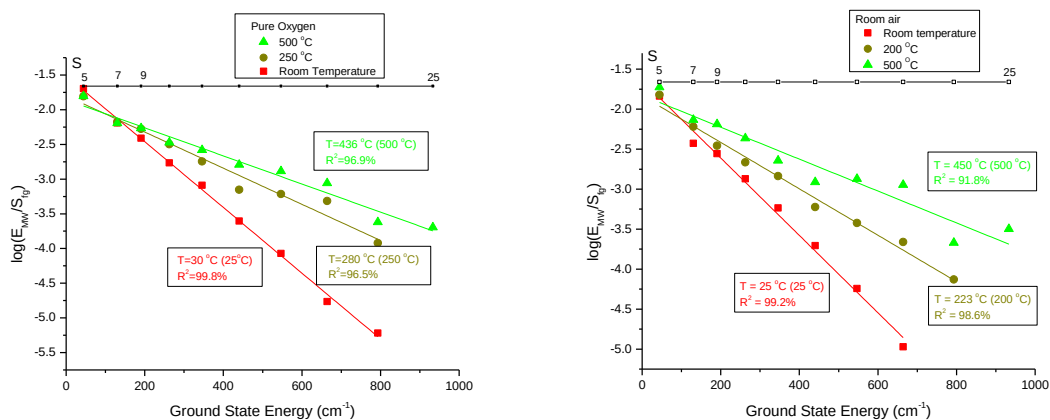


Figure 26. Boltzmann plots for oxygen temperature determination by rotational lines of S5–S25. (a) in pure oxygen and (b) in room air. The temperatures in parentheses are the furnace temperature values.

CHAPTER V
FLAME TEMPERATURE MEASUREMENTS BY RADAR
RESONANCE-ENHANCED MULTIPHOTON IONIZATION OF
MOLECULAR OXYGEN

This article, "Flame temperature measurements by radar resonance-enhanced multiphoton ionization of molecular oxygen", was received on 6 June 2012; revised on 29 August 2012; accepted on 30 August 2012, published 28 September 2012.

Author affiliations:

Yue Wu,¹ Jordan Sawyer,¹ Zhili Zhang,^{1,*} and Steven F. Adams²

¹*Mechanical, Aerospace and Biomedical Engineering, University of Tennessee of Tennessee, Knoxville TN 37996, USA*

²*Air Force Research Laboratory (AFRL/RZPE), Wright-Patterson AFB, Dayton OH 45433-7919, USA*

*Corresponding author: zzhang24@utk.edu

Applied Optics, Vol. 51, Issue 28, pp. 6864-6869 (2012)

<http://dx.doi.org/10.1364/AO.51.006864>

Abstract

Here we report nonintrusive local rotational temperature measurements of molecular oxygen, based on coherent microwave scattering (radar) from resonance-enhanced multiphoton ionization (REMPI) in room air and hydrogen/air flames. Analyses of the rotational line strengths of the two-photon molecular oxygen $C^3\Pi(v=2) \leftarrow X^3\Sigma(v'=0)$ transition have been used to determine the hyperfine rotational state distribution of the ground $X^3\Sigma(v'=0)$ state. Rotationally resolved 2+1 REMPI spectra of the molecular oxygen $C^3\Pi(v=2) \leftarrow X^3\Sigma(v'=0)$ transition at different temperatures were obtained experimentally by radar REMPI. Rotational temperatures have been determined from the resulting Boltzmann plots. The measurements in general had an accuracy of ± 60 K in the hydrogen/air flames at various equivalence ratios. Discussions about the decreased accuracy for the temperature measurement at elevated temperatures have been presented. © 2012 Optical Society of America

OCIS codes: 280.2470, 120.6780, 300.6410, 300.6350.

Introduction

The temperature near and on the surface of a burner provides the key boundary conditions for computation and modeling; however, it is extremely difficult to characterize the temperature using pure optical methods due to reflections and scattering from the burner surface. The possibility of measuring the vibrational and rotational temperatures of a species in air, such as oxygen [1] or nitrogen [2], near the burner surface is thus of importance for reacting environments,

supersonic flows, surface interactions, and tracking the evolution of species generated by photo-induced fragmentation.

Coherent microwave Rayleigh scattering (radar) from resonance-enhanced multiphoton ionization (REMPI) has recently been demonstrated to have the capability to achieve high spatial and temporal resolution measurements, which allow highly sensitive, nonintrusive, and spatially resolved diagnostics, and accurate determinations of concentration profiles without the use of physical probes or electrodes. Radar REMPI has been applied to the optical detection of argon [3], xenon [4], nitric oxide [5], carbon monoxide [6], oxygen atom [7], methyl radicals (CH_3) [8], and 1,4-diazobicyclooctane (DABCO) [9] in the gas cell, open air, weakly ionized plasma, and atmospheric pressure flames. Compared to the laser-induced fluorescence (LIF) system, temperature distribution within a few millimeters above the burner surface could be easily monitored by radar REMPI without considering the optical collection issues and the limitation of perturbations within the flame. Compared to conventional REMPI spectroscopy, radar REMPI is in situ and nonintrusive.

Additionally, it tracks the temporal evolution of the REMPI plasma. Previously, we have demonstrated that radar REMPI of molecular oxygen can be used as a molecular probe for temperature measurement [1]. Local temperatures above the burner could be measured by radar REMPI regardless of the process of combustion. While the general chemiluminescence methods are limited to the excited species within the flame, temperatures both in the flame front and beneath the flame can be monitored by probing the ground-state molecular oxygen, which is conveniently present in almost every air environment. We have achieved an accuracy of $\pm 60^\circ\text{C}$ in the closed cell filled with pure oxygen and $\pm 50^\circ\text{C}$ in the room air, with experiments conducted up to 500°C .

In this paper, the molecular oxygen REMPI spectral structure is discussed in detail. By using a frequency tunable laser, rotationally resolved 2+1 REMPI spectra of O_2 have been experimentally measured in hydrogen/air and methane/air flames in a calibrated Hencken burner. From the spectra and analyses of the rotational state distributions, the rotational temperatures of molecular oxygen and flames have thus been determined.

Molecular oxygen REMPI structure

The REMPI structure of O_2 can be summarized as the following. The molecular oxygen ground state, $X^3\Sigma(v'=0)$, can be best described as Hund's case (b), in which the projected component of orbital angular momentum on the molecular axis is $\Lambda'=0$, the projected component of the spin on the molecular axis Σ' can take -1, 0, 1, and the projected total angular momentum on the molecular axis Ω' is not defined [10]. The hyperfine splitting due to Λ' leads to the rotational

term values G_1 , G_2 , and G_3 in the ground state. The $O_2(X^3\Sigma(v'=0))$ ground-state term energy can be expressed as

$$\begin{aligned} G_1 &= B_v J(J+1) - D_v J^2(J+1)^2 + (2J+3)B_v - L - \sqrt{(2J+3)^2 B_v^2 + L^2 - 2LB_v} + G(J+1), \\ G_2 &= B_v J(J+1) - D_v J^2(J+1)^2, \\ G_3 &= B_v J(J+1) - D_v J^2(J+1)^2 + (2J+1)B_v - L - \sqrt{(2J-1)^2 B_v^2 + L^2 - 2LB_v} + GJ, \end{aligned}$$

where the molecular constants for the ground-state $X^3\Sigma(v'=0)$ are well known [11].

The excited $O_2(C^3\Pi(v=2))$ state, used as an intermediate state in this study, can be best described as Hund's case (a), which for $\Lambda=1$, Σ can take -1, 0, 1, and Ω can take 0, 1, 2, respectively. The coupling of these angular momenta results in hyperfine splitting and leads to the respective rotational term values F_1 , F_2 and F_3 in the C state. For the excited-state $C^3\Pi(v=2)$ of the molecular oxygen, the energy levels are thus calculated by

$$\begin{aligned} F_1(\Omega=0) &= n_{01} + B_{eff1} J(J+1) - D_{v1} J^2(J+1)^2, \\ F_2(\Omega=1) &= n_{02} + B_{eff2} J(J+1) - D_{v2} J^2(J+1)^2, \\ F_3(\Omega=2) &= n_{03} + B_{eff3} J(J+1) - D_{v3} J^2(J+1)^2, \end{aligned}$$

where the derived constants of the excited-state $C^3\Pi(v=2)$ of molecular oxygen have been published by Sur et al.[12,13]. It should be noted that there is a much greater uncertainty in the molecular constants for the $C^3\Pi(v=2)$, compared to those of the ground state. The values we adopted are listed in XXXX, based on our previous experimental and computational study of the REMPI spectra of molecular oxygen.

Both the ground and excited states contribute to the hyperfine structures in the REMPI spectra, which present a challenge in resolving the common two-photon rotational branches of O, P, Q, R, and S. The REMPI spectra include multiple lines for each branch due to the existence of hyperfine splitting of the ground (G_1 , G_2 and G_3) and the excited state (F_1 , F_2 and F_3). Here we adopted the convention of adding subscripts of hyperfine structures to the rotational branch, where, for example, S_{13} represents the S branch which originates from G_3 and transits to F_1 . The linewidth of the laser in this experiment is wide enough such that the spectrum cannot be resolved for the ground-state hyperfine splitting. The two-photon transition line strength, $T_{f,g}^2$, between the excited-state $C^3\Pi(v=2)$ of Hund's case (a) and the ground-state $X^3\Sigma(v'=0)$ of Hund's case (b) has been modeled by Wu *et al.* and Mainos [1,11] and is expressed as

$$T_{f,g}^2 = \sum_{k=0,2} \frac{|\beta_k^{(2)}|^2}{2k+1} (2J+1)(2J'+1)(2N'+1) \left[\begin{matrix} J' & S & N' \\ \Lambda'+\Sigma & -\Sigma & -\Lambda' \end{matrix} \right]^2 \left[\begin{matrix} J & k & J' \\ \Omega & -\Delta\Lambda & -\Lambda'-\Sigma \end{matrix} \right]^2 \quad (1)$$

where [...] is the Wigner 3-j symbol, J is the rotational quantum number, N is total angular momentum except the spin, $\beta_k^{(2)}$ is the polarization coefficient, primed

parameters are for the ground state of $X^3\Sigma$ and unprimed parameters are for the excited state of $C^3\Pi$. For linearly polarized light, terms of both $k=0$ and 2 contribute to the final line strength, $\beta_k^{(2)} = \sqrt{10/3}$, while for circularly polarized light, only $k=2$ contributes and $\beta_k^{(2)} = \sqrt{5}$.

The S_{21} branch was chosen for these analyses due to the distinctness in spectral position and intensity among the experimentally observable lines at relatively low temperature ($<700\text{K}$). The calculated rotational line strengths of selected S_{21} branch transitions based on Eq. (1) are shown in Table 3, as an example. Table 3 shows detailed information of the individual transitions, including transition wavelength, the J' rotational level of the ground state, the G_1 term energy of that ground-state rotational level, and the corresponding $T_{f,g}^2$ rotational line strength, which is used in the calculation of O_2 rotational temperature in Section 3.

At elevated temperature, the S branch lines become congested due to the overlap of multiple branches, including O and P branches, between 286 and 287.5 nm. A further shift in the population distribution toward higher rotational states due to increased temperature results in a different set of spectral peaks that is distinguishable between 285 and 286.5 nm, which is utilized for the elevated temperature extraction. The REMPI rotational lines used for temperature measurements greater than 700 K in the hydrogen/air flame are shown in Table 4. Based on the known standard temperature of the flames in the Hencken burner, rotational lines with maximum sensitivity within that temperature range were chosen.

The microwave scattering signal from the REMPI produced plasma is proportional to the total number of electrons inside the plasma [12], which is proportional to the total number of electron excitations to the continuum through the resonant two-photon transition followed by the single-photon ionization. The total number of electron excitations to the continuum is thus determined by the product of the number of molecules in the ground state and the rate of multiphoton ionization. An expression for the resulting microwave scattering signal for a given two-photon transition from state g to f can be written as

$$E_{MW} \propto N_e = N_0 \cdot T_{f,g}^{(2)} \cdot I^2 \cdot T_{f,i} \cdot I \cdot \exp\left(-\frac{E_g}{k_B T}\right), \quad (2)$$

where E_{MW} is the scattering microwave electric field, N_e is total electron number inside the plasma generated by REMPI, N_0 is the total number of oxygen molecules in the laser focal region, E_g is the energy of the ground state of $X^3\Sigma$, k_B is Boltzmann constant, T is temperature, I is the intensity of the laser beam, and $T_{f,i}$ is the ionization cross section from the excited state to the ionization continuum.

A rotational temperature can be extracted from the analysis of the ground state rotational energy distribution derived from the REMPI spectrum. The

thermal distribution of the rotational levels is given by a statistically weighted (i.e. quantum degenerated) Boltzmann factor of $J(J+1)\exp(-E_g / k_B T)$. The rotational level with the maximum population shifts toward higher J values with increasing temperature. This shift is reflected in the REMPI spectrum of the molecule. The variation of the intensity of the rotational lines in an electronic manifold is given by the thermal population distribution of the rotational levels. If $T_{f,i}$ is assumed to be constant over the limited laser wavelength scanning range and the ground-state population N_0 is constant during the scan time, the Boltzmann plots can be formulated as

$$\frac{\log\left(\frac{E_{MW}}{I^3 T_{f,g}^{(2)}}\right)}{E_g} \propto -\frac{1}{k_B T} \quad (3)$$

When a region of the spectrum including numerous rotational lines is measured, a statistical fit of the Boltzmann plot gives an accurate measurement of the rotational populations and thus the rotational temperature, i.e., the slope of the Boltzmann plot as shown in the Eq. (3).

Experimental setup

The experimental setup is shown in the Figure 27. A frequency-doubled Nd:YAG laser (Continuum Surelite SI-10) was used to pump a dye laser (Continuum ND6000, Rhodamine 6 G as the dye). The output of the dye laser was frequency doubled by an automatic frequency-doubling and tracking system (Continuum UVT-1). The laser output was then focused by a lens with a focal length of 10 cm to generate the REMPI plasma in pure oxygen and air at room and elevated temperatures. The gas cell is heated by a furnace, which consists of a concrete block heater with an accuracy of ± 1 K. Before entering the cell, the laser beam was split by a partially reflected mirror to monitor the laser power. Laser light scattered by the cell was collected by a photodiode to trigger the data acquisition system. The spectral wavelengths were calibrated according to well-known nitrogen rotational lines.

A microwave homodyne system was used to detect the REMPI plasma [13]. A 10 dBm tunable microwave source (HP 8350B sweep oscillator, set at ~ 10 GHz) was first split into two channels. One channel was used to illuminate the ionization point through a microwave horn (WR75, 15 dB 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 ~ 10 GHz. After the frequency was converted down 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 time-accurate microwave scattering signal was monitored by an oscilloscope. The microwave signal was also input into an automatic data acquisition system, which recorded the rotational spectrum of oxygen as the laser wavelength was scanned.

A Hencken burner with a 1 in. by 1 in. square exit geometry (Technologies for Research, Model: RT1×1) was used to generate a laminar and near adiabatic methane/air flame with sufficient optical access. This burner has been widely used as a test bed for laser diagnostic techniques [14–20]. The Hencken burner produces a unique, nearly adiabatic flame that is lifted from the burner surface since the fuel and oxidizer streams are separated until the exit of the burner. The fuel tubes have an inner diameter of approximately 0.54 mm and an outer diameter of approximately 0.83 mm. The oxidizer honeycomb is a hexagonal pattern with cell size of approximately 0.90 mm. The flame temperature in the Hencken burner is approximately at the adiabatic flame temperature [21]. This standard temperature is compared in the next section to our experimentally determined rotational temperature using radar REMPI of molecular oxygen.

Results and Discussion

Figure 28 shows the REMPI spectrum and Boltzmann plot for molecular oxygen in room air. At room temperature, the S_{21} branches of molecular oxygen are distinct as shown in the figure. The Boltzmann plot based on $S_{21}(J' = 3 - 25)$ shows the fitted temperature is 293 K, with an uncertainty of 2%.

Figure 29 shows the REMPI spectra of molecular oxygen in the hydrogen/air flames. The S_{21} branches are still distinct; however, the accuracy to determine the rotational temperature decreases, mainly due to the entanglement of many rotational lines in the region around 286 nm. As the temperature increases, the rotational level with the maximum population shifts toward higher J' values, which correspond to transitions around 286 nm. The entanglement of multiple rotational lines besides the S branches around this spectral region yields more uncertainties in the measurements.

The Boltzmann plots in Figure 30 show the temperature determination using only the most sensitive rotational lines, which are listed in Table 4 and include the branches of O and P in the range of 285–286.5 nm. Fairly good agreements between our molecular oxygen radar REMPI rotational temperature measurements and the adiabatic flame temperature have been achieved in the flames. As shown graphically in Figure 30, for equivalence ratios of 0.357 (H_2 :air = 2:14) and 0.536 (H_2 :air = 3:14) with respective adiabatic flame temperatures of 1281 K and 1658 K, the experimental O_2 rotational temperatures were found to be 1345 K and 1608 K, respectively. Table 5 gives the details about temperature measurements in pure oxygen, room air, and H_2 /air flame.

Conclusions

Nonintrusive local rotational temperature measurements of molecular oxygen, based on radar REMPI in pure oxygen, air, and the hydrogen/air flames were conducted with subsequent analysis of the rotational state distribution. Rotationally resolved 2+1 REMPI spectra of molecular oxygen ($C^3\Pi(v=2) \leftarrow X^3\Sigma(v'=0)$) at different temperatures have been obtained by radar REMPI. Rotational temperatures have been determined from the Boltzmann plots of various experiments. In the flame, a line-fitting procedure has been used to determine the temperature using select transition lines of multiple branches that overlap at elevated temperatures. The overall measurements have an accuracy of 60 K in the pure oxygen, 50 K in the room air for up to 773 K, and ± 60 K in the hydrogen/air flame.

Acknowledgments

This work is being supported by the National Science Foundation (NSF) CBET-1032523 and the Air Force Office of Scientific Research.

