



# Non-intrusive detection of combustion intermediates by photoionization via Rydberg states and microwave backscattering



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## ABSTRACT

A non-intrusive, in-situ detection technique for combustion intermediates in flame environments yields highly resolved spectra that are largely insensitive to molecular vibrations and thus temperature. The technique is based on laser photoionization of target compounds via Rydberg states, followed by detection of the laser-induced plasma with microwave radiation. The feasibility of this approach is tested on methyl radicals that are detected in methane, propane, and hexane fuel-rich flames. The methyl radicals are prepared in the 3s Rydberg state using photoexcitation at 216.4 nm. Using tunable VIS/IR radiation, the molecules are promoted from 3s to the 3p<sub>xy</sub> and 3p<sub>z</sub> Rydberg states. Photoionization out of the 3p states with 355 nm photons results in a small-volume plasma that is detected by microwave backscattering. The previously unobserved 3p<sub>xy</sub> state is found to have a binding energy of 2.57 eV.

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## 1. Introduction

Understanding the mechanisms of combustion reactions is of great importance for basic combustion science as well as for the development of efficient and clean engines [1]. Knowledge of the distribution of the combustion intermediates within a flame provides valuable insights into kinetic parameters and reaction mechanisms. The concentrations of combustion intermediates in flames are often determined using VUV photoionization mass spectrometry [2–6]. Using tunable far-UV radiation sources, it is possible to measure both the ionization potential and the mass of combustion intermediates, thus allowing for isomer-specific detection. While it is possible to map the concentrations of transients across a flame, photoionization mass spectrometry requires the extraction of combustion intermediates from the flame. The sampling cone perturbs the temperature and flow fields of the flame. Therefore, photoionization mass spectrometry may provide inaccurate results. Non-intrusive and in-situ detection is usually achieved by probing vibrational spectra using cavity ring-down spectroscopy (CRDS), coherent anti-Stokes Raman scattering (CARS), or degenerate four-wave mixing (DFWM) [see Ref. [7] and references therein]. However, those techniques are often challenged when one seeks detection of medium to large-sized

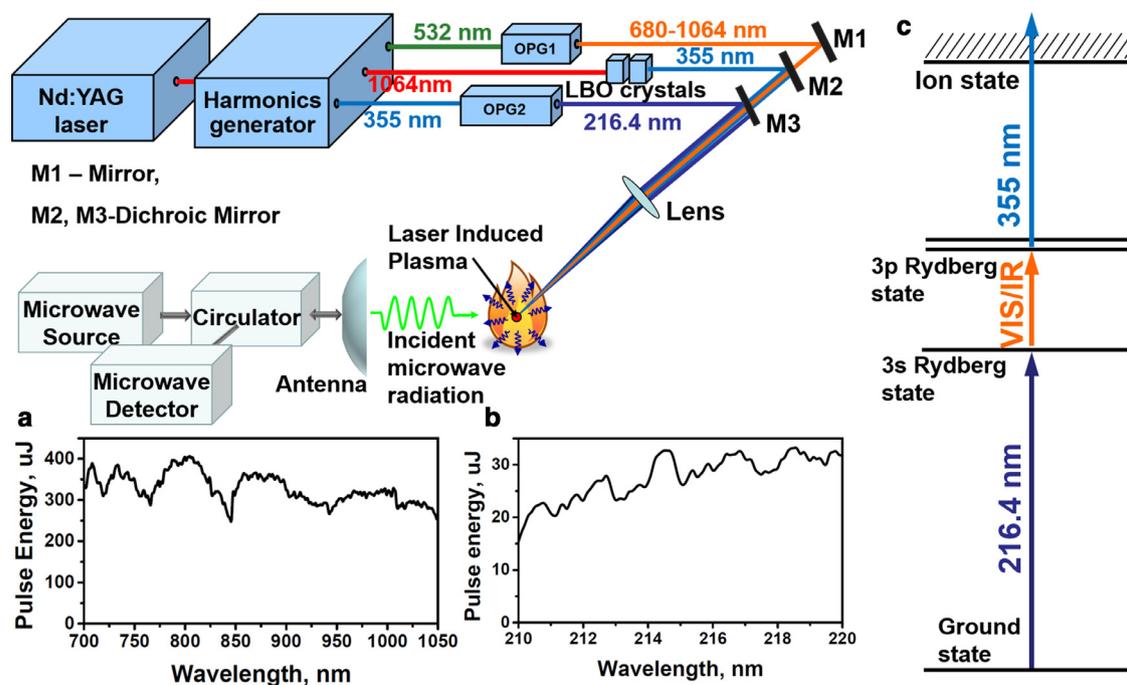
combustion intermediates in flames, since the complexity of vibrational spectra scales very unfavorably with both molecular size and the amount of vibrational energy available to the molecule. Laser-induced fluorescence (LID) has also limited applicability because fluorescence spectra are often broad and not characteristic and because many combustion intermediates do not fluoresce.

We propose here a technique for detection of combustion intermediates that utilizes resonance enhanced multiphoton ionization (REMPI) via molecular Rydberg states. Molecular Rydberg states are excited electronic states with wavefunctions resembling those of a hydrogen atom. Unlike valence electrons, Rydberg electrons do not contribute significantly to molecular bonding, so that the geometrical structures, and potential energy surfaces, of molecules in Rydberg states are nearly identical to those of the corresponding ion states [8]. Since the potential energy surfaces of all the Rydberg states and the corresponding ion state are nearly identical, the same is true for vibrational wavefunctions of all Rydberg states and an ion state.

