



# The kinetic study of excited singlet oxygen atom $O(^1D)$ reactions with acetylene

Chao Yan<sup>a,\*</sup>, Chu C. Teng<sup>b</sup>, Timothy Chen<sup>a</sup>, Hongtao Zhong<sup>a</sup>, Aric Rousso<sup>a</sup>, Hao Zhao<sup>a</sup>, Guoming Ma<sup>a,c</sup>, Gerard Wysocki<sup>b</sup>, Yiguang Ju<sup>a</sup>

<sup>a</sup> Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, 08544, USA

<sup>b</sup> Department of Electrical Engineering, Princeton University, Princeton, NJ, 08544, USA

<sup>c</sup> State Key Laboratory of Alternate Electrical Power System with Renewable Energy Sources, North China Electric Power University, Beijing 102206, China

## ARTICLE INFO

### Article history:

Received 29 March 2019

Revised 30 April 2019

Accepted 25 October 2019

### Keywords:

Singlet oxygen atom

Photolysis Herriott cell

Faraday rotation spectroscopy

Balanced detection

Plasma assisted combustion

## ABSTRACT

Understanding the multi-channel dynamics of  $O(^1D)$  reactions with unsaturated hydrocarbon molecules in low temperature reaction kinetics is critically important in stratospheric chemistry, plasma chemistry, plasma assisted fuel reforming, materials synthesis, and plasma assisted combustion. A photolysis flow reactor coupled with highly selective mid-infrared Faraday Rotation Spectroscopy (FRS) and direct ultraviolet-infrared (UV-IR) absorption spectroscopy (DAS) techniques was developed for the first time to study the multi-channel dynamics of excited singlet oxygen atom  $O(^1D)$  reactions with  $C_2H_2$  and the kinetics of subsequent reactions. Time-resolved species concentrations of OH,  $HO_2$  and  $H_2O$  were obtained and used to develop a validated kinetic model of  $O(^1D)$  reactions with  $C_2H_2$ . The branching ratios of  $O(^1D)$  reaction with  $C_2H_2$  and subsequent  $HO_2$  kinetics were also quantified. It is found that, contrary to  $O(^1D)$  reactions with saturated alkanes, OH formation via direct H abstraction by  $O(^1D)$  is negligible. The results revealed that two chain-branching and propagation reactions via direct  $O(^1D)$  insertion are the major pathways for radical production. The present study clearly demonstrated the advantage of radical detection and kinetic studies using FRS in the effective suppression of absorption interference from non-paramagnetic hydrocarbons.

© 2019 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

## 1. Introduction

The chemical behavior of electronically excited singlet oxygen atom,  $O(^1D)$ , is of considerable interest and remains experimentally attractive throughout the past few decades due to its substantial roles in establishing chemical composition of atmospheric chemistry, plasma fuel reforming, plasma assisted materials synthesis and plasma assisted combustion [1–5]. Numerous studies [3–5] have shown that  $O(^1D)$  atoms contribute significantly to enhance ignition, reform fuel, and reduce emissions. In particular,  $O(^1D)$  plays an important role in accelerating low temperature chain branching, leading to the formation of cool flames and warm flames [4,6]. Moreover,  $O(^1D)$  also contributes to the oxidation of leaked fuels and unburned hydrocarbons as well as the  $O_3$  cycle in the atmosphere [7,8]. As such, understanding the multi-channel dynamics of the  $O(^1D)$  reaction with fuel molecules and the low temperature reaction kinetics is critical. However,  $O(^1D)$  reactions

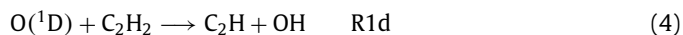
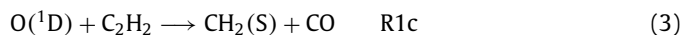
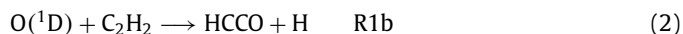
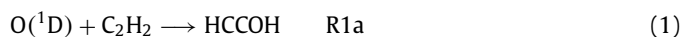
with fuels are complicated by its multi-channel behavior due to direct oxygen atom insertion process.

Early studies [9–14] of the reaction between  $O(^1D)$  with saturated hydrocarbons have been conducted to understand the role of  $O(^1D)$  initiated chain-branching reactions. In reaction dynamic studies, the products and branching ratios of the reaction channels are quite different because of the competition among different channels after oxygen atom insertion. In these reactions, the dominant reaction mechanism is the oxygen atom insertion into C-H bond, while direct H abstraction in the OH formation channel and oxygen atom insertion into the C-C bond are also important in some cases for larger hydrocarbons.

Unfortunately, for even a simple unsaturated hydrocarbon such as  $C_2H_2$ , the multi-channel dynamics of its reaction with  $O(^1D)$  and the kinetics of subsequent reactions are not well understood. Limited relevant studies [15–17] were performed to determine the overall rate constant and estimate the chain-branching products. The determined rate constant is  $k(O(^1D) + C_2H_2) = (3.1 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Based on this estimation [16], four potential reaction channels are considered in the current reaction mechanism:

\* Corresponding author.

E-mail address: [chaoy@princeton.edu](mailto:chaoy@princeton.edu) (C. Yan).



In addition, the radicals formed during these secondary chain-branching reactions initialize further chain-propagation and chain-branching reactions. Formation of radicals (e.g. OH and HO<sub>2</sub>) due to the subsequent hydrocarbon oxidation reactions are therefore extremely important. Understanding the multi-channel dynamics and subsequent reaction kinetics of O(<sup>1</sup>D) with C<sub>2</sub>H<sub>2</sub> is critical to understanding O(<sup>1</sup>D) kinetics with larger unsaturated fuels and unburned hydrocarbons typically containing alkenes and aldehydes.

Time-resolved diagnostics of radical species is crucial in kinetic studies due to the short-lived nature of free radicals. Many spectroscopic techniques have been adopted for radical species detection, the most notable examples include ultraviolet (UV) and mid-infrared (IR) tunable laser absorption spectroscopy (TDLAS), laser-induced fluorescent spectroscopy (LIF), and cavity ring-down spectroscopy (CRDS) [18–24]. For LIF, HO<sub>2</sub> is measured indirectly through chemical conversion to OH, and in many cases uncontrolled reactions involving the peroxy radicals introduce significant experimental uncertainty. Moreover, the sensitivity and uncertainty are limited by fluorescence quenching when the gas pressure is high. Therefore, calibrations are required at each pressure points [21,22].