References

1. Y. Wu, Z. Zhang, and S. F. Adams, "O₂ rotational temperature measurements by coherent microwave scattering from REMPI," *Chem. Phys. Lett.* **513**, 191–194 (2011).
2. S. Adams and J. Williamson, "Gas temperature measurement in atmospheric nitrogen discharge by laser REMPI-LIF technique," presented at the 63rd Annual Gaseous Electronics Conference and 7th International Conference on Reactive Plasmas, Paris, France, 4–8 Oct. 2010.
3. Z. Zhang, M. N. Shneider, and R. B. Miles, "Coherent microwave Rayleigh scattering from resonance-enhanced multiphoton ionization in argon," *Phys. Rev. Lett.* **98**, 265005 (2007).
4. Z. Zhang, M. N. Shneider, and R. B. Miles, "Experiments of microwave scattering of (3+1), (2+1) and (1+1) resonance enhanced multi-photon ionization," presented at the 38th AIAA Plasmadynamics and Laser Conference, Miami, Fla., 25–28 June 2007.
5. R. B. Miles, Z. Zhang, S. H. Zaidi, and M. N. Shneider, "Microwave scattering from laser ionized molecules: A new approach to nonintrusive diagnostics," *AIAA J.* **45**, 513–515 (2007).
6. A. Dogariu and R. B. Miles, "Detecting localized trace species in air using radar resonance-enhanced multi-photon ionization," *Appl. Opt.* **50**, A68–A73 (2011).
7. A. Dogariu, J. B. Michael, M. O. Scully, and R. B. Miles, "High-gain backward lasing in air," *Science* **331**, 442–445 (2011).
8. Y. Wu, A. Bottom, Z. Zhang, M. O. Timonhly, and R. K. Viswanath, "Direct measurement of methyl radicals in a methane/air flame at atmospheric pressure by radar REMPI," *Opt. Express* **19**, 23997–24004 (2011).
9. F. Rudakov and Z. Zhang, "Standoff detection of large organic molecules using Rydberg fingerprint spectroscopy and microwave Rayleigh scattering," *Opt. Lett.* **37**, 145–147 (2012).
10. G. Herzberg, *Molecular Spectra and Molecular Structure: Spectra of Diatomic Molecules*, 2nd ed. (Krieger, 1989), Chap. V, pp. 215–229.
11. C. Mainos, "Multiphoton rotational line strength in diatomic molecules and for states with Hund's case-(a) or case-(b) coupling," *Phys. Rev. A* **33**, 3983–3992 (1986).
12. Z. Zhang, "Coherent microwave scattering of laser-induced plasma," in *Mechanical and Aerospace Engineering* (Princeton University, 2008), pp. 36–46.
13. Z. Zhang and M. N. Shneider, "Measurement of plasma decay processes in mixture of sodium and argon by coherent microwave scattering," *Phys. Plasmas* **17**, 033108 (2010).
14. R. S. Barlow, R. W. Dibble, J.-Y. Chen, and R. P. Lucht, "Effect of Damkohler number on superequilibrium OH concentration in turbulent

- nonpremixed jet flames,” *Combust. Flame* **82**, 235–251 (1990).
15. F. Takahashi, W. J. Schmoll, and V. R. Katta, “Attachment mechanisms of diffusion flames,” *Symp. Int. Combust.* **27**, 675–684 (1998).
 16. J. Sakakibara and R. J. Adrian, “Whole field measurement of temperature in water using two-color laser induced fluorescence,” *Exp. Fluids* **26**, 7–15 (1999).
 17. J. Guasto and K. Breuer, “Simultaneous, ensemble-averaged measurement of near-wall temperature and velocity in steady micro-flows using single quantum dot tracking,” *Exp. Fluids* **45**, 157–166 (2008).
 18. X. Perpiñà, X. Jordà, M. Vellvehi, and J. Altet, “Hot spot analysis in integrated circuit substrates by laser mirage effect,” *Appl. Phys. Lett.* **98**, 164104 (2011).
 19. W. D. Kulatilaka, R. P. Lucht, S. F. Hanna, and V. R. Katta, “Two-color, two-photon laser-induced polarization spectroscopy (LIPS) measurements of atomic hydrogen in near-adiabatic, atmospheric pressure hydrogen/air flames,” *Combust. Flame* **137**, 523–537 (2004).
 20. S. Roy, T. R. Meyer, M. S. Brown, V. N. Velur, R. P. Lucht, and J. R. Gord, “Triple-pump coherent anti-Stokes Raman scattering (CARS): temperature and multiple-species concentration measurements in reacting flows,” *Opt. Commun.* **224**, 131–137 (2003).
 21. R. D. Hancock, K. E. Bertagnolli, and R. P. Lucht, “Nitrogen and hydrogen CARS temperature measurements in a hydrogen/air flame using a near-adiabatic flat-flame burner,” *Combust. Flame* **109**, 323–331 (1997).

Appendix

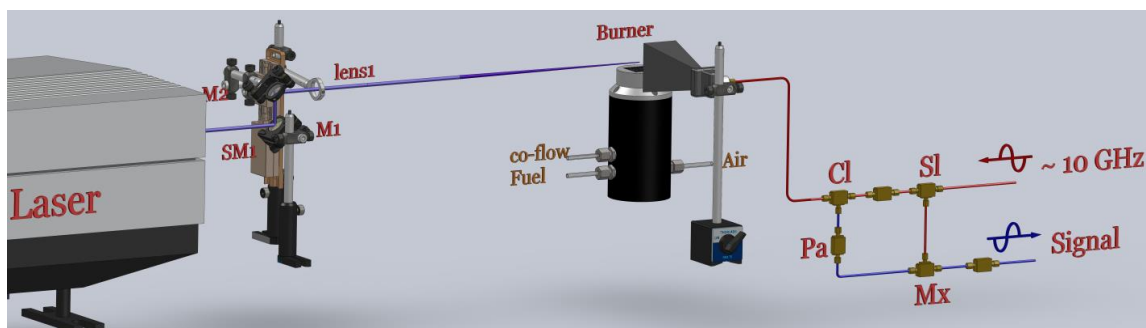


Figure 27. (Color online) Experimental setup for coherent microwave scattering from the REMPI of molecular oxygen, in flames.

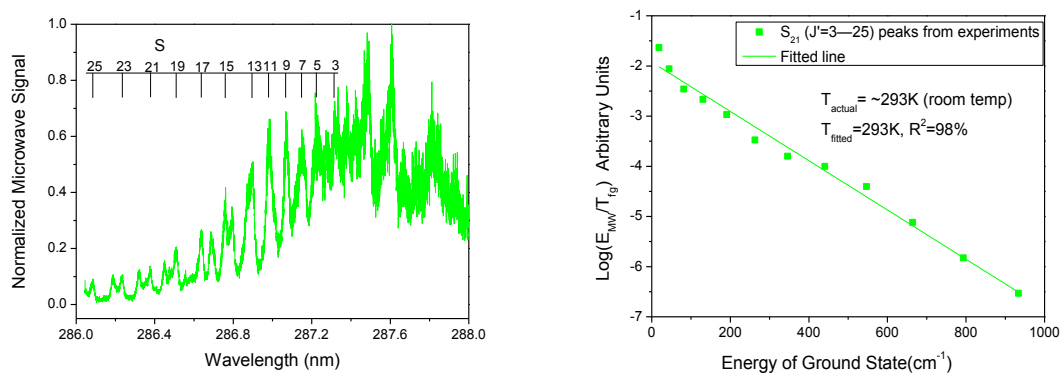


Figure 28. (Color online) (a) REMPI spectrum of molecular oxygen in room air and (b) temperature determination by the Boltzmann plot.

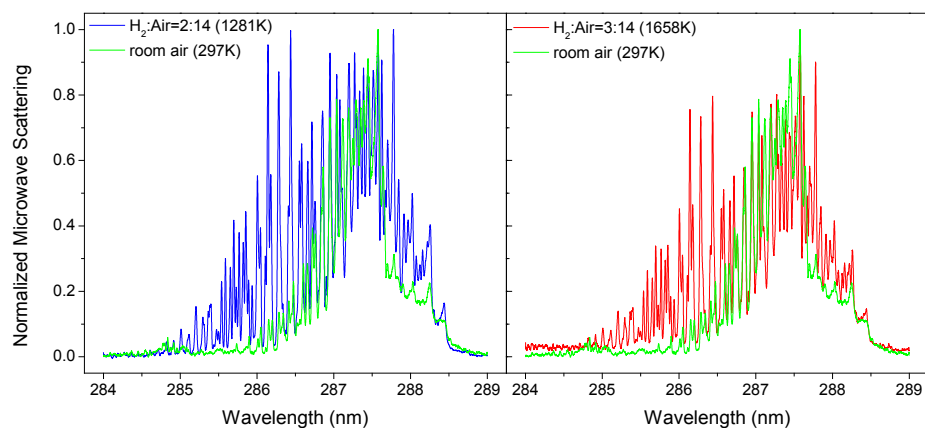


Figure 29. (Color online) REMPI spectrum of room air (green) compared to H_2 /air flame mixtures (blue 2:14 and red 3:14) with temperature determination by Boltzmann plot fit.

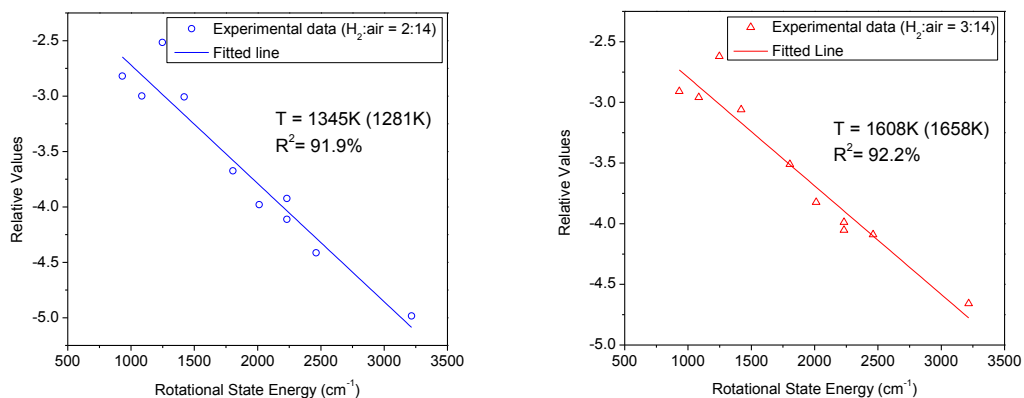


Figure 30. (Color online) Boltzmann plots, where T is the adiabatic flame temperature in the Hencken burner and in parentheses is the oxygen rotational temperature in the flames determine by the fit.

Table 2. Adopted Constants for $C^3\Pi(v=2)$ of Molecular Oxygen

cm^{-1}	$F_1(\Omega=0)$	$F_2(\Omega=1)$	$F_3(\Omega=2)$
n_0	69369(2)	69449(1)	69552(1)
B_{eff}	1.61(5)	1.65(1)	1.69(1)
D_v	$1.9(5)\times 10^{-5}$	$1.6(2)\times 10^{-5}$	$1.9(2)\times 10^{-5}$

Table 3. Selected Rotational Lines of S_{21} for Low Temperature Measurements

Wavelength (nm)	J'	$G_1(\text{cm}^{-1})$	$T_{f,g}^{(2)}$
286.09	25	933.38	14.73
286.24	23	793.08	13.73
286.38	21	664.15	12.73
286.52	19	546.62	11.72
286.65	17	440.49	10.72
286.78	15	345.79	9.72
286.88	13	262.54	8.71
286.99	11	190.74	7.70
287.09	9	130.42	6.69
287.18	7	81.57	5.66
287.26	5	44.20	4.62
287.34	3	18.33	3.50

Table 4. Selected Rotational Lines for Elevated Temperature Measurements

Branch	Wavelength (nm)	J'	$G_{\Omega+1}(\text{cm}^{-1})$	$T_{f,g}^{(2)}$
R ₃₂	285.36	41	2462.02	10.456
P ₃₁	285.37	48	3216.95	18.976
O ₁₂	286.05	39	2231.73	14.970
Q ₃₂	286.20	37	2012.57	18.740
P ₃₂	286.34	27	1085.03	9.630
O ₁₂	286.35	35	1804.59	17.740
Q ₃₁	286.45	26	931.19	13.754
P ₃₂	286.58	39	2231.73	20.5
P ₂₁	286.60	32	1420.03	20.247
Q ₁₂	286.62	29	1248.00	12.371

Table 5. Referenced and Measured Temperatures in Pure Oxygen, Room Air, and H₂/Air Flame

	Real (K)	Experimental (K)	Error	Percentage (%)
Pure oxygen	298	303	5	1.68
	523	553	30	5.74
	773	709	-64	-8.28
Room air	298	298	0	0.00
	473	496	23	4.86
	773	723	-50	-6.47
H ₂ /air flame	1281	1345	64	5.00
	1658	1608	-50	-3.02

CHAPTER VI
O₂ ROTATIONAL TEMPERATURE MEASUREMENTS IN AN
ATMOSPHERIC AIR MICRODISCHARGE BY RADAR
RESONANCE-ENHANCED MULTIPHOTON IONIZATION

This article, “O₂ rotational temperature measurements in an atmospheric air microdischarge by radar resonance-enhanced multiphoton ionization”, was received on 8 March 2013; accepted on 4 June 2013, published online 19 June 2013.

Author affiliations:

Jordan Sawyer,^{1, a)} Yue Wu,^{1, a)} Zhili Zhang,^{1, b)} and Steven F. Adams²

¹*Mechanical, Aerospace and Biomedical Engineering, University of Tennessee of Tennessee, Knoxville TN 37996, USA*

²*Air Force Research Laboratory (AFRL/RZPE), Wright-Patterson AFB, Dayton OH 45433-7919, USA*

a) The first two authors contributed equally to this work.

b) Corresponding author: z Zhang24@utk.edu

Journal of Applied Physics, Vol. 113, No. 233304, 2013

DOI: 10.1063/1.4811533.

Abstract

Nonintrusive spatially resolved rotational temperature measurements in an atmospheric air microdischarge are presented. The measurements were based on coherent microwave Rayleigh scattering (Radar) from resonance-enhanced multiphoton ionization of molecular oxygen. The open air DC microdischarge source operated in a stable “normal-glow” mode and pin-to-pin electrodes spaced 1.3 mm apart. The second harmonic of a tunable dye laser beam was focused between the two electrodes and scanned between 286 and 288 nm. Coherent microwave Rayleigh scattering was used to collect the two-photon rotational spectra of O₂ at $C^3\Pi(v=2) \leftarrow X^3\Sigma(v'=0)$ transitions. The Boltzmann plots from analyses of the O₂ rotational lines determined local rotational temperatures at various axial locations between the electrodes. The molecular oxygen rotational temperature varied from ~1150 K to ~1350 K within the discharge area. The measurements had an accuracy of ~±50 K. © 2013 AIP Publishing LLC.

Introduction

The advent of stable microdischarges dates back to the work of White in the 1950s [1] and gained much attention in spatially confined cavities in the 1990s [2, 3]. Numerous applications, including plasma ignition [4], vacuum ultraviolet (VUV) light sources [5], nanoparticle synthesis [6, 7], and biomedical research [8, 9], have been investigated. Microdischarge devices take advantage of the scaling of breakdown voltage with the product of pressure and gap distance (pd) as described by Paschen’s Law [10]. Typically, to maintain the stability of

“normal-glow” discharges at atmospheric pressure, the inter-electrode separation is confined to distances on the order of 1 mm or less [11]. This small spacing leads to the generation of a non-thermal or “cold” plasma. A striking property of these non-equilibrium plasmas is that the electron temperature, T_e , is often several orders of magnitude larger than the gas temperature, T_g [11, 12]. This excess electron energy can be channeled to drive specific optical or chemical processes at relatively low gas temperature, which opens microdischarges to the wide range of applications previously mentioned.

Although tremendous progress has been made in the area of plasma diagnostics in microdischarges [12], many fundamental properties, such as temperature, are still not satisfactorily measured. A non-thermal plasma is described, not by a single temperature, but by a set of temperatures including electron temperature (T_e) relating to the kinetic energy distribution of the electrons, as well as several molecular temperatures, T_{trans} , T_{vib} , and T_{rot} relating to the translational, vibrational, and rotational energies of the molecules. Typically, the temperature set in a non-thermal plasma will have the characteristic of $T_e \gg T_{vib} \gg T_{trans} = T_{rot}$, where T_{trans} and T_{rot} are commonly identified as the gas temperature, T_g . The gas temperature in these non-thermal plasmas can range from near room temperature for monatomic gases such as argon to above 2000 K in molecular gases such as air [11, 13] and is highly dependent on discharge source parameters such as electrical current.

Many optical diagnostics techniques for temperature measurements in plasmas are not well suited for microdischarge due to limited spatial resolution or a need for additional gas seeding. The most widely published diagnostic works involve determining rotational temperature by optical emission spectroscopy (OES) of the N_2 second positive system [14–16]. Unfortunately, the spatial and temporal resolutions achievable by these methods have stringent limitations. Additionally, OES is limited for certain species in the microplasma [17]. Another temperature measurement uses an analysis of broadening of the H_β transition of atomic hydrogen including Doppler, Stark, and van der Waals broadening. But it involves hydrogen seeding, which complicates the overall plasma composition [18]. Cavity Ringdown spectroscopy is a line-of-sight temperature measurement which has limited spatial resolution [17]. Overall, the diagnostic tools available for microdischarge analysis in atmospheric air are scarce and restricted, in some way, what can be accurately derived from the experimental process.

Here, coherent microwave scattering (Radar) from Resonance-Enhanced Multiphoton Ionization (REMPI) boasts excellent spatial and temporal resolutions. Radar REMPI has previously been demonstrated for local rotational temperature measurements of molecular oxygen in static cell [19] and flame [20] environments. In this work, Radar REMPI measurements of the local O_2 rotational temperature within an atmospheric air microdischarge are presented. These measurements are performed at eight axial locations between pin-to-pin electrodes; this allowed for an axial temperature distribution within the discharge region to be determined.