This results in several unique properties: first, most of the Frank–Condon envelope for Rydberg–Rydberg or Rydberg–ion transitions is enclosed in a very narrow band [no vibrational quantum number change is allowed ( $\Delta v=0$ )]. Therefore, transitions between two Rydberg states or between a Rydberg state and an ion state reveal *highly resolved spectra* [9–11]. This also implies that Rydberg spectra are *insensitive towards vibrational motion* that is, they are not sensitive to temperature. Secondly, since the number of molecular Rydberg states mirrors those of atoms, the complexity

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**Fig. 1.** Schematic diagram of the experimental setup (a) and photoionization scheme (c). The 70 mJ, 21 ps, 10 Hz output of the Nd:YAG laser is unconverted to produce three beams at 1064 nm, 532 nm, and 355 nm. The 355 nm-pumped OPG features a second harmonic generator unit and is tuned to produce 216.4 nm pulses that prepare the molecule in the 3s Rydberg state. The 532 nm-pumped OPG produces tunable radiation that is used to promote the molecules from the 3s to the 3p Rydberg states. Out of those states, the molecule is ionized via 355 nm photons that are produced by upconversion of 1064 nm photons using LBO crystals. The OPG outputs and the 355 nm pulses are overlapped in time using linear delay stages (not shown). The tuning curves for the two OPGs are shown in (b).

of Rydberg spectra does not scale with the molecular size, making the technique well suited for the detection of *large molecules* [12]. Finally, Rydberg orbitals extend across an entire molecule, thus providing sensitivity to the *global structure* of the molecule. Yet Rydberg spectra remain very sensitive to even minor changes in the molecular structure, including conformeric shapes [13–16]. Because the method can be implemented with ultrafast time resolution, it is also possible to apply the photoionization via Rydberg states to probe molecular structure and dynamics in highly energetic molecules [17–21]. The combination of high sensitivity to the molecular structure, insensitivity to vibrational motion, and applicability to large molecules makes it attractive to suggest photoionization through Rydberg states as a tool for detection of combustion intermediates.

We note that the insensitivity of Rydberg spectra to vibrational motion is based on an adiabatic approximation. If Rydberg states are short-lived or heavily mixed with valence states, the Rydberg–Rydberg transitions can be encumbered by vibrational motion. Furthermore, since the lifetimes of the excited electronic states typically depend on the amount of vibrational energy available to the molecule, the temperature of the molecules in a flame may affect the intensities of the Rydberg peaks and their widths.

Molecular Rydberg spectra are usually observed by photoionization coupled with mass spectrometry or photoelectron spectroscopy. When applied to combustion environments, both techniques would require extraction of combustion intermediates from the flame, thus preventing non-intrusive and in-situ detection. Recently we demonstrated that molecular Rydberg spectra could be acquired via microwave scattering from plasma produced by photoionization [22,23]. Detection is initiated by a microwave beam that is directed toward the ionization region [24]. The electrons generated through resonance-enhanced multiphoton ionization (REMPI) create a weakly ionized, small-volume plasma that scatters microwave radiation. The intensity of the scattering signal reflects the generation and evolution of the unbounded elec-

trons inside the plasma. As the photoionization laser wavelength is tuned through the resonances associated with Rydberg–Rydberg transitions, the total electron number in the plasma (and thus the intensity of scattered microwaves) changes, thereby revealing the Rydberg spectrum.

For a proof-of-a-feasibility demonstration we applied the photoionization via Rydberg states followed by detection of the laser-induced plasma to the detection of methyl radicals in methane, propane, and hexane flames. For methane and propane flames, we also performed spatially resolved measurements. The spectra show sharp peaks corresponding to transitions from 3s to 3p<sub>z</sub>, 3p<sub>xy</sub>, as well as higher-lying Rydberg states of the methyl radicals. We note here that the 3p<sub>xy</sub> Rydberg state in methyl radicals, while predicted computationally [25,26], appears not to have been previously observed experimentally. REMPI [27–30] as well as other techniques [31,32] have been applied to detection of methyl radicals. Those measurements were performed in methane flames, which represent a relatively straightforward environment that delivers high concentrations of methyl radicals. The photoionization through Rydberg states affords a high degree of selectivity that allows us to detect methyl radicals in more complex environments such as propane and hexane flames. We anticipate that the technique can be utilized for detection of polyatomic combustion intermediates in complex environments.

## 2. Experimental setup

Our experimental setup consists of two OPGs pumped by a 10 Hz, 21 ps, 70 mJ Nd:YAG laser (Ekspla PL2251C) and a microwave homodyne transceiver system (Fig. 1a). The harmonics generation produces three beams with wavelengths of 355 nm, 532 nm, and 1064 nm. The 355 nm and 532 nm beams are used to pump two optical parametric generators. The 1064 nm output is upconverted to produce 355 nm pulses. We will refer to the 532 nm pumped optical parametric generator (Ekspla PG501-DFG1) as OPG1. The

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