For CRDS, the acquisition interval is limited by the time required to have sufficient intensity build-up in the cavity and radical quenching on the sampling nozzle [23]. TDLAS in principle can provide much better time resolution; however, sensitive measurement of radicals (e.g. RO<sub>2</sub> and HO<sub>2</sub>) in both CRDS and TDLAS is challenging due to spectral contaminations from H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O, and other hydrocarbons in the mid-IR and UV regions [25,26]. Typically, the efficacy of TDLAS depends on identifying a spectral region free from unwanted absorption features, which becomes challenging in higher pressure experiments, and is compounded when using larger fuels with broadband spectral features [18,23,27].

To this end, Brumfield et al. first applied Faraday rotation spectroscopy (FRS) for HO<sub>2</sub> detection at the exit of a laminar flow reactor [27]. A modulated magnetic field was used to improve the detection limit and remove spectral interference. However, no time dependent measurements were attempted due to the slow field modulation.

In this work, we aim to study the multi-channel dynamics of excited singlet oxygen atom O(<sup>1</sup>D) reactions with C<sub>2</sub>H<sub>2</sub> and the kinetics of subsequent reactions via selective and time resolved detection of HO<sub>2</sub> and OH radicals by using FRS in a balanced detection scheme [28] to effectively cancel common-mode spectral interference.

## 2. Methodology

In this study, we developed a new photolysis flow reactor to study the reactions between O(<sup>1</sup>D) and C<sub>2</sub>H<sub>2</sub> by combining mid-infrared FRS with direct UV-IR TDLAS (Fig. 1).

The reactor is made of quartz tubing with an inner diameter of 56 mm. A pair of spherical mirrors with 250 mm focal length are installed at the both ends of the reactor 913 mm apart to form the multi-pass configuration (MPC), also called Herriot configuration for the QCLs (7.2 μm, Thorlabs and 2.8 μm, Nanoplus) beams. The mirror substrate is UV-grade CaF<sub>2</sub>, offering > 90 % transmission from UV to 7.1 μm. A protective gold coating extends 8 mm from

the edge of the mirror, leaving a 20° section transparent for the IR probe beam to couple into the photolysis cell. The uncoated central part of the spherical mirrors, 40 mm in diameter, allows for the UV photolysis beam to pass through the cell. Two dichroic mirrors (OMEGA OPTICAL) mounted at 45° are placed at the entrance and exit of the flow reactor to allow coupling of both UV photolysis beam and O<sub>3</sub> monitor beam (HG-1 Ocean Optics) in a single-pass configuration. A beam expander consisting of a UV coated plano-concave lens (f = −30 mm) and a UV coated plano-convex lens (f = 200 mm) were used to improve the homogeneity of the photolysis beam. The resulting photolysis beam profile was measured using an energy meter (NOVA II) combined with a diaphragm (ca. 1 mm) over the entire area of the beam. An iris diaphragm was installed at the entrance of the reactor with 18 mm diameter. Generally, the center part of the laser beam has better uniformity, therefore the iris diaphragm cut the laser beam and only allowed relatively uniform laser light passing through the reactor. The measured UV beam profile indicates that the uniformity across the reactor cross-section is ± 8.4 % from the mean value.

Currently the MPC is set up in a 21-pass configuration, resulting in an effective pathlength of 6.3 m after taking into consideration the overlap between the 25 mm diameter photolysis beam and the IR probe beam. The time resolved absorption signals of OH radicals and HO<sub>2</sub> radicals are measured using DFB-QCLs centered around the spectral regions of 3568.52 cm<sup>−1</sup> and 1396.91 cm<sup>−1</sup>, respectively. For HO<sub>2</sub> detection using FRS, the laser frequency is scanned over the absorption features of interest via current modulation at 10 kHz, and the concentration of HO<sub>2</sub> is obtained from spectral fitting with a time resolution of 100 μs. For OH detection, we identified an interference free region around 3568.52 cm<sup>−1</sup>, as a result better temporal resolution (up to 1 μs) can be obtained by operating the laser in continuous mode at fixed laser current.

A kinetic model is developed based on HP-Mech [29,30] with electronically excited species sub-mechanism. The updated HP-Mech was attached in the supplementary material, in which the O(<sup>1</sup>D) and electronically excited oxygen molecule O<sub>2</sub>(<sup>1</sup>Σ) quenching reactions and reactions with O<sub>3</sub>, H<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, CH<sub>2</sub>O, H, H<sub>2</sub>O, CH<sub>3</sub> and C<sub>2</sub>H<sub>2</sub> were considered. The half-life of diffusion time for major radicals and atoms out of photolysis beam (50 ms–100 ms) are more than five times larger than HO<sub>2</sub> radicals decay time (ca. 10 ms) and almost two orders longer compared with OH radical decay time (ca. 1 ms). Thus, the photolysis reactor could be simulated by using closed homogeneous batch reactor (0-D) in Chemkin.

The absolute concentrations of O(<sup>1</sup>D) and the absolute concentration of radicals are critical in order to determine the branching ratios of reaction O(<sup>1</sup>D) with C<sub>2</sub>H<sub>2</sub>. The absolute concentration of O(<sup>1</sup>D) was varied ca. 2 times and quantified by measuring the photon flux inside the reactor [1,26] using the absorption cross-section and the photolysis reaction pathway of O<sub>3</sub> at 266 nm at 60 Torr and 296 K. Ozone concentration is measured by a photomultiplier tube (Hamamatsu R7154) with amplifier (Hamamatsu C6271) using DAS signals from the monochromator (Acton 2500i). To avoid interferences from residual photolysis light or fluorescence from any surface, a 254 nm mercury line filter (Semrock) is installed before the monochromator. The major source of uncertainty in determining absolute concentration of O(<sup>1</sup>D) is quantifying the photolysis laser intensity inside the reactor. Therefore, we used *in-situ* laser light actinometry based on ozone depletion, which is relatively stable at these conditions, with detailed characterization of the cross-section at the monitoring wavelength of 253.65 nm (Mercury line) [31]. Ozone depletion in this measurement occurs in two stages, as seen in Fig. 2. The first stage is direct photolysis depletion: O<sub>3</sub> + hν → O(<sup>1</sup>D) + O<sub>2</sub> and O<sub>3</sub> + hν → O(<sup>3</sup>P) + O<sub>2</sub>. The second stage is chemical reaction consumption: a decay in ozone concentration due to excited oxygen atoms O(<sup>1</sup>D) and excited