Molecular oxygen structure and REMPI scheme

The 2+1 REMPI scheme used here in O_2 with an intermediate $C^3\Pi(v=2) \leftarrow X^3\Sigma(v'=0)$ transition was described in detail in our previous publications [19, 20]. The molecular oxygen ground state, $O_2(X^3\Sigma(v'=0))$, can be best described as Hund's case (b), and the $O_2(X^3\Sigma(v'=0))$ ground-state term energy can be expressed as

$$G_1 = B_v J(J+1) - D_v J^2(J+1)^2 + (2J+3)B_v - L - \sqrt{(2J+3)^2 B_v^2 + L^2 - 2LB_v} + G(J+1),$$

$$G_2 = B_v J(J+1) - D_v J^2(J+1)^2,$$

$$G_1 = B_v J(J+1) - D_v J^2(J+1)^2 + (2J+1)B_v - L - \sqrt{(2J-1)^2 B_v^2 + L^2 - 2LB_v} + GJ,$$

where the molecular constants above for the ground-state $X^3\Sigma(v'=0)$ are well known [21]. The molecular oxygen excited state $O_2(C^3\Pi(v=2))$, used as an intermediate state in the experiments, can be best described as Hund's case (a). The energy levels for the excited-state $O_2(C^3\Pi(v=2))$ are thus expressed by

$$F_1(\Omega=0) = n_{01} + B_{eff1} J(J+1) - D_{v1} J^2(J+1)^2,$$

$$F_2(\Omega=1) = n_{02} + B_{eff2} J(J+1) - D_{v2} J^2(J+1)^2,$$

$$F_3(\Omega=2) = n_{03} + B_{eff3} J(J+1) - D_{v3} J^2(J+1)^2,$$

where the derived constants of the excited-state $C^3\Pi(v=2)$ of molecular oxygen are listed in Table 6 based on our previous experimental and computational study of the REMPI spectra of molecular oxygen. Both the ground and excited states contribute to the hyperfine structures in the REMPI spectra. The two-photon transition line strength, $T_{f,g}^2$, between the excited-state $C^3\Pi(v=2)$ and the ground-state $X^3\Sigma(v'=0)$ has been modeled and expressed as

$$T_{f,g}^2 = \sum_{k=0,2} \frac{|\beta_k^{(2)}|^2}{2k+1} (2J+1)(2J'+1)(2N'+1) \left[\begin{matrix} J' & S & N' \\ \Lambda' + \Sigma & -\Sigma & -\Lambda' \end{matrix} \right]^2 \left[\begin{matrix} J & k & J' \\ \Omega & -\Delta\Lambda & -\Lambda' - \Sigma \end{matrix} \right]^2 \quad (1)$$

where [...] is the Wigner 3-j symbol, J is the rotational quantum number, N is total angular momentum except the spin, $\beta_k^{(2)}$ is the polarization coefficient, primed parameters are for the ground state of $X^3\Sigma$ and unprimed parameters are for the excited state of $C^3\Pi$. For linearly polarized light, terms of both $k=0$ and 2 contribute to the final line strength, $\beta_k^{(2)} = \sqrt{10/3}$, while for circularly polarized light, only $k=2$ contributes and $\beta_k^{(2)} = \sqrt{5}$.

In the previous O_2 rotational temperature study [19], the S_{21} branch was chosen for the temperature analyses due to the distinctness in spectral position and intensity among the experimentally observable lines at relatively low temperature (<700 K). At elevated temperature, the S branch lines become congested due to the overlap of multiple branches, including the other four common branches O, P, Q, and R [20]. Figure 31 shows a comparison of experimental spectra of molecular oxygen at low temperature in air (~300 K) and

at a moderately high temperature in an air microdischarge (~1200 K), respectively. The population distribution in the discharge was shifted toward higher rotational states due to the increased temperature, which visibly enhanced several spectral peaks between 286.0 and 288.0 nm and enabled more branches besides S_{21} to be involved in the higher temperature analyses in this paper.

The microwave scattering signal from the REMPI produced plasma is proportional to the total number of electrons inside the plasma, which is proportional to the total number of electron excitations to the continuum through the resonant two photon transition followed by the single photon ionization [22]. The total number of electron excitations to the continuum is thus determined by the product of the number of molecules in the ground state and the rate of multiphoton ionization. An expression for the resulting microwave scattering signal for a given two photon transition from state g to f can be written as

$$E_{MW} \propto N_e = N_0 \cdot T_{f,g}^{(2)} \cdot I^2 \cdot T_{f,i} \cdot I \cdot \exp\left(-\frac{E_g}{k_B T}\right) \quad (2)$$

where E_{MW} is the scattering microwave electric field, N_e is total electron number inside the plasma generated by REMPI, N_0 is the total number of oxygen molecules in the laser focal region, E_g is the energy of the ground state of $X^3\Sigma$, k_B is Boltzmann constant, T is temperature, I is the intensity of the laser beam, and $T_{f,i}$ is the ionization cross section from the excited state to the ionization continuum.

A rotational temperature can be extracted from the analysis of the ground state rotational energy distribution derived from the REMPI spectrum. The thermal distribution of the rotational levels is given by a statistically weighted (i.e. quantum degenerated) Boltzmann factor of $J(J+1)\exp(-E_g / k_B T)$. The rotational level with the maximum population shifts toward higher J values with increasing temperature. This shift is reflected in the REMPI spectrum of the molecule. The variation of the intensity of the rotational lines in an electronic manifold is given by the thermal population distribution of the rotational levels. If $T_{f,i}$ is assumed to be constant over the limited laser wavelength scanning range and the ground state population N_0 is constant during the scan time, the Boltzmann plots can be formulated as

$$\log(E_{MW} / I^3 T_{f,g}^{(2)}) / E_g \propto -(k_B T)^{-1}. \quad (3)$$

When a region of the spectrum including numerous rotational lines is measured, a statistical fit of the Boltzmann plot gives an accurate measurement of the rotational populations and thus the rotational temperature, i.e., the slope of the Boltzmann plot as shown in the Eq. (3).

Experimental setup

The experimental setup of O₂ rotational temperature measurement in a DC air microdischarge is shown in Figure 32. An Nd: YAG laser was used to pump a dye laser with Rhodamine 6G as the dye. The output of the dye laser was frequency doubled by an automatic second harmonic generation and tracking system allowing tunable ultraviolet radiation between 286 and 288 nm. The ultraviolet laser beam (6–8 mJ/pulse), from the tracking system, was first reflected by a pair of mirrors (M1 and M2) on a vertical transition stage, then focused by a lens ($f = 25$ mm) to generate the REMPI plasma within the atmospheric air microdischarge. As a rough estimate of the beam diameters, the waist size of the focused light beam is $1.5\text{ }\mu\text{m}$ with a depth of focus of $13\text{ }\mu\text{m}$ at the focal spot for an ideal Gaussian beam. A transition stage was employed in the experiment to vertically move the laser focal point precisely along the interelectrode axis using a stepper motor (SM1). The first eight sequential pictures in Figure 33 approximately show the position of laser focal points by generating laser-induced breakdown between the two electrodes.

A microwave homodyne system (MDS) was used to detect the REMPI plasma [23]. A 10 dBm tunable microwave source was first split into two channels. One channel was used to illuminate the ionization point through a microwave horn. 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 ~ 10 GHz. After frequency was converted down 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 time-accurate microwave scattering signal was monitored by an oscilloscope. The microwave signal was also input into an automatic data acquisition system, which recorded the rotational spectrum of oxygen as the laser wavelength was scanned.

A 5 kV maximum dc power supply was used in series with a 1 M Ω load resistor to energize the microdischarge. The air microdischarge was generated by a pin-to-pin electrode configuration with an inter-electrode gap of 1.30 mm. In the experiments, a 4.8 kV was applied by the dc power supplier, which provided the microdischarge with a reasonable electrical and spatial stability. The majority of the high voltage dropped across the load resistor with the remaining 78 ± 2 V dropping across the electrode gap while microdischarge current fluctuated between 4.60 mA and 4.73 mA. The microdischarge observed during the experiments is shown in the last two photographs in Figure 33. The plasma operated in a “normal glow” mode for REMPI temperature measurements. The discharge was reasonably stable and was not disturbed by the focused laser beam. However, when the laser beam focal spot was positioned too close to the anode or cathode, the microwave detection system obtained strong oscillating

signals. This was possibly caused by the high energy electrons and molecular ions from the REMPI process near anode and cathode, respectively. Hence, the temperature distribution was measured at eight different axial positions between the electrodes, equally spaced at 0.10 mm intervals, but with an offset distance of 0.28 mm from the anode and cathode. Images of air breakdown emission induced by the intense laser beam spot are shown in the first eight photographs of Figure 33, indicating the laser focal positions between the two electrodes with no discharge. Compared to the finite radial width of the microdischarge (<0.4 mm), the depth of focus of the laser beam ($13\text{ }\mu\text{m}$) was much smaller. So while the microdischarge was operating, the laser focal spot was centered radially in the plasma and confined to a region without a significant radial variation in temperature. With the microdischarge on, the focal region was pre-ionized by the plasma and the laser did not induce a more expansive breakdown, in the air, leaving the microwave scattering signal confined to the depth of focus region within the plasma. The environment inside the plasma was quite harsh and different from our previous experimental situations (i.e., pure oxygen in cell and room air); however, detection of the microwave radiation scattered by REMPI electrons was not impeded by background radiation from the air microdischarge. In fact, the spectra of O_2 were reasonably undisturbed by the microdischarge and fairly good and repeatable experimental data were obtained in this electrically and optically active environment (Figure 31). It is assumed that any heating of the air by the laser beam is negligible since the duty cycle of the laser pulse is small and relatively low average power compared to the microdischarge power.

Results and Discussion

Eight separate spectra of molecular oxygen were analyzed corresponding to the eight different axial positions probed in the microdischarge. The spectrum shown in Figure 34 is for the uppermost scanning position along the microdischarge axis which was 0.28 mm away from the anode. The red circle points in Figure 34 were the peak values extracted from the analysis of the molecular oxygen ground state rotational energy distribution derived from the REMPI spectrum. The transition assignments of these peak points are shown in Table 7.

After all the peak points were assigned in the eight spectra with the branch information shown in Table 7, Boltzmann plots of the selected rotational lines were generated as shown in the following Figure 35. In each Boltzmann plot, a linear curve fit was applied to the peak values of the selected rotational lines. The R-squared value and slope of the fitted line are shown in the left bottom corner of each figure. The temperature at each scanning point was determined by the slope of the linear curve fit.

The O_2 rotational temperature distribution within the microdischarge was derived from the Boltzmann plots in Figure 35, which provided a determination of the O_2 ground-state population distributions at the local positions in the

atmospheric microdischarge. The axial temperature distribution of the microdischarge was obtained and is shown in Fig. 6. Due to the characteristics of the Boltzmann plot and linear fit, the variation in rotational temperature was highly sensitive to small changes in the slope of the fitted line. Hence this approach could precisely track temperature variation, however, the temperature uncertainties were relatively large ($\sim \pm 50$ K in Figure 36) as a trade-off in accuracy. The scanning resolution was 0.10 mm, as mentioned above. This resolution was small enough to reveal the basic envelope of the temperature distribution for a normal glow discharge within 1.30 mm between two electrodes with a pin-to-pin configuration.

Within our pin-to-pin electrode configuration, depending on the applied voltage and current through the gap, the microdischarge can operate in different modes, including a normal glow discharge or an arc discharge mode, where the gas temperature is dependent on the mode. Since the experiment here is operating in a relatively low-temperature standard glow discharge mode, the present temperature measurement is comparable to previous measurements by Laux et al [12] and Staack et al [16]. The spatial temperature variations roughly correspond to different regions of negative glow (NG), Faraday space (FS), and positive column (PC) within the normal glow discharge.

Conclusions

This work presents a new diagnostic tool for determining local rotational temperatures in atmospheric air microdischarges. Radar REMPI measurements were made at eight different axial locations in a stable “normal-glow” microdischarge between two pin electrodes. Local rotational temperatures were obtained from the 2p1 REMPI spectra of molecular oxygen $C^3\Pi(v=2) \leftarrow X^3\Sigma(v'=0)$ transition as determined by Radar REMPI. The axial temperature distribution within the microdischarge with a 1.3 mm electrode spacing was determined.

Acknowledgements

This work was supported by NSF CBET-1032523 and Air Force Office of Scientific Research.

References

1. A. D. White, "New hollow cathode glow discharge," *J. Appl. Phys.* **30**(5), 711–719 (1959).
2. K. H. Schoenbach, R. Verhappen, T. Tessnow, F. E. Peterkin, and W. W. Byszewski, "Microhollow cathode discharges," *Appl. Phys. Lett.* **68**(1), 13–15 (1996).
3. F. Iza, G. J. Kim, S. M. Lee, J. K. Lee, J. L. Walsh, Y. T. Zhang, and M. G. Kong, "Microplasmas: sources, particle kinetics, and biomedical applications," *Plasma Process. Polym.* **5**(4), 322–344 (2008).
4. S. V. Pancheshnyi, D. A. Lacoste, A. Bourdon, and C. O. Laux, "Ignition of propane–air mixtures by a repetitively pulsed nanosecond discharge," *IEEE Trans. Plasma Sci.* **34**(6), 2478–2487 (2006).
5. B. Ren'an, S. Mingdong, W. Zhongrui, J. Jing, H. Wenbo, Q. Feng, W. Wenjiang, and Z. Jintao, "Development of 146nm vacuum UV light source," *Phys. Procedia* **32**, 477–481 (2012).
6. W.-H. Chiang and R. M. Sankaran, "Microplasma synthesis of metal nanoparticles for gas-phase studies of catalyzed carbon nanotube growth," *Appl. Phys. Lett.* **91**(12), 121503-3 (2007).
7. C. Richmonds and R. M. Sankaran, "Plasma-liquid electrochemistry: Rapid synthesis of colloidal metal nanoparticles by microplasma reduction of aqueous cations," *Appl. Phys. Lett.* **93**(13), 131501-3 (2008).
8. J. Goree, L. Bin, D. Drake, and E. Stoffels, "Killing of *S. Mutans* bacteria using a plasma needle at atmospheric pressure," *IEEE Trans. Plasma Sci.* **34**(4), 1317–1324 (2006).
9. J. Y. Kim, Y. Wei, J. Li, and S.-O. Kim, "15- μ m-sized single-cellular level and cell-manipulatable microplasma jet in cancer therapies," *Biosens. Bioelectron.* **26**(2), 555–559 (2010).
10. F. Paschen, "Ueber die zum Funkenubergang in Luft, Wasserstoff und Kohlensaure bei verschiedenen Drucken erforderliche Potentialdifferenz," *Ann. Phys.* **273**(5), 69–96 (1889).
11. R. Foest, M. Schmidt, and K. Becker, "Microplasmas, an emerging field of low-temperature plasma science and technology," *Int. J. Mass Spectrom.* **248**(3), 87–102 (2006).
12. C. O. Laux, T. G. Spence, C. H. Kruger, and R. N. Zare, "Optical diagnostics of atmospheric pressure air plasmas," *Plasma Sources Sci. Technol.* **12**(2), 125 (2003).
13. K. H. Becker, K. H. Schoenbach, and J. G. Eden, "Microplasmas and applications," *J. Phys. D: Appl. Phys.* **39**(3), R55 (2006).
14. A. N. Goyette, J. R. Peck, Y. Matsuda, L. W. Anderson, and J. E. Lawler, "Experimental comparison of rotational and gas kinetic temperatures in N_2 and He- N_2 discharges," *J. Phys. D: Appl. Phys.* **31**(13), 1556 (1998).
15. H. Nassar, S. Pellerin, K. Musiol, O. Martinie, N. Pellerin, and J. M. Cormier,

- "N₂⁺/N₂ ratio and temperature measurements based on the first negative N₂⁺ and second positive N₂ overlapped molecular emission spectra," J. Phys. D: Appl. Phys. **37**(14), 1904 (2004).
16. D. Staack, B. Farouk, A. F. Gutsol, and A. Fridman, "Spatially resolved temperature measurements of atmospheric-pressure normal glow microplasmas in air," IEEE Trans. Plasma Sci. **35**(5), 1448–1455 (2007).
 17. G. D. Stancu, F. Kaddouri, D. A. Lacoste, and C. O. Laux, "Atmospheric pressure plasma diagnostics by OES, CRDS and TALIF," J. Phys. D: Appl. Phys. **43**(12), 124002 (2010).
 18. Z. Xi-Ming, C. Wen-Cong, and P. Yi-Kang, "Gas temperature, electron density and electron temperature measurement in a microwave excited microplasma," J. Phys. D: Appl. Phys. **41**(10), 105212 (2008).
 19. Y. Wu, Z. Zhang, and S. F. Adams, "O₂ rotational temperature measurements by coherent microwave scattering from REMPI," Chem. Phys. Lett. **513**(4–6), 191–194 (2011).
 20. Y. Wu, J. Sawyer, Z. Zhang, and S. F. Adams, "Flame temperature measurements by radar resonance-enhanced multiphoton ionization of molecular oxygen," Appl. Opt. **51**(28), 6864–6869 (2012).
 21. C. Mainos, "Multiphoton rotational line strength in diatomic-molecules and for states with Hunds-case-(a) or Hunds-case-(B) coupling," Phys. Rev. A **33**(6), 3983–3992 (1986).
 22. Z. Zhang, "Coherent microwave scattering of laser-induced plasma," in Mechanical and Aerospace Engineering (Princeton University, 2008), pp. 36–46.
 23. Z. L. Zhang and M. N. Shneider, "Measurement of plasma decay processes in mixture of sodium and argon by coherent microwave scattering," Phys. Plasmas **17**(3), 033108 (2010).

Appendix

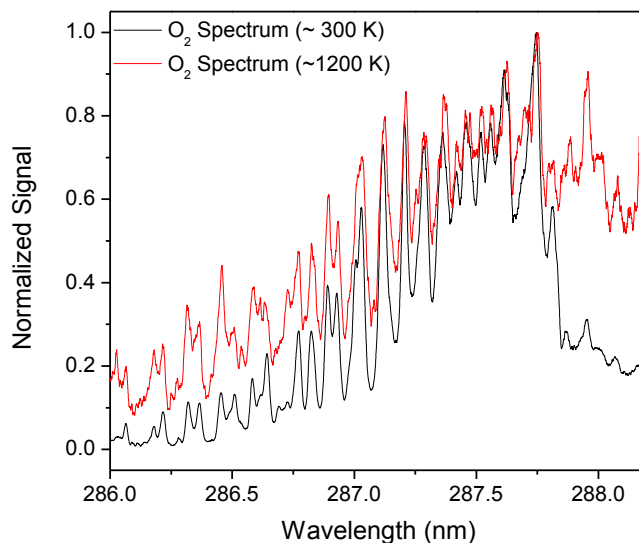


Figure 31. Spectra of molecular oxygen in atmospheric air (300 K) and air microdischarge (1200 K).