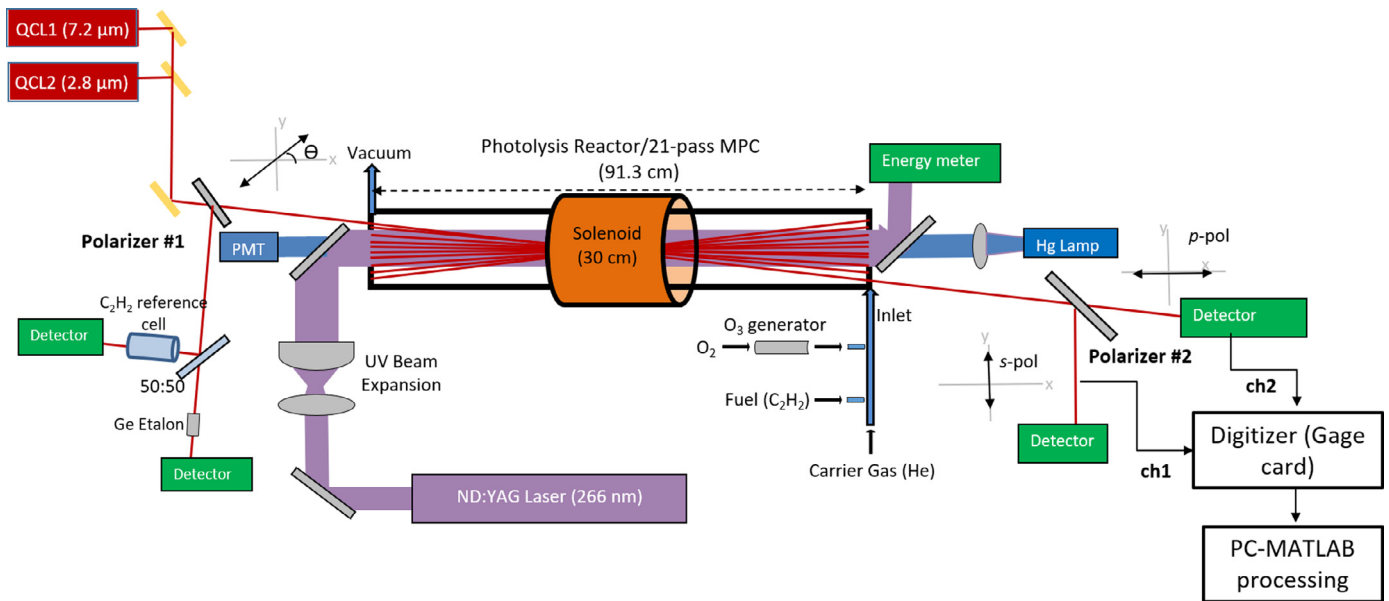


Fig. 1. Experimental setup schematic.

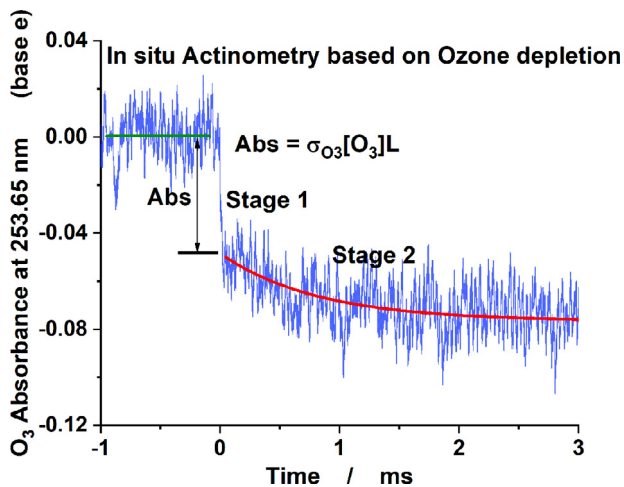


Fig. 2. In-situ actinometry based on ozone depletion. Ozone is detected at the monitoring wavelength of 253.65 nm (Mercury line). Ozone depletion in this measurement occurs in two stages. The first stage is direct photolysis depletion; the second stage is secondary chemical reaction consumption. Green line is linear fitting before UV photolysis. Red line is fitted by HP-Mech which photon fluence is fitting parameter.

oxygen molecules  $O_2(^1\Sigma)$  interaction with  $O_3$ . The main reactions for stage 2 are:  $O(^1D) + O_2 \rightarrow O(^3P) + O_2(^1\Sigma)$ ,  $O_2(^1\Sigma) + O_3 \rightarrow O(^3P) + 2O_2$  and  $O(^1D) + O_3 \rightarrow 2O_2$ . The photon fluence  $F$  (photons  $cm^{-2}$ ) can be calculated based on the absorbance (Abs):

$$F = \frac{Abs}{\sigma_{O_3,253.65} * L * [O_3] * \sigma_{O_3,266}} \quad (5)$$

where the ozone absorption cross-sections at 253.65 nm and 266 nm are:

$$\sigma_{O_3,253.65} = (1.136 \pm 0.012) \times 10^{-17} cm^2 molecule^{-1} \quad (6)$$

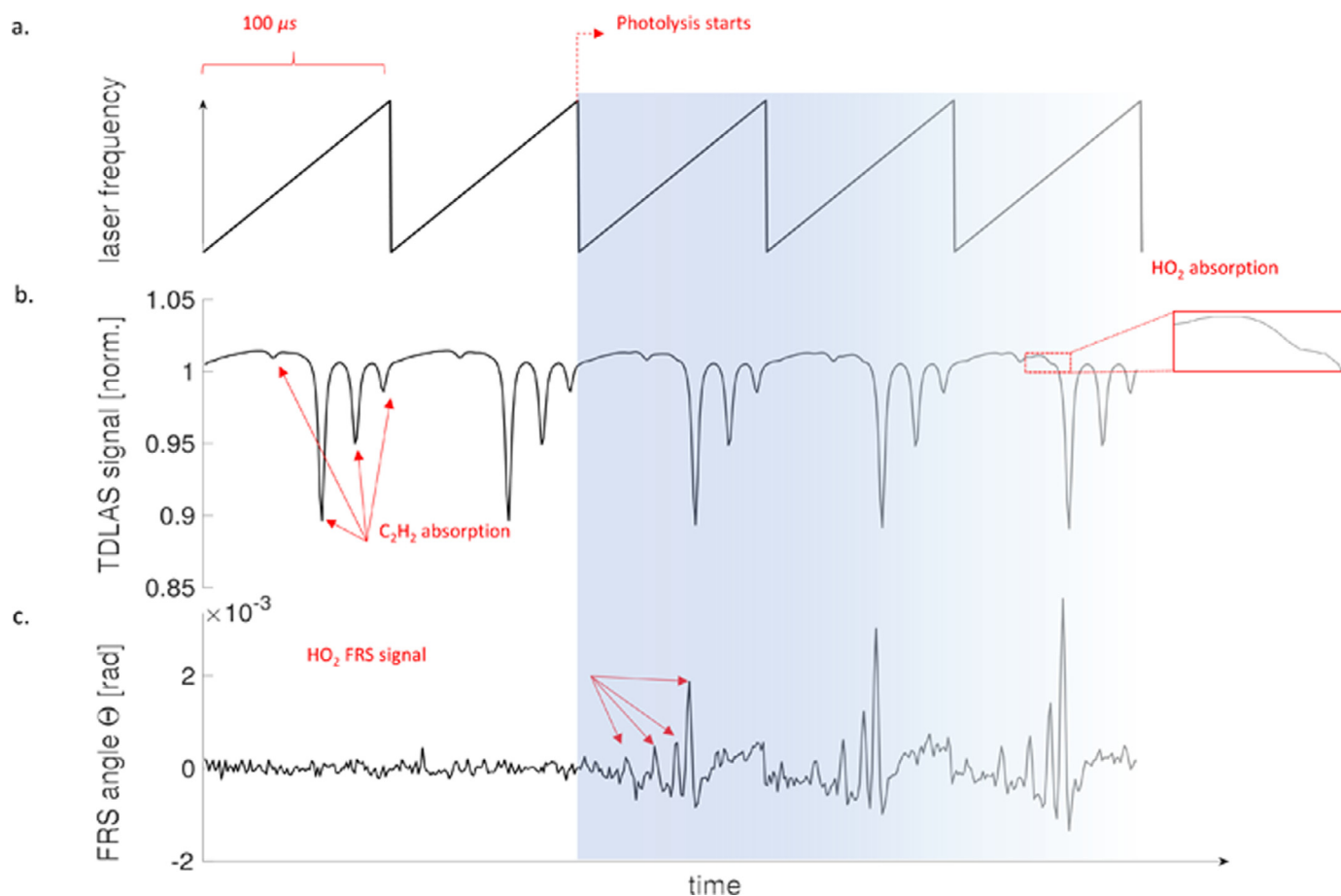
$$\sigma_{O_3,266} = (9.04 \pm 0.64) \times 10^{-18} cm^2 molecule^{-1} \quad (7)$$

$L = 913$  mm is the length of the reactor, and  $[O_3]$  is the concentration. Actinometry measurements were performed before spectroscopy experiments to provide the absolute concentration of  $O(^1D)$  atoms.

In the presence of a paramagnetic species such as  $HO_2$ , magnetically induced circular birefringence (MCB) causes rotation of the polarization plane of linearly polarized light, which leads to the FRS signal. As Fig. 1 shows, a solenoid is used to generate an axial magnetic field (370 Gauss) along the direction of laser propagation within the flow reactor. A pair of wire-grid polarizers are used: one defines the incident linear polarization, and the second serves as an analyzer to convert laser polarization rotation into intensity changes that can be detected using photodetectors. In this case, the analyzer (Polarizer #2) axis is rotated at an angle of  $45^\circ$  with respect to the initial polarizer (Polarizer #1), hence the exit beam is split into the s and p orthogonal polarizations in the transmitted and reflected beam. In this balanced detection configuration, the FRS signal is obtained from the differential measurement between the s and p polarizations while other signals, including non-paramagnetic absorptions, appear as common mode signal [32,33].

The advantage of this detection scheme is demonstrated in Fig. 3, where we compare the TDLAS absorption spectra and FRS spectra observed at  $7.2 \mu m$  under the same experimental conditions. Figure 3(a) shows the saw-tooth laser frequency scanning across the  $HO_2$  transitions at a rate of 10 kHz, leading to an acquisition time of 100  $\mu s$  for each spectrum. A total of 5 consecutive spectra are shown here, with ozone photolysis initiated after the second ramp. The TDLAS spectra is shown in panel (b), where 4  $C_2H_2$  lines are clearly visible and labeled in the figure. After the photolysis reactions, the  $HO_2$  absorption signal appears near a dominant  $C_2H_2$  transition as also labeled in panel (b). At 60 Torr, the  $HO_2$  signal is still distinguishable from  $C_2H_2$  but is already affected by the  $C_2H_2$  lines. This spectral interference is effectively suppressed in the FRS signal as shown in panel (c), where  $HO_2$  formation is clearly visible after photolysis starts.  $HO_2$  concentration is determined by least mean square fitting to the FRS spectrum using HITRAN line parameters. Due to the use of helium as the bath gas, collisional line-broadening parameters deviate from the air-broadening coefficients provided by HITRAN. Based on a well-calibrated frequency axis using a Germanium etalon, the actual broadening coefficient is determined during the nonlinear fitting procedure based on the best fit to the measured spectrum.