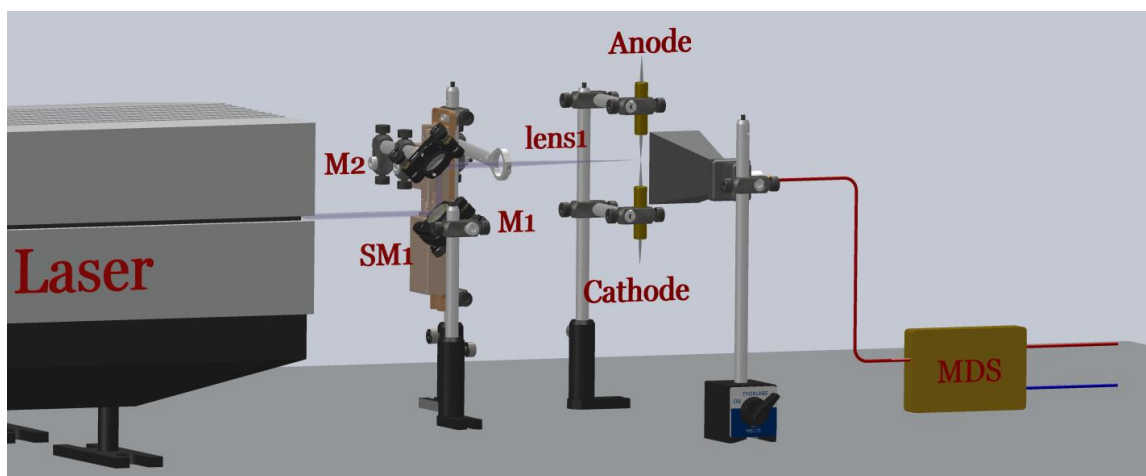


Figure 32. Experimental setup, the microdischarge was generated by two pin electrodes, microwave detection system (MDS) was used to collect the REMPI signal in the microdischarge.

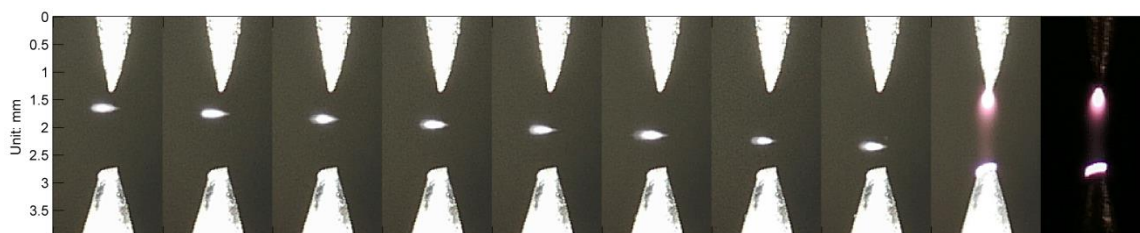


Figure 33. The first eight sequential photographs show the different scanning positions between the two electrodes without the microdischarge; the ninth and tenth photographs show the microdischarge (glow discharge) with and without camera light, respectively.

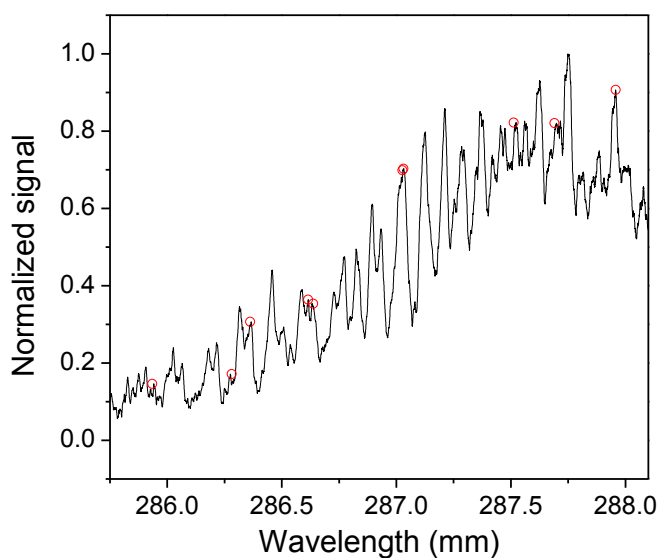
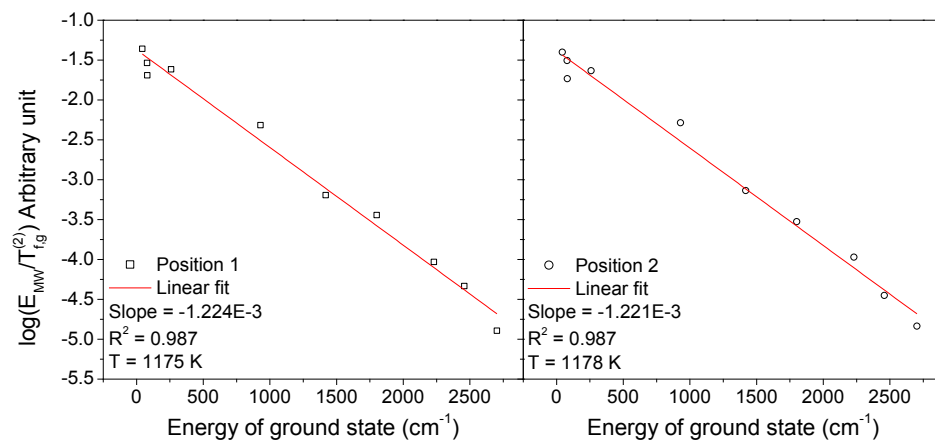
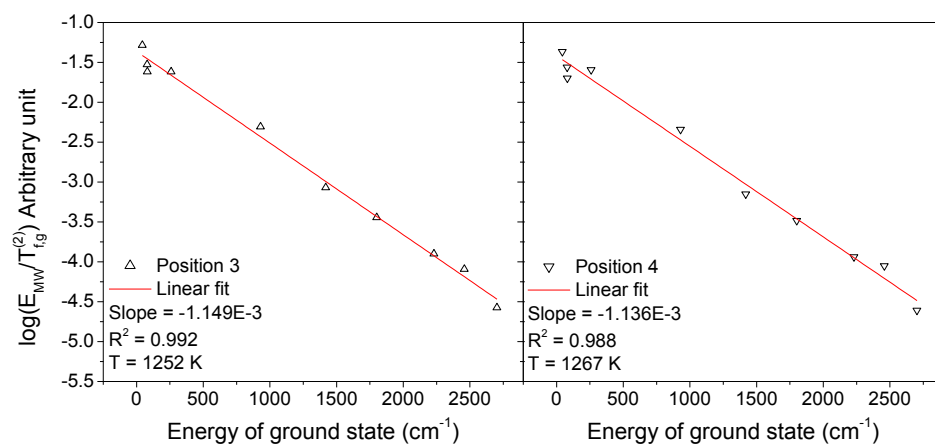


Figure 34. Spectrum of molecular oxygen in an atmospheric microdischarge.

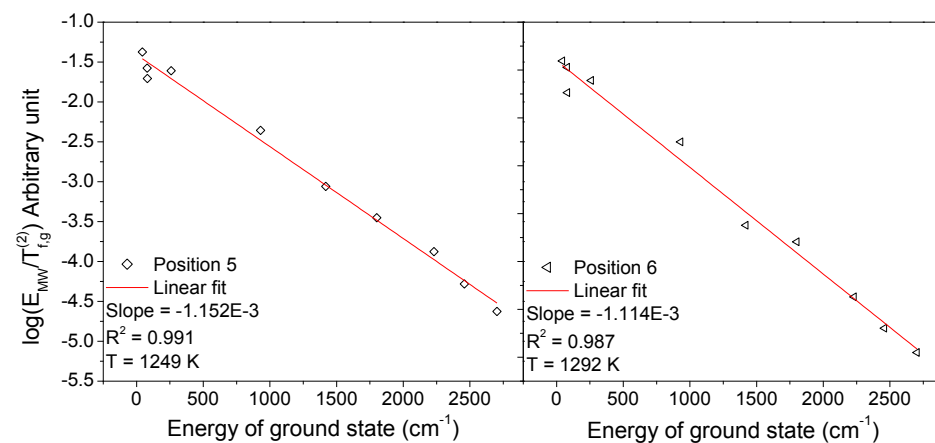
Figure 35(a)-(d). Boltzmann plots at different positions in the atmospheric microdischarges.



(a)

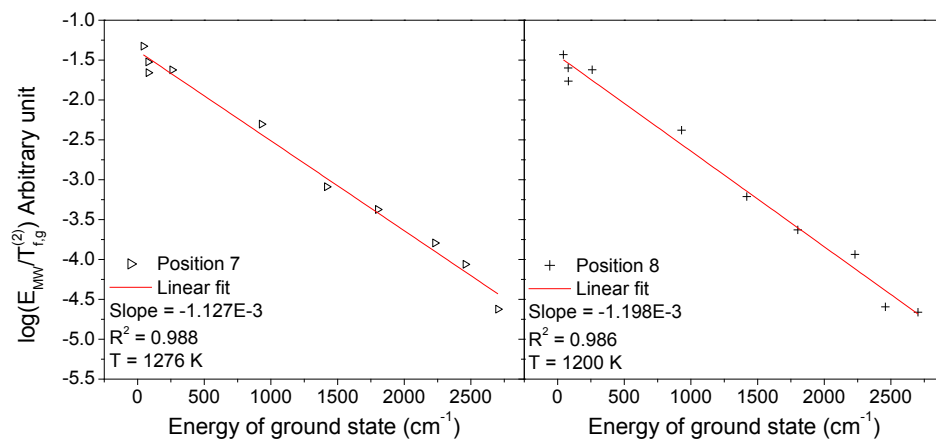


(b)



(c)

Figure 35. Continued



(d)
Figure 35. Continued

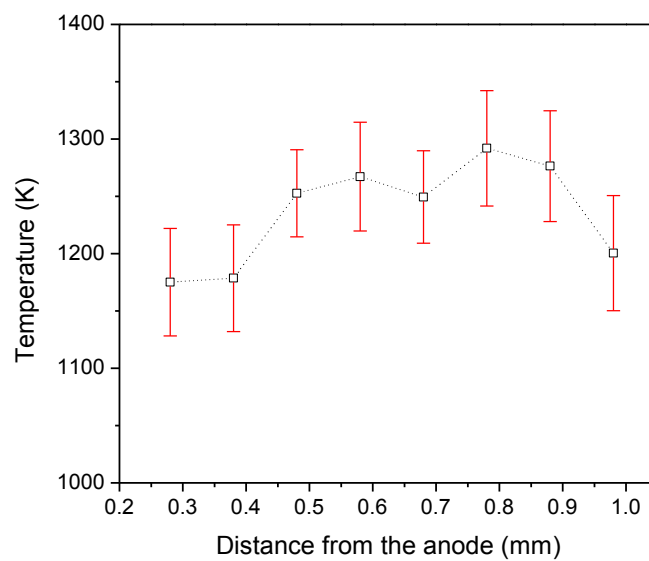


Figure 36. The temperature distribution in the microdischarge was determined by eight points between anode and cathode at equal intervals of 0.10 mm.

Table 6. Adopted constants for $C^3\Pi(v=2)$ of molecular oxygen

cm^{-1}	$F_1(\Omega=0)$	$F_2(\Omega=1)$	$F_3(\Omega=2)$
n_0	69369(2)	69449(1)	69552(1)
B_{eff}	1.61(5)	1.65(1)	1.69(1)
D_v	$1.9(5)\times 10^{-5}$	$1.6(2)\times 10^{-5}$	$1.9(2)\times 10^{-5}$

Table 7. Selected rotational lines for temperature measurements in the microdischarge.

Branch	J'	Wavelength (nm)	$G_1(\text{cm}^{-1})$	$T_{f,g}^{(2)}$
R ₃₁	42	285.935	2459.69	11.129
P ₃₂	43	286.282	2703.41	22.927
R ₁₁	36	286.362	1802.31	9.630
R ₁₂	39	286.615	2231.73	20.500
R ₁₁	32	286.637	1420.02	8.631
R ₁₁	26	287.027	931.19	7.132
S ₃₁	8	287.031	79.55	3.269
P ₃₂	5	287.512	44.20	3.200
R ₁₁	14	287.690	260.46	4.138
S ₂₁	7	287.958	81.57	3.706

CHAPTER VII
O₂ ROTATIONAL TEMPERATURE DETERMINATION BY
EMPIRICAL ANALYSES OF $C^3\Pi(v' = 2) \leftarrow X^3\Sigma(v'' = 0)$ TRANSITIONS

This article, “O₂ Rotational Temperature Determination by Empirical Analyses of $C^3\Pi(v'=2) \leftarrow X^3\Sigma(v''=0)$ Transitions”, was accepted by Applied Spectroscopy waiting for press.

Author affiliations:

Steven F. Adams,¹ Yue Wu,² and Zhili Zhang,^{2, a)}

¹*Air Force Research Laboratory (AFRL/RZPE), Wright-Patterson AFB, Dayton OH 45433-7919, USA*

²*Mechanical, Aerospace and Biomedical Engineering, University of Tennessee of Tennessee, Knoxville TN 37996, USA*

a) Corresponding author: zzhang24@utk.edu

Applied Spectroscopy, in press

Abstract

The spectra of molecular oxygen through $C^3\Pi(v'=2) \leftarrow X^3\Sigma(v''=0)$ transitions have been obtained by coherent microwave Rayleigh scattering (Radar) from resonance enhanced multi-photon ionization (REMPI). Measurements of rotational temperatures of molecular oxygen have been demonstrated based on the empirical analyses of the O₂ spectra without the requirement of highly resolved rotational features. Three methods, including (1) linewidth fitting, (2) linear fitting, and (3) area fitting have been investigated for temperature measurements within pure oxygen, ambient air, and H₂/air and CH₄/air flame environments. The first two methods were applied in a moderately low temperature environment with measurement uncertainties less than 11% and 26%, respectively. The area fitting method covered a wider temperature range, from room temperature (~ 300 K) to flame temperature (~1700 K), with minimal dependence on the fine structures of the O₂ spectra. Less elaborate than Boltzmann plot analyses of ultrafine rotational lines from congested upper rotational energy levels in O₂($C^3\Pi(v'=2)$), these empirical analyses are predictably sensitive to the thermal distribution of molecular oxygen, and have been successfully demonstrated as simple and quick methods for remote gas-phase temperature measurement.

OCIS codes: (120.6780) Temperature; (070.4790) Spectrum analysis; (300.6410) Spectroscopy, multiphoton; (300.6350) Spectroscopy, ionization.

Introduction

In recent decades, temperature measurements have been widely studied in various gas-phase environments; such as stagnant gas, nonreactive gas flow,

glow discharges, combustion systems, etc. As the second most common component of the Earth's atmosphere, molecular oxygen plays a key role as the main oxidizer in chemical reactions to produce heat and energy. Hence, O₂ rotational temperature extraction in various environments has been studied over the past 30 years, applying various optical techniques including Raman spectroscopy [1], emission spectroscopy [2, 3], laser-induced fluorescence (LIF) [4], coherent anti-Stokes Raman scattering (CARS) [5], and laser absorption spectroscopy (LAS) [6]. Although proven accurate, the quantitative LAS technique is limited in spatial resolution, and the collisional quenching effects must be carefully characterized in the LIF-based technique. When comparing recent CARS work to the conventional optical emission and Raman spectroscopy, the signal intensity and signal noise ratio (SNR) of CARS have been dramatically improved. At present, CARS is widely used in temperature measurements of laboratory flames [7] and advanced high-pressure combustor facilities [8], although both require precise optical alignment and sophisticated fitting models.

Most techniques mentioned above obtain the temperature information from intricate fits to Boltzmann plots based on the thermal distribution of the O₂ population within tabulated vibrational and rotational levels. These techniques have been applied in various environments such as O₂, air, microdischarges, and atmospheric flames. A 2+1 photon REMPI technique with an intermediate transition of $C^3\Pi(v'=2) \leftarrow X^3\Sigma(v''=0)$ in molecular oxygen has been used in the past by applying a Boltzmann plot analysis to assign temperatures in oxygen-containing environments [9-11]. As applied in this manner, this REMPI technique requires relatively high spectral resolution of the fine/hyper-fine structures of molecular oxygen. Meanwhile, the selection of the appropriate rotational transition is critical for accuracy in this Boltzmann point-fitting method engaging with two photon absorption process. It is even more difficult to achieve an accurate fit of the entire spectrum with a complex transition model. In this paper, the rotational temperatures are extracted from molecular oxygen resonant enhanced multi-photon ionization (REMPI) spectra detected by coherent microwave Rayleigh scattering (Radar) and analyzed through relatively simple empirical fitting models. A synthetic analysis of a low-resolution spectrum without detailed rotational structure is presented for quick and accurate temperature measurements in pure oxygen (O₂), ambient air, and atmospheric flames, ranging from room temperature to ~1700 K.

As a non-intrusive, *in situ* optical diagnostic tool, Radar REMPI has demonstrated its capability to successfully detect various gas-phase species including argon [12], xenon, CO [13], NO [14], O atom [15], CH₃ [16], O₂(a¹Δg) [17] and 1,4-diazobicyclooctane [18]. In this work, the molecular oxygen spectra were obtained with a single laser pulse by 2+1 REMPI with a two photon absorption transition from the O₂(X³Σ) ground state to the O₂(C³Π) intermediate state followed by a one photon ionization step. As an alternative to temperature measurements using the Boltzmann distribution principle in our previous

publications [9-11], the empirical analyses of the low-resolution spectra are presented here. Three methods based on low-resolution spectral analyses have been demonstrated to achieve quick temperature extractions within O₂, ambient air, and CH₄/air and H₂/air flames with a relatively standard laser system (i.e. convenient Rhodamine 610 dye, single laser beam, and typical laser linewidth). The empirical equations generated for temperature measurements are provided, along with the associated error factors.