It should be noted that at higher pressures, collisional line broadening will result in more severe overlap between this interference and the  $HO_2$  absorption signal, therefore the immunity

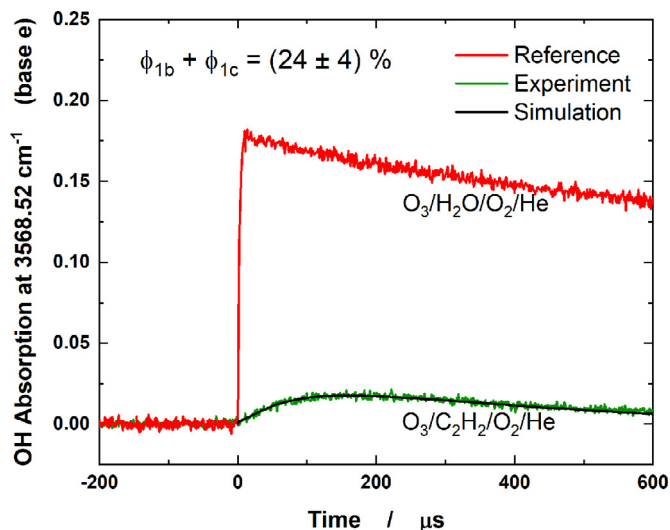


**Fig. 3.** Illustration of spectral interference removal using FRS. (a) Continuous linear laser frequency scanning at a rate of 10 kHz from 1396.8  $\text{cm}^{-1}$  to 1396.95  $\text{cm}^{-1}$ . A total of 5 consecutive spectra are recorded with UV photolysis initiated after the second ramp. (b) TDLAS spectra containing both  $\text{C}_2\text{H}_2$  and  $\text{HO}_2$  absorption signal with prominent  $\text{C}_2\text{H}_2$  features in the same spectral region. A zoomed view of  $\text{HO}_2$  absorption is shown to emphasize the magnitude of spectral interference compared to the  $\text{HO}_2$  signal using TDLAS. (c) FRS spectra measured in the same experimental condition as (b). Note the absence of non-paramagnetic  $\text{C}_2\text{H}_2$  absorptions.

to spectral interference from non-paramagnetic species makes FRS a uniquely suitable technique for *in-situ* measurements of radical species over a wide range of experimental conditions (e.g. with varying pressure and different fuels). In addition, given the clean signal spectrum achievable using FRS, spectral line-fitting is not required to isolate the  $\text{HO}_2$  signal, which would be critical in the case shown in panel (b). Hence line-locked harmonic detection can be performed using fast laser wavelength modulation (e.g. at 100 kHz) to further improve sensitivity and time resolution of FRS detection [34].

In addition to  $\text{HO}_2$ , time-resolved concentration measurements of OH and  $\text{H}_2\text{O}$  are also required for modeling the chemical reaction pathways. In the current setup, another QCL at 2.8  $\mu\text{m}$  is used for measuring OH and  $\text{H}_2\text{O}$  generated during the reactions following ozone photolysis. Since negligible spectral interference between OH and nearby water lines is observed at the current pressure conditions (60 Torr–150 Torr), TDLAS is used for detecting both OH and  $\text{H}_2\text{O}$ . QCL laser frequency fluctuations up to 0.003 nm is observed during the OH measurements. Since this fluctuation is 4 times smaller than the full width at half maximum (FWHM) of OH absorption profiles at 60 Torr and 296 K according to HITRAN simulations, insignificant influence to concentration retrieval is assumed. The absorption cross-section of the OH radical at 3568.52  $\text{cm}^{-1}$  is calibrated using well studied chemical reactions  $\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2$  and  $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$  (Fig. 4). The obtained absorption cross section is:

$$\sigma_{\text{OH}, 3568.52 \text{ cm}^{-1}} = (3.1 \pm 0.5) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1} \quad (8)$$



**Fig. 4.** Comparison of the 60 Torr experimental data and simulation based on updated HP-Mech.  $[\text{C}_2\text{H}_2] = 1.69 \times 10^{16} \text{ molecules cm}^{-3}$ ,  $[\text{O}_2] = 6.32 \times 10^{15} \text{ molecules cm}^{-3}$ ,  $[\text{O}_3] = 2.94 \times 10^{14} \text{ molecules cm}^{-3}$ ,  $[\text{H}_2\text{O}] = 9.23 \times 10^{16} \text{ molecules cm}^{-3}$ ,  $[\text{O}(^1\text{D})] = 5.88 \times 10^{13} \text{ molecules cm}^{-3}$ . The time-resolved measurements of OH radicals. The absorption cross-section of the OH radical at 3568.52  $\text{cm}^{-1}$  is calibrated using well studied chemical reactions  $\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2$  and  $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$  (Reference). In this experimental condition, the recombination channel is dominant (branching ratio  $\phi_{1a} = 76\%$ ), while channel  $\text{O}(^1\text{D}) + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H} + \text{OH}$  (R1d) can be neglected.

It should be noted, however, that with minor modifications to the current system, OH detection using FRS can be implemented to allow measurements at higher reactor pressures where interference becomes significant. The absorption cross section of  $\text{H}_2\text{O}$  at  $3568.29 \text{ cm}^{-1}$  is:

$$\sigma_{\text{H}_2\text{O}}, 3568.29 \text{ cm}^{-1} = 2.45 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1} \quad (9)$$

at 60 Torr, which is taken from the HITRAN database [35].

All the experiments were carried out at 60 Torr and 150 Torr pressure and ambient temperature. The gas flow rates were controlled by mass flow controllers (MKS instruments). Helium was used as the bath gas to dilute the reactant mixtures with total flow rate in the range of 2300 sccm – 12300 sccm. Liquid  $\text{H}_2\text{O}$  (10 – 30  $\mu\text{l} / \text{min}$ ) was injected through a precision syringe pump (Harvard Apparatus, Model PHD 2200), which was delivered through a capillary tube into a heated pre-vaporization chamber maintained at  $90^\circ\text{C}$ .  $\text{O}_3$  was produced by an ozone generator (Ozone Solutions, TG-20) from the downstream of  $\text{O}_2$  flow. The Nd:YAG laser (Quantel Laser, Qsmart 850) was operated at 0.2 – 1 Hz repetition rate. The Q-switch output signal was used as trigger signal for oscilloscope to acquire data.