Experimental Setup

The main part of the experimental setup is shown in Figure 37. A Nd: YAG laser (Continuum Surelite SL I-10, 10 Hz) with a second harmonic generator was utilized as the energy source to pump a dye laser (Continuum ND 6000 with Rhodamine 610 dye). The output beam of the dye laser was then frequency doubled by a crystal auto-tracking system (Continuum UVT-1). The energy of the ultraviolet laser beam was 6~8 mJ/pulse. The incident beam was focused by a focal lens ($f = 100$ mm) into one of two regions, depending on the configuration: (1) at the center of a quartz cell mounting inside a furnace for the O₂ and ambient air temperature experiments and (2) 100 mm above the Hencken burner surface for the flame temperature experiments. With the furnace configuration, the O₂ and ambient air at 1 atm were heated up from room temperature (~21 °C) up to 500 °C in the quartz cell. The Hencken burner configuration was used to generate a near-adiabatic, flat flame with methane and hydrogen as the fuel, respectively, to provide combustion environments with higher temperature values. Both of these two configurations offered an environment where the gas temperature was well known and calibrated from previous studies. This provided an excellent standard test-bed for the Radar REMPI empirical analyses.

At the laser focal point with intensive photon energy, the O₂ plasma was generated by 2+1 REMPI through a resonant two photon absorption process with the $C^3\Pi \leftarrow X^3\Sigma$ electronic transition of O₂ and the followed ionization with third photon of the same energy. Since the size of the plasma is much smaller than the microwave wavelength, the microwave scattering falls into the Rayleigh regime with the electric field amplitude of the plasma proportional to the number of electrons. A 10-dBm tunable microwave source (HP 8350B sweep oscillator, set at ~10 GHz) was applied in the homodyne transceiver detection system (MDS) shown in Figure 38. The microwave source was first split into two channels. One of them was used to illuminate the ionization point through a microwave horn (WR75, 15-dB 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 ~10 GHz. After the frequency was converted down 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 beam to maximize the scattering signal.

Results and Discussions

The empirical analyses of $C^3\Pi(v'=2) \leftarrow X^3\Sigma(v''=0)$ transitions of molecular oxygen directly depend on the thermal distribution and the transition characteristics. Previous publications [9-11] provide detailed theory and molecular constants for simulation of the $C^3\Pi(v'=2) \leftarrow X^3\Sigma(v''=0)$ two-photon spectral band, which consists of multiple branches for the various allowed rotational level combinations (ΔJ) between the states. As shown in Figure 39, the spectral band heads, which include the O branches ($\Delta J = -2$), are located at the low energy side (34600-34800 cm^{-1}), while the S branches ($\Delta J = +2$) are well expanded at high energy side ($>34800 \text{ cm}^{-1}$). In the band heads, the majority of the transitions are overlapped and tangled together with low temperature sensitivity due to the laser linewidth and signal convolution. However, the S branches are much more sensitive to temperature changes with individual peaks well separated at higher energy level. The remaining branches are mainly located in the center of the spectral band. The result of the convolution of transitions over all the branches is the hill-shaped O_2 2+1 REMPI spectrum, as shown in Figure 39.

Based on the given structures of the $C^3\Pi(v'=2) \leftarrow X^3\Sigma(v''=0)$ two-photon spectrum, empirical temperature measurements were conducted using three types of data analyses. Synthetic analyses of experimentally obtained low-resolution spectra have been conducted using the following methods; (1) linewidth fitting, (2) linear fitting and (3) area fitting. The O_2 REMPI spectrum (black line) shown in Figure 39 was obtained in an O_2 environment at 773 K and 1 atm. To show the possibilities of using a low-resolution spectrum, the smoothed spectrum (red bold line) was a moving-average over 500 points of the original data collected by the auto acquisition system. Both the linewidth fitting and linear fitting were applied to the smoothed low-resolution spectra with the error analysis depending on the spectral resolution. The area fitting method was applied to the higher-resolution spectra which extended the temperature measurement range from room temperature ($\sim 300 \text{ K}$) to flame temperature ($\sim 1700 \text{ K}$). In contrast with Boltzmann plot analyses of ultrafine rotational lines from congested rotational energy levels of $C^3\Pi(v'=2)$, the empirical methods do not require the resolution of the individual rotational lines and can thus provide temperature information by coarse scanning. Neither do they need high precision determination of individual rotational levels as used in Boltzmann plots, which usually account for another source of error.

Linewidth Fitting Method

The linewidth fitting method was applied in temperature measurements of O₂ and ambient air at 1 atm. The values of full width at half maximum (FWHM) were calculated for several spectral peaks within the smoothed O₂ rotational spectra. The mean values of the experimental FWHM data are shown as the black hollow squares in Figure 40 with the horizontal error bar depending on the level of smoothing (100 - 1000 data points). The black horizontal error bars indicate that the FWHM values are dependent on the spectral resolution, with large error at high temperature. The empirical equations of the temperature measurement were then polynomial fitted with respect to the FWHM values of the experimental spectra of molecular oxygen in those two conditions.

$$T_{O_2} = -0.03079x^2 + 19.75x - 2199(K) \quad (1)$$

$$T_{Air} = -0.2586x^2 + 119.0x - 12911(K) \quad (2)$$

From the curves of empirical equations (1) and (2) shown in Figure 40, there exists clear differences in temperature measurements between O₂ and ambient air using the FWHM data. The molecular nitrogen (78.09 %), argon (0.93 %) and water vapor (~1 %) must be considered as factors in the buffer gas collisional effect in ambient air. After the empirical equations (1) and (2) were obtained from the experimental data, they were then used to extract temperatures from O₂ spectra with various spectral resolutions (shown as the red hollow squares in Figure 40).

The percent errors of the temperatures obtained using the empirical equations in O₂ and ambient air are shown in Table 8. For the O₂ case, the overall percent error is $\pm 11\%$, whereas in ambient air it is $\pm 26\%$ at elevated temperatures (≥ 473 K) and even higher at room temperature.

When applying either equations (1) or (2) in the linewidth fitting method, the temperature measurement is relatively sensitive at low temperatures (≤ 700 K). As the temperature reaches higher values, this method provides less sensitivity and lower accuracy since rotational lines are populated more evenly at higher temperatures than those at lower temperatures. Thus, the linewidth fitting method can be adequately applied to low temperature measurements using low-resolution spectra with no requirements on complex model fitting involving fine/hyper fine structures of molecular oxygen.

Linear Fitting Method

The linear fitting method was applied to the temperature measurement in O₂ and ambient air as well. In contrast to linewidth fitting, thousands of data points were used in the linear fitting to extract the temperature from O₂ spectra. The right side ($34800 \text{ cm}^{-1} - 35200 \text{ cm}^{-1}$) of the spectrum shown in Figure 39, representing higher energy transitions, with S branches dominating the spectral shape, was

involved to extract the data slope information highly related to the O₂ rotational temperature. Within the normalized spectral profile, the data selection threshold was set at 30%-80% of the peak values with the spectra smoothed over 100 to 1000 points. The black hollow square and circle data shown in Figure 41 indicate the mean values of the line slopes with their error bar dependent on the spectral resolution. The unique empirical equation for both pure O₂ and ambient air was expressed as

$$T = 1.539 \times 10^7 x^2 + 2.893 \times 10^5 x + 1.607 \times 10^3 \text{ (K)} \quad (3)$$

Once constructed from the spectral slope information, this empirical equation was used to calculate temperatures for O₂ and ambient air conditions. The accuracy of the empirical equation shown in Figure 41 is seen to be acceptable within the experimental uncertainties, which depend on the spectral resolution. The red hollow square and circle data are the temperatures calculated for O₂ and ambient air, respectively.

The percent errors of the temperature values calculated from the empirical equation based on the linear fitting method is shown in Table 9, with less than $\pm 10\%$ error for both O₂ and ambient air conditions.

With the inclusion of more spectral peaks at high energy level, the linear fitting reduces the degree of uncertainty, improves the accuracy with less error associated with smoothing effects and spectral resolution, and better represents of the complete thermal distribution of the oxygen population. The effects of collisional broadening and overlapping of fine/hyper-fine structures do not significantly affect the linear fitting process. The linear fitting method, like linewidth fitting, can be accomplished with a relatively standard laser system (i.e. with a typical laser linewidth) and the spectral resolution requirement is fairly modest.

Area Fitting Method

The area fitting was applied to measure the temperature, not only in O₂ and ambient air at low temperature range, but also in H₂/air and CH₄/air flames with higher temperature values. Due to the unique structure of the REMPI spectrum in molecular oxygen, the area fitting method has been demonstrated to be a viable technique for the remote temperature measurement over a wide temperature range and in dramatically different environments.

O₂ Radar REMPI spectra obtained in O₂, ambient air and atmospheric flames are shown in Figure 42 with the data smoothed over 100 points. As discussed earlier, the O branches of the $C^3\Pi(v'=2) \leftarrow X^3\Sigma(v''=0)$ transition are crowded within the lower energy band head region of the spectrum and are less sensitive to temperature, while the S branches are expanded into the higher energy spectral region and exhibit strong temperature dependence. Hence, the three strongest S branch peaks were chosen to be utilized in the area fitting method. The spectra were first normalized by the peak value of O₁₁ branch and

the total area of the three S branch peaks were measured and are shown in Figure 43. A polynomial function was used to fit the area data and an empirical equation is expressed as:

$$T = 0.002155x^2 + 1.241x + 248.0 (K) \quad (4)$$

The empirical Eqn. (4) can be applied to measurements ranging from room temperature up to flame temperatures, which is a vastly greater coverage compared to the linewidth and linear fitting methods. Similar to the linear fitting method, this area method also reduces the effects of collisional broadening on the temperature calculation. However, fine structures were used in the area fitting analyses which required sufficient spectral resolution in experimental data. Thus the area fitting method has a requirement for a moderately narrow laser linewidth and also a relatively fast laser wavelength scanning rate.

In the previous work [9-11], the temperature measurements in pure O₂, air-like gas, ambient air, microdischarges and flame environments have been accomplished by using Boltzmann principle. The rotational branches must be carefully selected during the temperature calculation. However, in this paper, the empirical analyses have been applied without the complicated modelling and critical rotational branches selection. The ideal of such technique is quite similar to the single-shot rotational Raman thermometry which has been used in the temperature measurements in turbulent flames.[19] The complicated experimental setups and sophisticated models are not required any more in the experiments. The temperature measurements could be easily accomplished based on the empirical analyses with a simple laser system, which reduces the requirements for the laser diagnostics on temperature measurements in real critical testing environments.

Conclusion

Rotational temperatures were derived from the empirical analyses of spectra of molecular oxygen obtained by 2+1 Radar REMPI in O₂, ambient air and H₂/air and CH₄/air flames. The O₂ rotational temperatures were extracted by three demonstrated methods including (1) linewidth fitting, (2) linear fitting and (3) area fitting. The first two methods (linewidth and linear fitting) resulted in relatively accurate temperature measurements from room temperature to ~770K using low-resolution spectra with minimal requirements on laser linewidth, while the third method (area fitting) also provided accurate results in an expanded temperature range up to 1700K, but required greater resolution of the fine structure of the O₂ spectrum. All of the methods were based on the generation of empirical equations that could then be simply applied to the synthetic analyses of further O₂ spectral data from various environments.

Acknowledgements

This work is being supported by NSF CBET-1032523, Air Force Office of Scientific Research and Air Force Research Laboratory.

References

1. Hickman, R.S. and L. Liang, *Comparison of Temperature-Measurement of Oxygen in 0-0 and 0-1 Rotational Bands Using Laser Raman-Spectroscopy*. Review of Scientific Instruments, 1974. **45**(12): p. 1580-1582.
2. Touzeau, M., et al., *Spectroscopic Temperature-Measurements in Oxygen Discharges*. Journal of Physics D-Applied Physics, 1991. **24**(1): p. 41-47.
3. Macko, P. and P. Veis, *Time resolved O-2(b(1)Sigma(+)(g)) rotational temperature measurements in a low-pressure oxygen pulsed discharge. Simple and quick method for temperature determination*. Journal of Physics D-Applied Physics, 1999. **32**(3): p. 246-250.
4. Grinstead, J.H., G. Laufer, and J.C. Mcdaniel, *Rotational Temperature-Measurement in High-Temperature Air Using Krf Laser-Induced O2 Fluorescence*. Applied Physics B-Photophysics and Laser Chemistry, 1993. **57**(6): p. 393-396.
5. Meyer, T.R., et al., *Dual-pump dual-broadband CARS for exhaust-gas temperature and CO2-O-2-N-2 mole-fraction measurements in model gas-turbine combustors*. Combustion and Flame, 2005. **142**(1-2): p. 52-61.
6. Philippe, L.C. and R.K. Hanson, *Laser-Diode Wavelength-Modulation Spectroscopy for Simultaneous Measurement of Temperature, Pressure, and Velocity in Shock-Heated Oxygen Flows*. Applied Optics, 1993. **32**(30): p. 6090-6103.
7. Roy, S., et al., *Temperature measurements in reacting flows by time-resolved femtosecond coherent anti-Stokes Raman scattering (fs-CARS) spectroscopy*. Optics Communications, 2008. **281**(2): p. 319-325.
8. Thariyan, M.P., et al., *Dual-pump coherent anti-Stokes Raman scattering system for temperature and species measurements in an optically accessible high-pressure gas turbine combustor facility*. Measurement Science & Technology, 2011. **22**(1).
9. Wu, Y., Z.L. Zhang, and S.F. Adams, *O-2 rotational temperature measurements by coherent microwave scattering from REMPI*. Chemical Physics Letters, 2011. **513**(4-6): p. 191-194.
10. Sawyer, J., et al., *O-2 rotational temperature measurements in an atmospheric air microdischarge by radar resonance-enhanced multiphoton ionization*. Journal of Applied Physics, 2013. **113**(23).
11. Wu, Y., et al., *Flame temperature measurements by radar resonance-enhanced multiphoton ionization of molecular oxygen*. Applied Optics, 2012. **51**(28): p. 6864-6869.
12. Zhang, Z.L., M.N. Shneider, and R.B. Miles, *Coherent microwave rayleigh scattering from resonance-enhanced multiphoton ionization in argon*. Physical Review Letters, 2007. **98**(26).
13. Dogariu, A. and R.B. Miles, *Detecting localized trace species in air using radar resonance-enhanced multi-photon ionization*. Applied Optics, 2011.

- 50**(4): p. A68-A73.
14. Miles, R.B., et al., *Microwave scattering from laser ionized molecules: A new approach to nonintrusive diagnostics*. Aiaa Journal, 2007. **45**(3): p. 513-515.
 15. Dogariu, A., et al., *High-Gain Backward Lasing in Air*. Science, 2011. **331**(6016): p. 442-445.
 16. Wu, Y., et al., *Direct measurement of methyl radicals in a methane/air flame at atmospheric pressure by radar REMPI*. Optics Express, 2011. **19**(24): p. 23997-24004.
 17. Wu, Y., Z.L. Zhang, and T.M. Ombrello, *Spatially resolved measurement of singlet delta oxygen by radar resonance-enhanced multiphoton ionization*. Optics Letters, 2013. **38**(13): p. 2286-2288.
 18. Rudakov, F. and Z.L. Zhang, *Standoff detection of large organic molecules using Rydberg fingerprint spectroscopy and microwave Rayleigh scattering*. Optics Letters, 2012. **37**(2): p. 145-147.
 19. Kojima, J. and Q.V. Nguyen, *Single-shot rotational Raman thermometry for turbulent flames using a low-resolution bandwidth technique*. Measurement Science & Technology, 2008. **19**(1).

Appendix

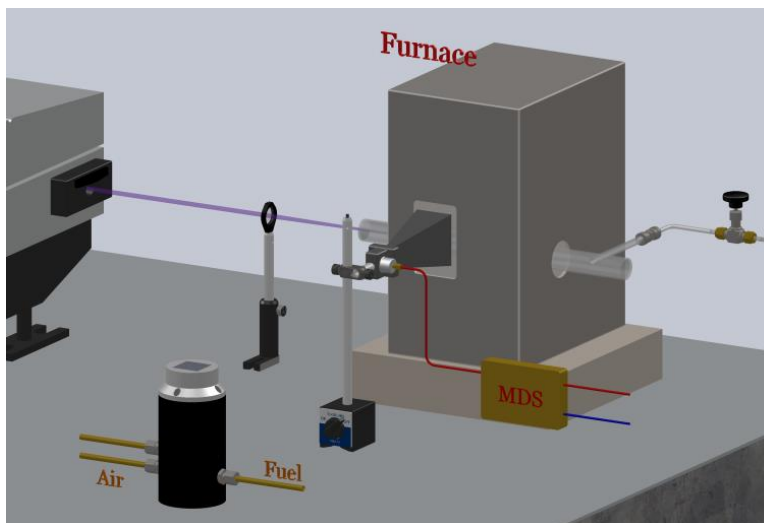


Figure 37. (Color online) The experimental setup for molecular oxygen temperature measurements within (1) O_2 and ambient air in quartz cell, respectively; and (2) CH_4/air and H_2/air flames generated by the Hencken burner, respectively.

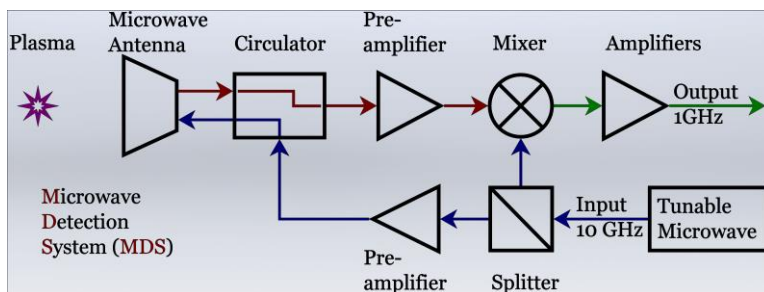


Figure 38. (Color online) The schematic diagram of the microwave homodyne transceiver detection system.