The concentration of  $\text{O}_3$  in the gas mixture in the range of  $(1.2 - 3.3) \times 10^{14} \text{ molecules cm}^{-3}$ , allowing only a small fraction of the photolysis beam (less than 30%) to be absorbed to maintain homogeneous photolysis light throughout the reactor. The concentration of  $\text{C}_2\text{H}_2$  in the range of  $(1.2 - 2.5) \times 10^{16} \text{ molecules cm}^{-3}$ , which was in excess compared to that of  $\text{O}(^1\text{D})$  ( $(3.8 - 7.5) \times 10^{13} \text{ molecules cm}^{-3}$ ).  $\text{O}_2$  concentration was in the range of  $(2.4 - 6.5) \times 10^{15} \text{ molecules cm}^{-3}$ . The photon fluence inside the reactor was in the range of  $(2.1 - 3.7) \times 10^{16} \text{ photons cm}^{-2}$ .

Reagents: All gases used in this study were obtained from Air-gas. Ultra High Purity (UHP) helium 99.9995 % purity was used as the bath gas in all the experiments. Atomic Absorption (AA) grade acetylene 99.6% purity was well mixed with the bath gas before entering the reactor. UHP oxygen 99.994% purity was the precursor for ozone generation. Deionized water was injected through precision syringe pump after freeze-pump-thaw procedure degassed.

### 3. Results and discussion

Transient absorption profiles of OH and  $\text{HO}_2$  were measured at 60 Torr pressure and ambient temperature, which are shown in Figs. 4–6. To determine the branching ratios of reaction  $(\text{O}(^1\text{D}) + \text{C}_2\text{H}_2)$ , a reaction mechanism based on the HP-mech was used to model and simulate the experimental profiles. The transient absorption profiles were simulated by numerical solutions of a system of differential equations corresponding to the reaction mechanism using Chemkin-Pro software [36].

The reaction rate constants used in the reaction mechanism and absorption cross sections were taken from literature and measured in the current work. The updated HP-Mech reaction mechanism used in the model are listed in the supporting documents. The formation of OH radicals is dominated by the reaction of  $\text{H} + \text{O}_3$  and most H atoms react with  $\text{O}_3$  molecules. The H atoms are contributed by the initial dissociation of the HCCOH and two major secondary reactions ( $\text{HCCO} + \text{O}_2$  and  $\text{CH}_2 + \text{O}_2$ ) in which HCCO radicals are the major products of dissociation of HCCOH (reaction R1b) and majority  $\text{CH}_2(\text{S})$  formed in reaction R1c are quenched by He and  $\text{C}_2\text{H}_2$  to form  $\text{CH}_2$  in less than 1  $\mu\text{s}$  time scale. The total contribution of all other reactions in terms of formation of OH is less than 6% at 60 Torr and ambient temperature. The decay of OH radicals is almost entirely controlled by the two reactions (the major channel:  $\text{C}_2\text{H}_2 + \text{OH}$  and the minor channel:  $\text{HO}_2 + \text{OH}$ ). The rest of the reactions in the mechanism (updated HP-Mech) only places minor roles and can make some small corrections.

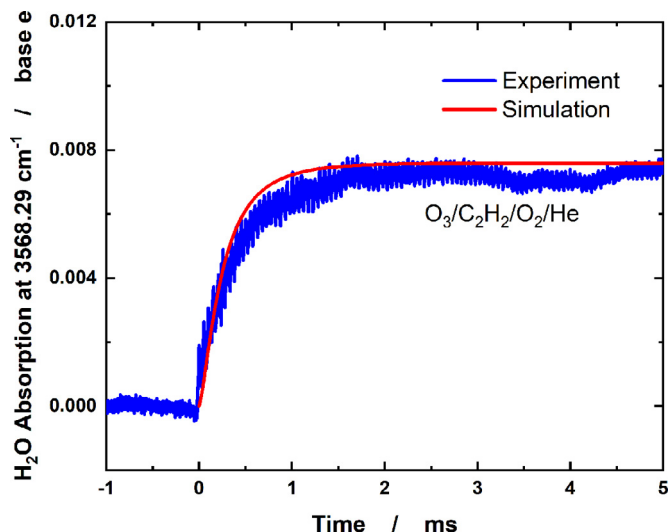


Fig. 5. The time-resolved measurement of  $\text{H}_2\text{O}$  was measured at  $3568.29 \text{ cm}^{-1}$  wavenumber. There is good agreement between the experimental measurement and theoretical simulation based on the updated HP-Mech.  $[\text{C}_2\text{H}_2] = 1.42 \times 10^{16} \text{ molecules cm}^{-3}$ ,  $[\text{O}_2] = 6.27 \times 10^{15} \text{ molecules cm}^{-3}$ ,  $[\text{O}_3] = 1.26 \times 10^{14} \text{ molecules cm}^{-3}$ ,  $[\text{O}(^1\text{D})] = 4.50 \times 10^{13} \text{ molecules cm}^{-3}$ .

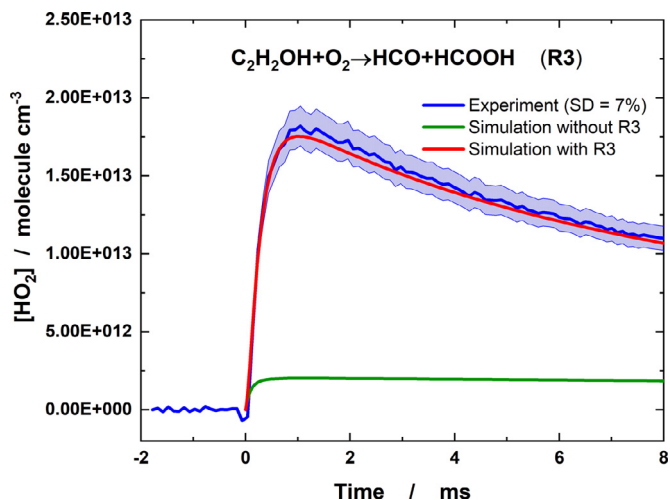


Fig. 6. The temporal profile of  $\text{HO}_2$  concentration with a gas mixture of  $\text{C}_2\text{H}_2/\text{O}_2/\text{O}_3/\text{He}$ .  $[\text{C}_2\text{H}_2] = 2.40 \times 10^{16} \text{ molecules cm}^{-3}$ ,  $[\text{O}_2] = 3.58 \times 10^{15} \text{ molecules cm}^{-3}$ ,  $[\text{O}_3] = 3.28 \times 10^{14} \text{ molecules cm}^{-3}$ ,  $[\text{O}(^1\text{D})] = 9.34 \times 10^{13} \text{ molecules cm}^{-3}$ . A key elementary reaction R3 ( $\text{C}_2\text{H}_2\text{OH} + \text{O}_2$ ) dominates the  $\text{HO}_2$  formation. The rate constant is determined by comparing the experimental profile with the updated HP-Mech simulation.

The initial concentration of  $\text{O}(^1\text{D})$  can be quantified based on the photon fluence, the concentration of  $\text{O}_3$ , and the quantum yield of photodissociation of  $\text{O}_3$  at wavelength 266 nm (4th harmonic Nd:Yag laser). The reaction of  $\text{O}(^1\text{D})$  with  $\text{C}_2\text{H}_2$  is fast and dominant in the current gas mixture system. The lifetime of this reaction is very short (less than 1  $\mu\text{s}$ ). The branching ratios of this reaction are the fitting parameters in this study. The quenching of  $\text{CH}_2(\text{S})$  by He and  $\text{C}_2\text{H}_2$  can be finished less than 1  $\mu\text{s}$  time scale. Over 50 transient species in the reaction mechanism are listed in the supporting documents, such as OH,  $\text{HO}_2$ ,  $\text{CH}_2$ , H, O, HCO,  $\text{CH}_2\text{O}$ , and  $\text{H}_2\text{O}$ . The concentration of stable molecules,  $\text{O}_2$ ,  $\text{C}_2\text{H}_2$ , and  $\text{O}_3$  are present in large excess of the transient species (20 ~ 1000 times). Therefore, the majority initial formed HCCO,  $\text{CH}_2(\text{S})$ , and H in the reaction 1 could convert to OH radicals by the reactions with stable molecule ( $\text{HCCO} + \text{O}_2$ ,  $\text{CH}_2 + \text{O}_2$ , and  $\text{H} + \text{O}_3$ ). By comparing the experimental transient profiles of OH radicals with model

**Table 1**

Branching ratios of reaction 1 at 60 Torr and 296 K. The detailed HP-Mech is listed in the supporting materials. Units are in moles, cubic centimeters, seconds and cal/mole.

Number	Reaction	A	n	Ea	Comments
R1a	$O(^1D) + C_2H_2 \rightarrow HCCOH$	$1.8 \times 10^{14}$	0	0	84% of $k_{1total}$
R1b	$O(^1D) + C_2H_2 \rightarrow HCCO + H$		0	0	$\phi_{1b} + \phi_{1c} = (16 \pm 4)\%$
R1c	$O(^1D) + C_2H_2 \rightarrow CH_2(S) + CO$		0	0	$\phi_{1b} + \phi_{1c} = (16 \pm 4)\%$
R2	$C_2H_2 + OH + M \rightarrow C_2H_2OH + M$	$2.28 \times 10^{19}$	0	1071	Refs. [38,39]
R3a	$C_2H_2OH + O_2 \rightarrow HCO + HCOOH$	$0.74 \times 10^{12}$	0	0	Refs. [40]
R3b	$C_2H_2OH + O_2 \rightarrow HCOHCO + OH$	$2.97 \times 10^{12}$	0	0	Refs. [40]

simulation using updated HP-Mech, the overall branching ratio of R1b and R1c can be determined.

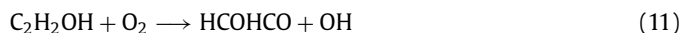
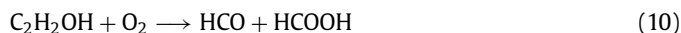
In Fig. 4, the OH radical absorption was measured at  $3568.52 \text{ cm}^{-1}$  at 60 Torr and ambient temperature in a  $C_2H_2/O_3/O_2/He$  gas system. It is interesting to note in Fig. 4 that the peak of OH production is observed 200  $\mu\text{s}$  after photolysis, which indicates that the channel  $O(^1D) + C_2H_2 \rightarrow C_2H + OH$  (R1d) via H abstraction reaction channel forming OH can be neglected because these channels would result in much faster OH rise (ca. 1  $\mu\text{s}$ ). This result is different from the previous studies of  $O(^1D)$  reaction with saturated hydrocarbons [9,14,37], suggesting the uniqueness of  $O(^1D)$  reaction with alkyne.

According to the simulation based on the reaction mechanism (HP-Mech), the chain branching and propagation channels 1b and 1c, as mentioned in the introduction, have similar sensitivities of OH formation, while the channel 1a is dominant chain termination pathway. As a result, through an adjustment of the ratio of branching ratio  $\phi_{1a}/(\phi_{1b} + \phi_{1c})$ , the agreement between simulation and experimental data was greatly improved. However, only an overall chain branching ratios,  $\phi_{1b} + \phi_{1c}$ , can be determined since both of the channel 1b and 1c result in the fast OH radical formations. The derived branching ratio of channel 1a is 84% and the overall branching ratio of channel 1b and channel 1c is  $(16 \pm 4)\%$  under 60 Torr and ambient temperature conditions. Under higher pressure experiments condition (150 Torr), the measured overall branching ratio of Channel 1b and 1c is  $(10 \pm 3)\%$ . Unimolecular reaction with chemical activation can be analyzed by the ratios of stabilization/dissociation. The collision efficiency and bath gas number density are linearly proportional to the ratio of stabilization/dissociation. Comparing with experiments between 60 Torr and 150 Torr conditions, the decomposition channels are decreased. It should be noted that the HP-Mech was updated in this study, some key elementary reactions were either added or corrected based on most recent literature values (shown in Table 1).

Figure 5 shows the  $H_2O$  formation measured using TDLAS at  $3568.29 \text{ cm}^{-1}$  to validate the updated kinetic mechanism (HP-Mech) which including the branching ratios of  $O(^1D)$  reaction with  $C_2H_2$  and key elementary reactions shown in Table 1. The reaction of  $CH_2 + O_2 \rightarrow H_2O + CO$  is the major  $H_2O$  formation channel at the initial 150  $\mu\text{s}$  time range and the reaction of  $OH + HO_2 \rightarrow H_2O + O_2$  is the major  $H_2O$  formation reaction over 150  $\mu\text{s}$  to 5 ms time range. The simulation agrees well with experimental measurements, especially during the initial  $H_2O$  rise but slightly over-predicts the  $H_2O$  concentration at around 1 ms. Signal fluctuation is observed from the minor drifting of the laser wavelength which can not be subtracted by the background measurements.