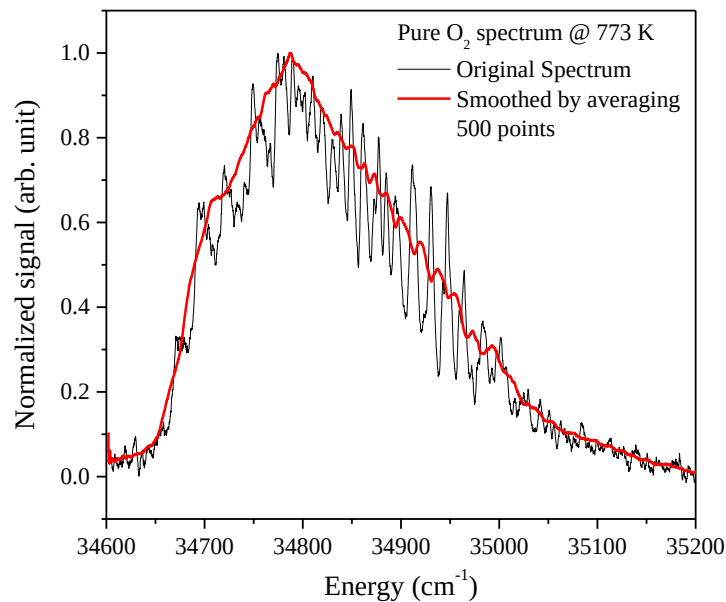


Figure 39. (Color online) The O₂ 2+1 REMPI spectra obtained in O₂ at 773 K and 1 atm. The black line is the original experimental spectrum and the red line is smoothed by moving-averaging 500 points from the original data.

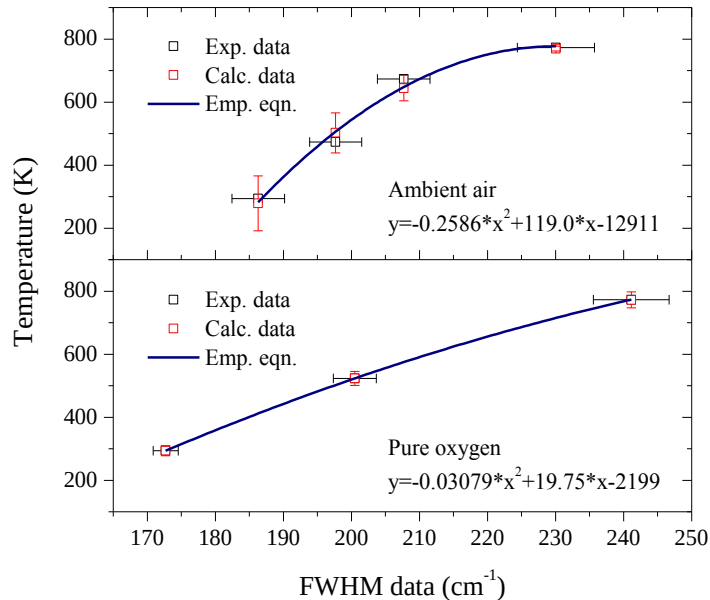


Figure 40. O₂ rotational temperature determination by empirical equations for O₂ and ambient air, respectively, with temperature range varying from 294 K ~ 773 K.

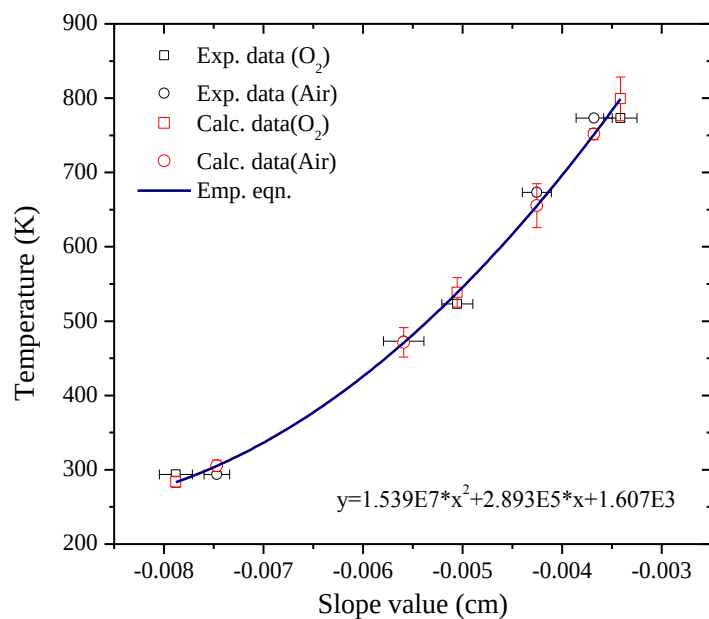


Figure 41. (Color online) O₂ rotational temperature empirical equation obtained for O₂ and ambient air, respectively, using spectral slope linear fitting method. The range of temperature is 294 K ~ 773 K.

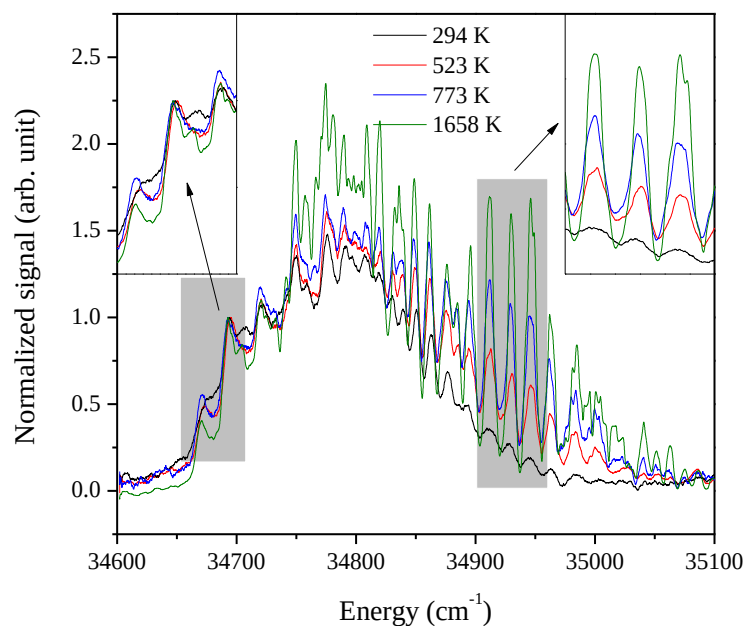


Figure 42. (Color online) Selected O₂ rotational spectra used in the area fitting method.

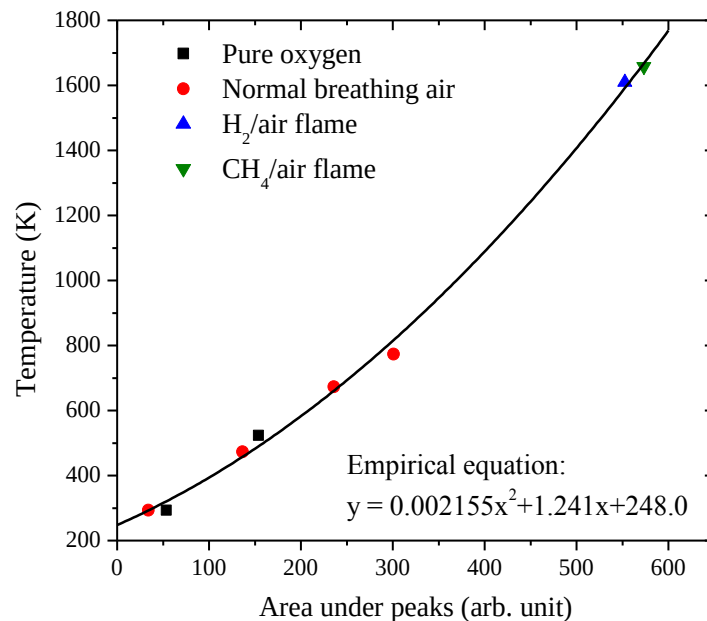


Figure 43. The empirical equation obtained with a wider temperature range (~300 K to ~1700 K) from the area fitting method within O₂, ambient air, H₂/air and CH₄/air flames.

Table 8. Percent errors of temperature calculated using the linewidth fitting method in O₂ and ambient air

Percent Error (%)					
O ₂			ambient air		
T (K)	max	min	T (K)	Max	min
294	10.15	-8.14	294	20.94	-76.42
523	6.32	-6.92	473	25.19	-25.78
773	5.41	-4.05	673	6.25	-13.05
			773	0.48	-2.16

Table 9. Percent errors of temperature using linear fitting method in O₂ and ambient air

Percent Error (%)					
O ₂			ambient air		
T (K)	max	min	T (K)	Max	min
294	2.2730	-6.7794	294	9.1612	1.2362
523	9.9115	-2.5193	473	9.8760	-5.4540
773	9.9217	-1.3962	673	4.8126	-7.4014
			773	5.0891	-7.6884

CHAPTER VIII
ROTATIONAL TEMPERATURE MEASUREMENTS IN O₂ BY
RADAR REMPI

This article, “Rotational Temperature Measurements of O₂ by Radar REMPI”, was just finished and will be submitted to journal publication soon.

Author affiliations:

Yue Wu,¹ and Zhili Zhang,^{1, a)}

¹*Mechanical, Aerospace and Biomedical Engineering, University of Tennessee of Tennessee, Knoxville TN 37996, USA*

a) Corresponding author: zzhang24@utk.edu

Abstract

The O₂ rotational temperature has been measured using coherent microwave Rayleigh scattering from Resonance-Enhanced Multi-Photon Ionization (Radar REMPI). Since the Rydberg state $(3s\sigma)C^3\Pi_g$ has been selected as the intermediate state of O₂ in the 2+1 REMPI process, the rotational-resolved spectra from two-photon $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow\leftarrow X^3\Sigma_g^-(v''=0)$ transition have been obtained in several conditions including pure O₂, air-like gas, ambient air and flame environments from room temperature (294K) to flame temperature (1658 K). The O₂ REMPI spectral model has been built up to simulate the experimental data which is dependent on the temperature. The model has been calibrated at an ideal temperature condition (~5 K) and then accomplished the temperature measurements with the overall error percentage less than $\pm 10\%$. The O₂ REMPI spectral model has been first reported in the community as a demonstration for the rotational temperature measurement with a wide temperature testing range. Further fine tunes of the model will be accomplished based on more experimental data in both low temperature (<300 K) and high temperature ranges (>1300 K).

Introduction

We wish to report here the first temperature measurement (~300 K ~1700 K) based on the detailed rotational analysis and spectrum fitting of $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow\leftarrow X^3\Sigma_g^-(v''=0)$ transition in pure O₂, air-like gas, ambient air, and flame environments by using coherent microwave Rayleigh scattering (Radar) from Resonance-Enhanced Multi-Photon Ionization (REMPI). As the second most common component of the Earth's atmosphere, molecular oxygen plays the key roles in biology, chemistry, engineering and *et al.*. The electronic structure of O₂ was comprehensively reviewed by Krupenie in 1972 [1], since then many interesting theoretical and experimental studies have been developed in order to further characterize the *gerade* Rydberg states [2-11]. After the first experimental observation of electronic states of oxygen in the 8.4-8.8 eV region

achieved by Cartwright et al [12], the $(3s\sigma)^1\Pi_g$ and $(3s\sigma)^3\Pi_g$ Rydberg states, as the lowest members of the *gerade* Rydberg series converging to the ground electronic state of the O_2^+ , have been carefully examined through the rotational analysis of two photon transition from $X^3\Sigma_g^-$ and $a^1\Delta_g$ to $(3s\sigma)^{1,3}\Pi_g$ states using resonant REMPI spectroscopy, which is inaccessible in one-photon spectroscopy [2-4, 8, 11]. In particular, the qualitative and quantitative analysis and results of perturbations and Rydberg-valence interactions in $(3s\sigma)^{1,3}\Pi_g$ states provided the spectroscopic study and fundamental basis for the rotational temperature measurement in O_2 by using $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow\leftarrow X^3\Sigma_g^-(v''=0)$ two-photon transition model.

In order to apply the rotational analysis and Boltzmann effect to the temperature measurement in O_2 , the transition cross section and rotational-resolved spectrum are the two key and essential factors. In the previous work by Johnson et al. [8] the four lowest vibrational levels of $d^1\Pi_g$ and $C^3\Pi_g$ were assigned in the composite spectrum of O_2 $X^3\Sigma_g^-$ by 2+1 REMPI process at room temperature. Due to the selection rule of ΔS , transitions from the $X^3\Sigma_g^-$ to $(3s\sigma)^3\Pi_g$ state are generally more intense than transitions to the $(3s\sigma)^1\Pi_g$ state. However, when the initial states is the lowest excited state, $a^1\Delta_g$ state, the pattern of weak and strong bands is reversed [8]. Though the cross section of O_2 $a^1\Delta_g$ is one order magnitude higher than that of O_2 $X^3\Sigma_g^-$, the REMPI signal intensity of singlet oxygen is much lower, considering its low concentration and high reactive as the lowest electronically excited state of O_2 in ambient air [13]. Hence, $(3s\sigma)^3\Pi_g$ states have been selected, as the intermediate state for the two photon absorption from O_2 $X^3\Sigma_g^-$ state. The first optical spectrum of the $(3s\sigma)^3\Pi_g$ state was reported by Sur [2]. Due to the interaction with the nearby valence state, only the $v'=2$ vibrational level shows rotationally resolved structure. Other vibrational bands are all diffuse. So in this paper, the temperature measurements were conducted based on the 2+1 REMPI process from $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow\leftarrow X^3\Sigma_g^-(v''=0)$ transition.

In the last four decades, several interesting diagnostic tools, including the electron impact excitation [12], low energy electron scattering spectroscopy [14], REMPI with time-of-flight mass spectrometer [4-6] and photoelectron spectroscopy (PES) [9], have been utilized in the studies of the electronically excited states and Rydberg states of O_2 . In particular, the REMPI technique has been applied in the study of $(3s\sigma)^{1,3}\Pi_g$ Rydberg states and their Rydberg-valence interactions. The rotational analyses were explored either in jet-cooled gas beam (~ 5 K) [4, 5] or at room temperature [7] focusing on the study of Rydberg-valence interaction and spectroscopic constant analysis with lower rotational levels. There is no need to elaborate the importance of these fundamental studies on Rydberg states of O_2 any further, in fact, such theoretical and experimental

analyses have not yet been developed in engineering and industry for practical application until recently years Radar REMPI was used in the temperature measurements in pure O₂, ambient air, microwave discharge and hydrogen/air flame based on the Boltzmann effect [15-17]. As a non-intrusive diagnostic tool, Radar REMPI technique [18] has not only been applied in the fundamental plasma studies [19], but also been used in the practical region as an *in situ* detection tool with low requirements of optical access and easily experimental setup while processing highly-resolved spatial resolution [20, 21]. For instance, only one laser beam is engaged in the experiment which simplifies the experimental setup. Meanwhile only one optical access is required while the concern for the optical output is unnecessary. Such unique feature is quite different from laser absorption spectroscopy (LAS) [22], laser induced fluorescence (LIF) [23], Coherent anti-Stokes Raman spectroscopy (CARS) [24], Raman thermometry [25] and other interesting laser diagnostic tools. The microwave wave is working as the remote non-intrusive detection tool which can pass through many materials (i.e., the fiber glass using as the heat insulation component in such experiment).

The challenges of building an O₂ 2+1 REMPI spectral model have been existed in the community for many decades and some critical considerations were mentioned by Johnson *et al.*. For instance, the main issues during simulation studies are including the accuracy of the two photon Honl-London formulas for the description of REMPI process, the high laser beam intensity and pulse duration [8]. Considering such challenges and difficulties, a demonstration of 2+1 REMPI spectral model has been built based on the time perturbation theory in this paper. The diatomic constants of the ground state of O₂ $X^3\Sigma_g^-$ and the intermediate Rydberg state $(3s\sigma)^3\Pi_g$ states were obtained from the previous theoretical and experimental data. The two-photon line strength of the $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow\leftarrow X^3\Sigma_g^-(v''=0)$ transition has been calculated based on the coupling transition of Hund's case-(a) and Hund's case-(b) [26]. The details of the model have been introduced in this paper which can be found in previous works as well [15-17, 27]. The temperature measurements were performed in various conditions including pure oxygen, air-like gas (N₂:O₂=4:1), ambient air and flame environment from ~300 K to ~1700 K. Such model has been confirmed by the previous experimental results done by Sur *et al.* in a supersonic beam with the rotational temperature at ~5 K [3]. This is the first demonstration for using rotational analysis and 2+1 REMPI spectral model fitting in the temperature measurements with a wide detection temperature window (~300 K to ~1700 K) at various environmental conditions by using Radar REMPI in two-photon $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow\leftarrow X^3\Sigma_g^-(v''=0)$ transition.

Experimental setup

As mentioned in the introduction, the Radar REMPI has low requirements for the optical access. The similarity of the experimental setups in previous works proved such technique easy-setup and robust features in different local testing environments [13, 16, 20, 21]. Here we just briefly introduced the experimental setup for temperature measurements in pure O₂, air-like gas and ambient air. The setup for the temperature measurement in flame can be found similarly in the previous publication [17].

The key part of the experimental setup is shown in Figure 44. A Nd: YAG laser (Continuum Surelite SL I-10, 10 Hz) with a second harmonic generator was utilized as the energy source (532 nm) to pump a dye laser (Continuum ND 6000 with Rhodamine 6G as the dye). The output beam (568 ~ 578 nm) was then frequency doubled by an auto-tracking system with the usage of a KDP crystal (Continuum UVT-1). The energy of the ultraviolet laser beam (284 ~ 289 nm) was 6~8 mJ/pulse which was used in the excitation and ionization of ground state O₂ through 2+1 REMPI process. Only 15%~20% of UV photons have been absorbed during the process and over 80% energy passed through the local testing point. The incident beam was simply focused by a focal lens ($f = 300$ mm) at the center of a quartz cell with temperature controlling by a pair of cylindrical furnace. The testing gas (pure O₂, air-like gas or ambient air) was heated up from room temperature (294 K) up to 1273 K in the quartz cell. The cylindrical furnaces offered a stable test environment with temperature fluctuation less than ± 1.0 %. The temperature in the CH₄/air and H₂/air flames were calculated by the Reaction software based on the GRI 3.0 mechanism.

At the beam focal point, the O₂ plasma was generated by 2+1 REMPI through a resonant two photon absorption process in the $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow \leftarrow X^3\Sigma_g^-(v''=0)$ transition of O₂ and the followed ionization with a third photon of the same energy (~4.3 eV). Since the size of the plasma is much smaller than the microwave wavelength, the microwave scattering falls into the Rayleigh regime with the electric field amplitude of the plasma proportional to the number of electrons [18]. The principle of Radar REMPI was shown in the subplot of Figure 44. A 10-dBm tunable microwave source (HP 8350B sweep oscillator, set at ~10 GHz) was applied in the homodyne transceiver detection system (MDS). The microwave source was first split into two channels. One of them was used to illuminate the ionization point through a microwave horn (WR75, 15-dB 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 ~10 GHz. After the frequency was converted down 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 beam to maximize the scattering signal.

O₂ Structure and REMPI Scheme

Ground state oxygen is a bi-radical showing the paramagnetic behavior of oxygen. The two unpaired oxygens each have a spin state of 1/2 for total resultant spin S of 1, making ground state oxygen a triplet $(2S+1) = 3$. It can be best described as Hund's case (b), and the ground state energies of these three spin states of $O_2(X^3\Sigma_g^-(v''=0, J''))$ for a specific N value are as follows [28]:

$$G_1(J = N + 1) = G_2(J = N) - \lambda + \gamma(N + 1) + B_v(2N + 3) - [\lambda^2 - 2\lambda B_v + B_v^2(2N + 3)^2]^{1/2}$$

$$G_2(J = N) = B_v N(N + 1) - D_v N^2(N + 1)^2$$

$$G_3(J = N - 1) = G_2(J = N) - \lambda - \gamma N - B_v(2N - 1) + [\lambda^2 - 2\lambda B_v + B_v^2(2N - 1)^2]^{1/2}$$

The diatomic constants for these expressions are well known which are available in the database of National Institute of Standards and Technology (NIST). [29]

Meanwhile, the $^3\Pi_g$ Rydberg state of O_2 is a triple as well which is best described as Hund's case (a) as the intermediate upper level. It is found that the $^3\Pi_g$ Rydberg state is very diffuse and has rotationally resolved structure for the $v'=2$ level only. The excited state energies of $O_2(C^3\Pi_g(v'=2, J'))$ are fitted by least squares to the polynomials as follows:

$$F_1 = n_{01} + B_{eff1}J'(J' + 1) - D_{v1}J'^2(J' + 1)^2,$$

$$F_2 = n_{02} + B_{eff2}J'(J' + 1) - D_{v2}J'^2(J' + 1)^2,$$

$$F_3 = n_{03} + B_{eff3}J'(J' + 1) - D_{v3}J'^2(J' + 1)^2,$$

where the derived constants are listed in Table 10 based on the previous experimental and computational study of the REMPI spectra of O_2 . [11, 15-17]

In the two-photon transition $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow \leftarrow X^3\Sigma_g^-(v''=0)$, since the $^3\Pi$ and $^3\Sigma$ states approaches case (a) and case (b), respectively, the band structure is more complicated than other transitions (i.e. $^2\Pi \leftarrow ^2\Sigma$). Three sub-bands are expected as $^3\Pi_0 \leftarrow ^3\Sigma^-$, $^3\Pi_1 \leftarrow ^3\Sigma^-$, and $^3\Pi_2 \leftarrow ^3\Sigma^-$. In each sub-band there are nine branches, three for each triplet component of the lower state. Thus there are in all 27 branches [30]. In addition, the O, P, Q, R, and S branches are expected according to the selection rule ($\Delta J=0, \pm 1, \pm 2$). For instance, in an S branch ($\Delta J=+2$), a two-photon transition from ground state G_1 to intermediate state F_3 giving rise to S_{31} .

The 2+1 REMPI process is schematically expressed in Figure 45. The two-photon transition $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow \leftarrow X^3\Sigma_g^-(v''=0)$ was accomplished by first two-photon absorption process with total energy ~ 8.6 eV. The weakly-ionized plasma was then generated by a following photon with the same photon energy ~ 4.3 eV. The rotational-resolved hyperfine structures in such REMPI process have been expected according to the characteristics of both triplet ground state and Rydberg state. The two-photon rotational line strength in diatomic oxygen for states with Hund's case (a) and case (b) coupling were expressed as follow:

$$T_{f,g}^{(2)} = \sum_{k=0,2} \frac{|\beta_k^{(2)}|^2}{2k+1} \cdot (2J'+1) \cdot (2J''+1) \cdot (2N''+1) \cdot \left[\begin{matrix} J'' & S' & N'' \\ \Lambda'' + \Sigma' & -\Sigma' & -\Lambda'' \end{matrix} \right]^2 \left[\begin{matrix} J' & k & J'' \\ \Omega' & -\Delta\Lambda & -\Lambda'' - \Sigma' \end{matrix} \right]^2$$

where [...] is the Wigner 3-j symbol, J is the rotational quantum number, N is total angular momentum except the spin, $\beta_k^{(2)}$ is polarization coefficient, double-primed parameters denote the ground state of $X^3\Sigma_g^-$ and primed parameters denote the Rydberg state of $(3s\sigma)C^3\Pi_g$. For linearly polarized light, terms of both $k=0$ and 2 contribute to the final line strength, $\beta_k^{(2)} = \sqrt{10/3}$, while for circularly polarized light, only $k=2$ contributes and $\beta_k^{(2)} = \sqrt{5}$. [26]

The homodyne transceiver detection system was utilized to collect the signal. The microwave scattering signal from the REMPI produced plasma is proportional to the total number of electrons inside the plasma, which is proportional to the total number of electron excitations to the continuum through the resonant two-photon transition followed by the single photon ionization. The total number of electron excitations to the continuum is thus determined by the product of the number of molecules in the ground state and the rate of multiphoton ionization. An expression for the resulting microwave scattering signal for a given two-photon transition from $X^3\Sigma_g^-$ state to $(3s\sigma)C^3\Pi_g$ state can be written as

$$E_{MW} \propto N_e = N_0 \cdot T_{f,g}^{(2)} \cdot I^2 \cdot T_{i,f}^{(1)} \cdot I \cdot \exp(-E_g / k_B T)$$

where E_{MW} is the scattering microwave electric field, N_e is the total electron number inside the plasma generated by REMPI, N_0 is the total number of oxygen molecules in the laser focal region, E_g is the energy of the ground state $X^3\Sigma_g^-$, k_B is the Boltzmann constant, T is the temperature value, I is the intensity of the laser beam, and $T_{i,f}^{(1)}$ is the ionization cross section from the excited state to the ionization continuum.

The rotational temperature of O_2 can be inferred from the rotational analysis on the thermal distribution of the ground state $X^3\Sigma_g^-$ according to the Radar RMEPI spectrum. Such thermal distribution of the rotational levels is given by a statistically weighted (i.e., quantum degenerated) Boltzmann factor of $J'(J'+1)\exp(E_g / k_B T)$. In the O_2 REMPI spectrum, the significant intensity increasing of the hyperfine structures at higher J'' levels are occurring with increasing temperature which are the synactic effect between the thermal distribution of the molecules and the transition line strength of each rotational level. If $T_{i,f}^{(1)}$ is assumed to be constant over the limited laser wavelength scanning range and the ground state population N_0 is constant during the scan time, the spectrum is only depended on the rotational temperature of O_2 . Based on such principle, the Boltzmann plots were applied to extract the temperature information from the selected rotational lines and the rotational temperature could be calculated according to the slope of the Boltzmann plots in our previous works [15-17]. In this paper, the whole spectrum of O_2 was involved in the temperature

measurements based on the O₂ REMPI spectral model. Compared to the previous work, there is no need to take great effect to select the specific rotational branches or single lines with high temperature sensitivities, instead, the whole set of rotational levels are considered in the model which has been developed to calculate the rotational temperature based on the REMPI spectrum which is the convolution result of all 27 transition branches.

Experimental Results and Discussion

In this paper, the O₂ REMPI spectral model was first reported as a demonstration for the rotational temperature calculation based on the whole spectral fitting technique. Some parts of the model have been carefully treated, some parts have been simplified which might be considered in the development of the model in the near future.

(1) The constants of the energy in ground state and excited state were obtained from the database of NIST. Small changes have been made based on the experimental results.

(2) Both thermal and laser broadening have been considered in the model while the oxygen attachment, detachment, third body recombination, species collision and spectra line shifting effects were not involved in the model.

(3) The life time of the Rydberg state was fitted by experimental results and the constants with large uncertainties could be found in previous publications which have no sufficiently theoretical support.

(4) Sur et al. have given evidence for Rydberg-valence interactions in the $(3s\sigma)C^3\Pi_g$ Rydberg state [3], however, this interaction is relatively weak and resulted only in selective broadening of the spectral linewidth [8]. Hence, the interaction effects between the Rydberg state and valence state have not been considered in the model.

Although fairly large uncertainties exist in the theory with spectroscopic constants poorly supported by experiments, the O₂ REMPI spectral model has been first carried out here as a proof-of-principle technique for the rotational temperature measurement based on rotational-resolved REMPI spectrum. Such model was first verified and fine-tuned based on the previous experimental results done by Sur *et al.* as shown in Figure 46.[3] The upper black data is the O₂ spectrum obtained in a supersonic beam with O₂ rotational temperature of ~5K. Since the rotational temperature is extremely low, all three components, F_1 , F_2 , and F_3 can be clearly seen in the spectrum. The lower red data is the simulation results using the O₂ REMPI model. The model well predicted the spectrum of O₂ in the low temperature value although two hyperfine lines have been convoluted together in the simulation results. The peak positions are not accurately matched due to the uncertainty of the upper and lower level energy distributions.

After the O₂ REMPI model was confirmed by the experimental results at extremely low temperature (~5 K), the buffer gas pressure and collision effect were studied. As the O₂ spectra shown in Figure 47, which were obtained in four different conditions in a quartz cell at room temperature (294 K). The experimental conditions are shown as follows:

- (1) 20 Torr pure O₂ in the quartz cell at 294 K,
- (2) 100 Torr pure O₂ in the quartz cell at 294 K,
- (3) 100 Torr air-like gas (N₂:O₂=4:1) in the quartz cell at 294 K,
- (4) 100 Torr ambient air in the quartz cell at 294 K.

Since the O₂ spectra in all these four conditions are well agreed with each other, some assumptions have been made:

(1) The spectrum has little effect on the pressure and molecule collision with respect to the number density of O₂, the electron-O₂ attachment is very weak in these conditions.

(2) Including N₂, Ar, CO₂ and other components in the air, these molecules have little effect on the O₂ REMPI spectrum.

(3) There exists resonant- and avalanche-ionization amplification effect at low pressure condition [31] and such effect becomes fewer at higher pressure conditions. The phenomenon is observed in the N₂ 2+2 REMPI spectrum from 284.5 to 285 nm which has few effect on the main O₂ transition bands studied in this paper.

The O₂ temperature measurements were conducted in such four conditions with the temperature varying from the room temperature to 1273 K. The spectra obtained at higher temperature conditions were also well agreed with each other including 473K, 673K, 873K, 1073K and 1273K with increased pressure according to the ideal gas law in the closed quartz cell.

The experimental results of the O₂ rotational temperature measurements based on the O₂ REMPI spectral model are shown in Figure 48 from subplot (a) to (h). In each plot, the black line is the averaged spectral result from four spectra obtained in the different conditions mentioned above. The red line is the O₂ REMPI spectrum simulation result. The experimental temperature and calculated rotational temperature of O₂ are both labeled in the figure. Eight different temperatures have been measured in the quartz cell and flame environments. The temperature range is from 294K to 1273K in the quartz cell limited by the heating capability of the furnace. Two flame conditions were demonstrated with higher temperature values i.e., 1610 K in CH₄/air flame and 1658 K in H₂/air flame. The comparison results between the experiments and simulations are shown in Table 11.

As the results shown in Table 11, the error of rotational temperature measurement of O₂ is less than ±10% with the temperature range of 294 K to 1658 K. Since the model was confirmed by the experimental results obtained in the supersonic beam (~5 K), here we assume this O₂ REMPI model could be used in different testing conditions from ambient air to flame environment with a wide temperature measurement range expanding from 5K to ~1700 K.

According to Figure 46 and Figure 48(a) ~ (h), the rotational branches are extended to higher energy levels due to the increase of the temperature. Several branches show the strong temperature sensitivity feature especially in the 286 ~ 286.5 nm region. From 286 nm to higher energy level, the spectrum displays a decreasing in intensity with increasing J'' value at a rate greater than that accounting for Boltzmann effect in the ground state. At even higher energy level from 285 nm to 284 nm, the rotational structures were not displayed in the experimental results at higher temperature conditions because of the short life time of the excited O₂ at the Rydberg state with high J' values.

Clearly, the spectra obtained in the quartz cell have good agreement with simulation results as shown in Figure 48(a) to Figure 48(f). However, in the real flame environment, the practical measurement conditions are much rougher than that in the quartz cell. While being in the flame environment, the spectral intensities do not match well between the experimental results and the O₂ spectrum simulation especially at 287 ~ 288nm region. In fact, as the rotational structures are well-expanded in the higher energy level, the model still has the capability to fit the experimental results and give acceptable simulation results that fairly well-agreed with the experimental results in flame environment (Figure 48 (g) and Figure 48 (h)).

Conclusion

Based on the rotational analysis, the Rydberg state $(3s\sigma)C^3\Pi_g(v'=2)$ has been selected as the intermediate state for the two-photon $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow\leftarrow X^3\Sigma_g^-(v''=0)$ transition which give birth to the rotational-resolved spectra through 2+1 REMPI process. The temperature measurements have been conducted in different conditions including pure O₂, air-like gas, ambient air and flame environments. The O₂ REMPI model has been built up to simulate the experimental spectra and extract the temperature information based on the whole spectral fitting process. The model was calibrated by previous experimental data at a low temperature condition (~ 5K). The model has been used in the rotational temperature measurements with a temperature range of ~300K to ~1700 K. The error percentage of the measurement is less than $\pm 10\%$ from pure O₂, air-like gas, ambient air to complicated flame environments. The O₂ REMPI model for the two-photon $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow\leftarrow X^3\Sigma_g^-(v''=0)$ transition is first reported here as a demonstration in the rotational temperature measurements in various environments. The model will be fine-tuned with more data results in both low temperature (< 300 K) and high temperature (> 1300 K) regions.

Acknowledgements

Funding for this research was provided by the AFOSR under Contract No. FA9550-14-1-0329 under Dr. Chiping Li.

References

1. Krupenie, P. H., "The Spectrum of Molecular Oxygen." *Journal of Physical and Chemical Reference Data*, Vol. 1, No. 2, 1972, pp. 423-534.
2. Sur, A., Ramana, C. V., and Colson, S. D., "Optical-Spectra of the Lowest-Pi-G Rydberg States in O-2." *Journal of Chemical Physics*, Vol. 83, No. 2, 1985, pp. 904-905.
3. Sur, A., et al., "Rydberg-Valence Interactions in the Pi-G States of O-2." *Journal of Chemical Physics*, Vol. 84, No. 1, 1986, pp. 69-72.
4. Sur, A., Friedman, R. S., and Miller, P. J., "Rotational Dependence of the Rydberg Valence Interactions in the 1-Pi-G States of Molecular-Oxygen." *Journal of Chemical Physics*, Vol. 94, No. 3, 1991, pp. 1704-1711.
5. Sur, A., Nguyen, L., and Nikoi, N., "Franck-Condon Overlap Integrals between the 3s-Sigma 3-Pi-G Rydberg and the 1-3-Pi-G Valence States of O2." *Journal of Chemical Physics*, Vol. 96, No. 9, 1992, pp. 6791-6795.
6. Loo, R. O., et al., "Multiphoton Ionization of O-2chi-3-Sigma-G-, A1-Delta-G, and B 1-Sigma-G+ Via the 2-Photon Resonant Ns-Sigma-G, Nd-Sigma-G, and Nd-Pi-G Rydberg Levels." *Journal of Chemical Physics*, Vol. 91, No. 9, 1989, pp. 5185-5200.
7. Ogorzalek-Loo, R. R., Ph.D. Thesis, Cornell University, 1989.
8. Johnson, R. D., Long, G. R., and Hudgens, J. W., "2 Photon Resonance Enhanced Multiphoton Ionization Spectroscopy of Gas-Phase O2 Alpha-1-Delta-G between 305-350 Nm." *Journal of Chemical Physics*, Vol. 87, No. 4, 1987, pp. 1977-1981.
9. Morrill, J. S., et al., "Two-photon REMPI spectra from a(1)Delta(g) and b(1)Sigma+(g) to d(1)Pi(g) in O-2." *Journal of Molecular Spectroscopy*, Vol. 219, No. 2, 2003, pp. 200-216.
10. Morrill, J. S., et al., "The (X (2)Pi(g)) ns sigma(g) (1,3)Pi(g) Rydberg states of O-2: Spectra, structures, and interactions." *Journal of Chemical Physics*, Vol. 111, No. 1, 1999, pp. 173-185.
11. Lewis, B. R., et al., "Perturbations in the 3s sigma(g) (1,3)Pi(g) Rydberg states of O-2: Bound-bound interactions with the second (1)Pi(g) and (1)Delta(g) valence states." *Journal of Chemical Physics*, Vol. 111, No. 1, 1999, pp. 186-197.
12. Cartwrig.Dc, et al., "Theoretical and Experimental (Electron-Impact) Studies of Low-Lying Rydberg States in O2." *Physical Review A*, Vol. 8, No. 5, 1973, pp. 2436-2448.
13. Wu, Y., Zhang, Z. L., and Ombrello, T. M., "Spatially resolved measurement of singlet delta oxygen by radar resonance-enhanced multiphoton ionization." *Optics Letters*, Vol. 38, No. 13, 2013, pp. 2286-2288.
14. York, T. A. and Comer, J., "Electron Energy-Loss Studies of Molecular-Oxygen in the Region 6.0-16.1 Ev Using a Multidetector Electron Spectrometer." *Journal of Physics B-Atomic Molecular and Optical Physics*,

- Vol. 16, No. 19, 1983, pp. 3627-3639.
15. Wu, Y., Zhang, Z. L., and Adams, S. F., "O-2 rotational temperature measurements by coherent microwave scattering from REMPI." *Chemical Physics Letters*, Vol. 513, No. 4-6, 2011, pp. 191-194.
 16. Sawyer, J., et al., "O-2 rotational temperature measurements in an atmospheric air microdischarge by radar resonance-enhanced multiphoton ionization." *Journal of Applied Physics*, Vol. 113, No. 23, 2013.
 17. Wu, Y., et al., "Flame temperature measurements by radar resonance-enhanced multiphoton ionization of molecular oxygen." *Applied Optics*, Vol. 51, No. 28, 2012, pp. 6864-6869.
 18. Zhang, Z. L., Shneider, M. N., and Miles, R. B., "Coherent microwave rayleigh scattering from resonance-enhanced multiphoton ionization in argon." *Physical Review Letters*, Vol. 98, No. 26, 2007.
 19. Shneider, M. N., Zhang, Z., and Miles, R. B., "Plasma induced by resonance enhanced multiphoton ionization in inert gas." *Journal of Applied Physics*, Vol. 102, No. 12, 2007.
 20. Wu, Y., et al., "Direct measurement of methyl radicals in a methane/air flame at atmospheric pressure by radar REMPI." *Optics Express*, Vol. 19, No. 24, 2011, pp. 23997-24004.
 21. Wu, Y. and Zhang, Z., "Two-dimensional quantitative measurements of methyl radicals in methane/air flame." *Applied Optics*, Vol. 54, No. 2, 2015, pp. 157-162.
 22. Sanders, S. T., et al., "Diode-laser absorption sensor for line-of-sight gas temperature distributions." *Applied Optics*, Vol. 40, No. 24, 2001, pp. 4404-4415.
 23. Thurber, M. C., Grisch, F., and Hanson, R. K., "Temperature imaging with single- and dual-wavelength acetone planar laser-induced fluorescence." *Optics Letters*, Vol. 22, No. 4, 1997, pp. 251-253.
 24. Hancock, R. D., Bertagnolli, K. E., and Lucht, R. P., "Nitrogen and hydrogen CARS temperature measurements in a hydrogen/air flame using a near-adiabatic flat-flame burner." *Combustion and Flame*, Vol. 109, No. 3, 1997, pp. 323-331.
 25. Kojima, J. and Nguyen, Q. V., "Single-shot rotational Raman thermometry for turbulent flames using a low- resolution bandwidth technique." *Measurement Science & Technology*, Vol. 19, No. 1, 2008.
 26. Mainos, C., "Multiphoton Rotational Line Strength in Diatomic-Molecules and for States with Hunds-Case-(a) or Hunds-Case-(B) Coupling." *Physical Review A*, Vol. 33, No. 6, 1986, pp. 3983-3992.
 27. Adams, S. F., Williamson, J. M., and Fisher, D. M., "Rotational temperature analysis of N-2 by resonant enhanced multi-photon ionization with fluorescence detection." *Journal of Applied Physics*, Vol. 110, No. 8, 2011.
 28. Brown, J. M. and Carrington, A., *Rotational Spectroscopy of Diatomic Molecules*, CAMBRIDGE UNIVERSITY PRESS, Cambridge, 2003, 752-759.

29. Laher, R. R. and Gilmore, F. R., "Improved Fits for the Vibrational and Rotational-Constants of Many States of Nitrogen and Oxygen." *Journal of Physical and Chemical Reference Data*, Vol. 20, No. 4, 1991, pp. 685-712.
30. Herzberg, G., *Molecular Spectra and Molecular Structure. Volume I: Spectra of Diatomic Molecules.*, 2nd ed., D. Van Nostrand, 1950, 264.
31. Wu, Y., et al., "Resonant- and avalanche-ionization amplification of laser-induced plasma in air." *Journal of Applied Physics*, Vol. 116, No. 14, 2014.

Appendix

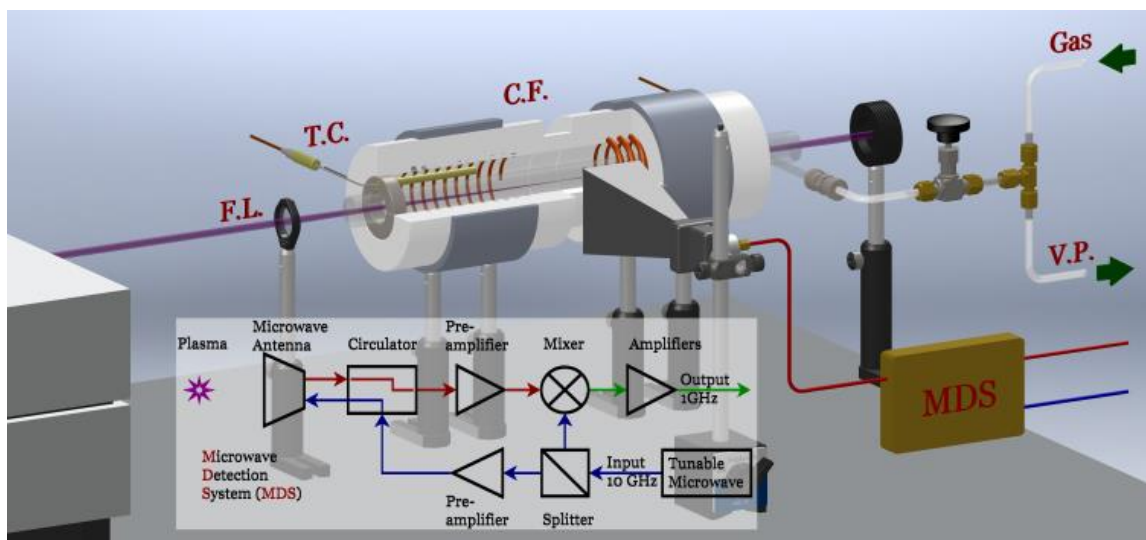


Figure 44. The experimental setup for temperature measurements of target gas species (i.e. pure O₂, air-like gas and ambient air) in a quartz cell heating by a pair of cylindrical furnace.

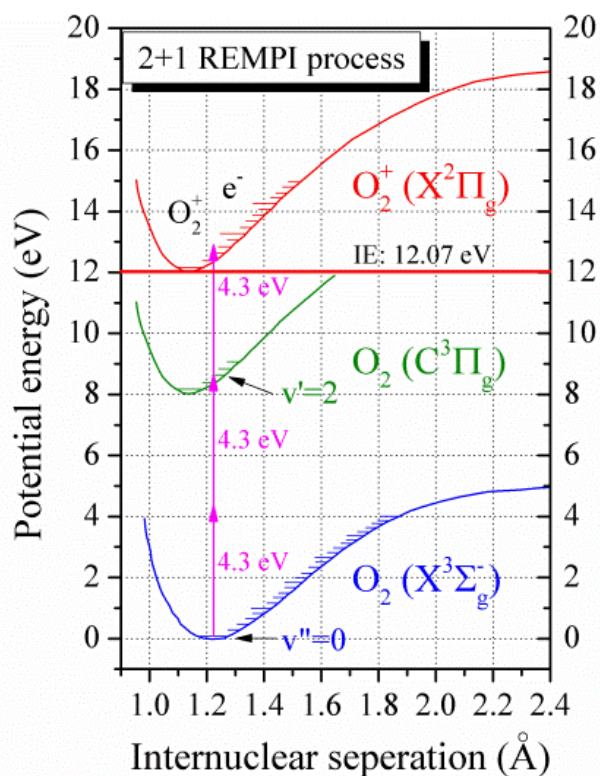


Figure 45. The potential energy of molecular oxygen for each state including (1) the ground state $O_2(X^3\Sigma_g^-)$, (2) the intermediate Rydberg state $O_2(C^3\Pi_g)$, and (3) the $O_2^+(X^2\Pi_g)$ state above the ionization level (12.07 eV). The 2+1 REMPI process is schematically expressed in the plot.

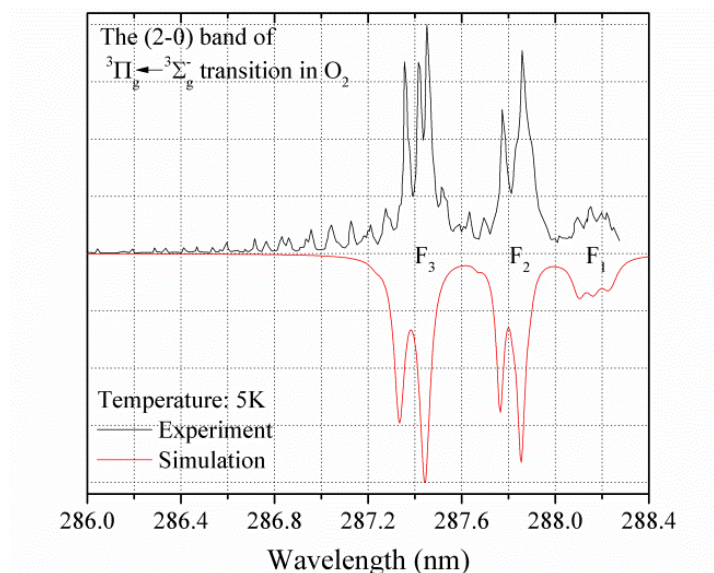


Figure 46. The rotational spectra of the $(3s\sigma)C^3\Pi_g(v'=2) \leftarrow X^3\Sigma_g^-(v''=0)$ transition. The upper spectrum was obtained in a supersonic beam with rotational temperature $\sim 5K$. The lower spectrum was simulation results based on the O_2 RMEPI model.

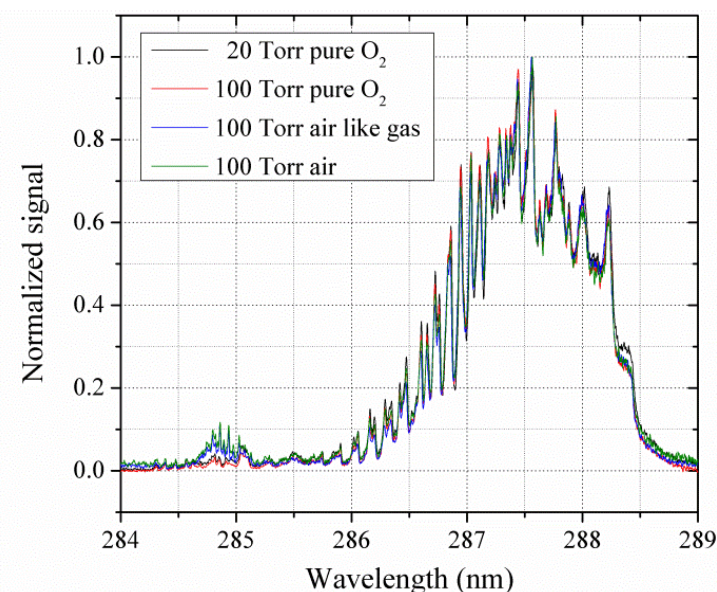
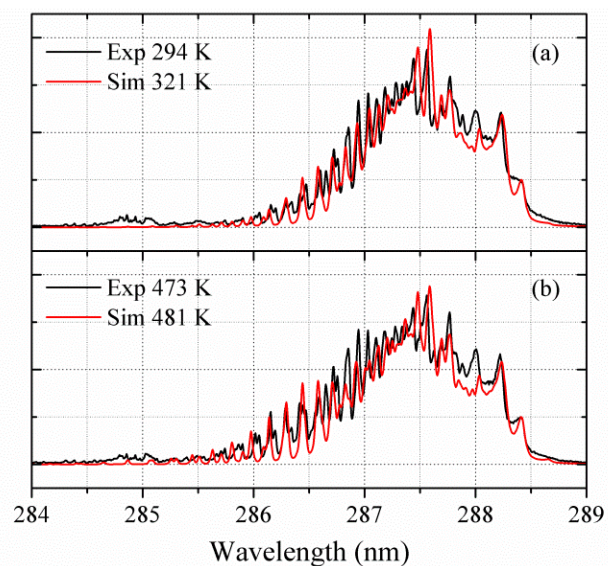
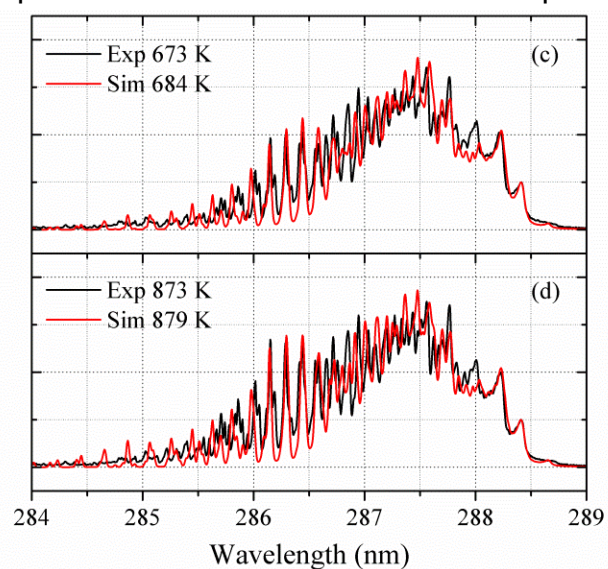


Figure 47. The O_2 REMPI spectra at room temperature (294 K). Four different conditions were explored in order to confirm that there is no effect on the pressure and other gas species.

Figure 48(a)-(h). The spectral comparison between experimental results and simulation calculations.

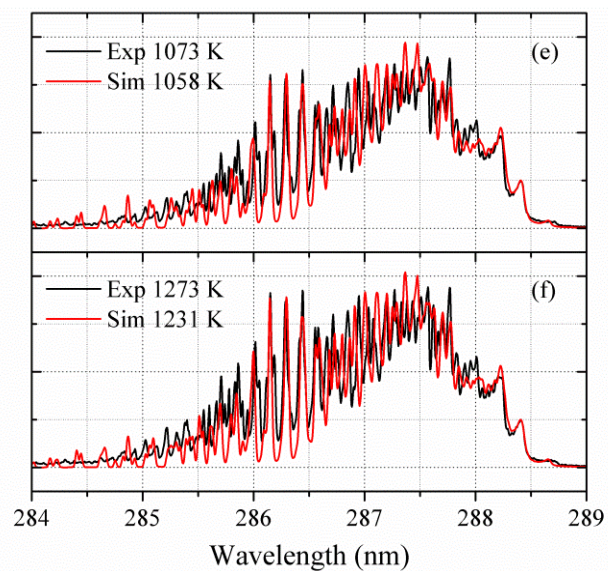


(a) The O_2 REMPI spectrum at 294 K with calculated temperature 321 K.
 (b) The O_2 REMPI spectrum at 473 K with calculated temperature 481 K.



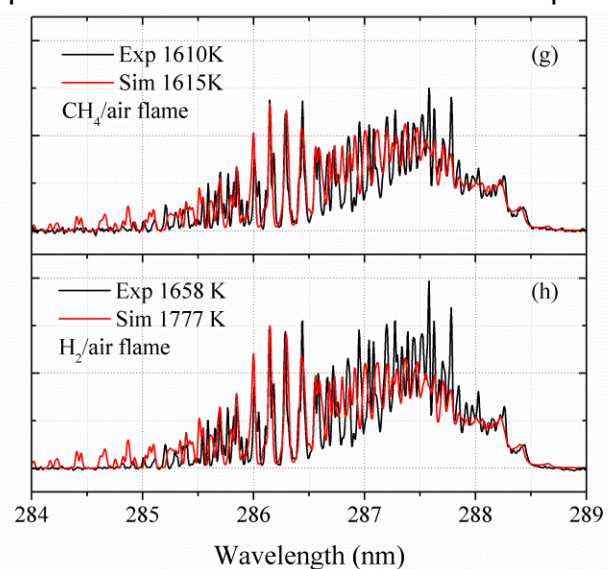
(c) The O_2 REMPI spectrum at 673 K with calculated temperature 684 K.
 (d) The O_2 REMPI spectrum at 873 K with calculated temperature 879 K.

Figure 48. Continued



(e) The O_2 REMPI spectrum at 1073 K with calculated temperature 1058 K.

(f) The O_2 REMPI spectrum at 1273 K with calculated temperature 1231 K.



(g) The O_2 REMPI spectrum at 1610 K with calculated temperature 1615 K in a CH_4 /air flame environment.

(h) The O_2 REMPI spectrum at 1658 K with calculated temperature 1777 K in a CH_4 /air flame environment.

Figure 48. Continued

Table 10. Adopted constants for $O_2(C^3\Pi_g(v' = 2))$

cm^{-1}	F_1	F_2	F_3
n_0	69369	69449	69552
B_{eff}	1.630	1.653	1.691
D_v	1.9×10^{-5}	1.6×10^{-5}	1.9×10^{-5}

Table 11. The comparison between experimental temperatures and O_2 REMPI model simulation results.

Figure 48	Experiment	Simulation	Error (%)
(a)	294 K	321 K	9.18
(b)	473 K	481 K	1.69
(c)	673 K	684 K	1.63
(d)	873 K	879 K	0.69
(e)	1073 K	1058 K	-1.40
(f)	1273 K	1231 K	-3.30
(g)	1610 K	1615 K	0.31
(h)	1658 K	1677 K	7.18

CONCLUSION

In this thesis, eight chapters are focusing on two main parts: (1) the methyl radical detection and (2) the O_2 rotational temperature measurements. Except the last paper, the rest have been already published in different journals. Hence, the detailed conclusions can be found in each chapter. From the arrangement of these chapters, the readers could know the development and progresses that the author has done. The CH_3 were first successfully detected in CH_4 /air flame and then quantitative 1D and 2D experiments have been continuously studied as a demonstration to measure the concentration of CH_3 in real flame environments. The second part is focusing on the temperature measurement based on rotational spectrum of molecular oxygen. The Boltzmann plot method has been first used in the experiments to extract the temperature information from pure O_2 , ambient air, microdischarge and flames. Then the empirical analysis has been demonstrated to calculate the temperature with low requirements on fine structures of O_2 spectrum which is expected to be applied in industry area someday. In the last chapter, the O_2 REMPI spectrum model has been build and calibrated by previous reference. This new model was used to simulate the O_2 spectrum in different temperature fitting the experimental results. This model has been successfully used to fit the O_2 spectrum and measure the rotational temperatures in a variety of environments. More work need to be done to improve the model in the future in order to apply such O_2 temperature measurement technique to scientific and industrial areas.

VITA

Yue Wu was born in Suzhou, China. He lived and study in Suzhou for 19 years and then went to college at Nanjing, China. He got Bachelor and Master of Science in Nanjing University of Aeronautics and Astronautics in 2007 and 2010 respectively. The major was Automobile Engineering. After that he went to University of Tennessee to pursue a Ph.D. degree on Mechanical Engineering. The main research is focused on the laser diagnostics on combustion.