The path flux analysis indicated that the original mechanism constructed using HP-Mech and ozone measurements with additional reactions involving  $O(^1D)$  has little sensitivity to the production of  $HO_2$ , suggesting the absence of some critical reaction channels for  $HO_2$ . A key reaction of  $C_2H_2OH$  with  $O_2$  has been added into the reaction mechanism which directly influences the

formation of  $HO_2$ :



In fact, Fig. 6 shows dramatically improved agreement between  $HO_2$  measurements and the model prediction after including reaction  $C_2H_2OH + O_2 \rightarrow HCO + HCOOH$  (R3a) and  $C_2H_2OH + O_2 \rightarrow HCOHCO + OH$  (R3b). The reaction R3 is directly sensitive towards the HCO radical production, which is one of the most important intermediates in  $HO_2$  formation. The experimental errors were mainly introduced from magnetic field ( $\pm 10 \text{ G}$ ) and pathlength ( $\pm 21 \text{ cm}$ ) uncertainty, in total 7%. Sensitivity analysis has been carried out for all reactions in the reaction mechanism. Among the reactions included in the mechanism, some reactions have only marginal importance, while most of them are not important at all. Turning off all other  $HO_2$  formation channels results in the change of the peak value of  $HO_2$  not exceeding 15 %.

The branching ratios and rate constants of key reactions examined in this study are summarized in Table 1.

#### 4. Conclusion

In conclusion, the kinetics of  $O(^1D)$  reactions with  $C_2H_2$  are studied through quantitative time-resolved measurements of  $HO_2$ , OH, and  $H_2O$  in a newly developed photolysis flow reactor. In particular, selective and time-resolved detection of  $HO_2$  was successfully demonstrated through use of Faraday rotation spectroscopy by the suppression of spectral interference from non-paramagnetic hydrocarbon absorption via balanced detection. The branching ratios of  $O(^1D)$  reactions with  $C_2H_2$  as well as its subsequent reaction kinetics are quantified.

With the adoption of these reaction channels and the measured reaction rates and branching ratios, an updated kinetic model for  $O(^1D)$  reactions with  $C_2H_2$  based on HP-Mech is developed. The updated model significantly improved the prediction of experimental results of OH,  $HO_2$ , and  $H_2O$ . The results also demonstrate that the new experimental apparatus combining TDLAS with FRS in the photolysis reactor has the potential for sensitive measurements of many species, (e.g. OH,  $HO_2$ ,  $H_2O$ ,  $CH_2O$ ,  $C_2H_2$ , and  $O_3$ ) for the study more complicated chemical kinetics and dynamics involving  $O(^1D)$  reaction with large unsaturated hydrocarbons and oxygenated fuels. Furthermore, understanding of  $O(^1D)$  reactions with fuels provides a key sub-mechanism of reaction kinetics for combustion, plasma chemistry, materials synthesis, and atmospheric chemistry.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgment

This project is supported by the NSF grants CBET 1903362 and 1507358, DOE grant DE-SC0020233 of Plasma Science Center, Princeton SEAS innovation grant, ACEE center grant, and Exxon Mobile research grant.

## Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2019.10.034.

## References

- [1] E.J. Dunlea, A. Ravishankara, Kinetic studies of the reactions of  $O(^1D)$  with several atmospheric molecules, *Phys. Chem. Chem. Phys.* 6 (9) (2004) 2152–2161.
- [2] S. Vranckx, J. Peeters, S. Carl, Kinetics of  $O(^1D) + H_2O$  and  $O(^1D) + H_2$ : absolute rate coefficients and  $O(^3P)$  yields between 227 and 453 K, *Phys. Chem. Chem. Phys.* 12 (32) (2010) 9213–9221.
- [3] Y. Ju, W. Sun, Plasma assisted combustion: Dynamics and chemistry, *Prog. Energy Combust. Sci.* 48 (2015) 21–83.
- [4] S. Yang, S. Nagaraja, W. Sun, V. Yang, Multiscale modeling and general theory of non-equilibrium plasma-assisted ignition and combustion, *J. Phys. D: Appl. Phys.* 50 (43) (2017) 433001.
- [5] S. Yang, X. Gao, V. Yang, W. Sun, S. Nagaraja, J.K. Lefkowitz, Y. Ju, Nanosecond pulsed plasma activated  $C_2H_4/O_2/Ar$  mixtures in a flow reactor, *J. Propuls. Power* (2016) 1240–1252.
- [6] W. Sun, X. Gao, B. Wu, T. Ombrello, The effect of ozone addition on combustion: Kinetics and dynamics, *Prog. Energy Combust. Sci.* 73 (2019) 1–25.
- [7] M.J. Prather, Time scales in atmospheric chemistry: coupled perturbations to  $N_2O$ ,  $NO_y$ , and  $O_3$ , *Science* 279 (5355) (1998) 1339–1341.
- [8] S. Gligorovski, R. Strekowski, S. Barabati, D. Vione, Environmental implications of hydroxyl radicals (OH), *Chem. Rev.* 115 (24) (2015) 13051–13092.
- [9] C. Lin, W. DeMore, Reactions of atomic oxygen ( $1D$ ) with methane and ethane, *J. Phys. Chem.* 77 (7) (1973) 863–869.
- [10] A. Luntz, Chemical dynamics of the reactions of  $O(^1D_2)$  with saturated hydrocarbons, *J. Chem. Phys.* 73 (3) (1980) 1143–1152.
- [11] H. Yamazaki, R. Cvetanović, Collisional deactivation of the excited singlet oxygen atoms and their insertion into the CH bonds of propane, *J. Chem. Phys.* 41 (12) (1964) 3703–3710.
- [12] X. Yang, Multiple channel dynamics in the  $O(^1D)$  reaction with alkanes, *Phys. Chem. Chem. Phys.* 8 (2) (2006) 205–215.
- [13] H.-G. Yu, J.T. Muckerman, Mrci calculations of the lowest potential energy surface for  $CH_3OH$  and direct ab initio dynamics simulations of the  $O(^1D) + CH_4$  reaction, *J. Phys. Chem. A* 108 (41) (2004) 8615–8623.
- [14] S.-i. Wada, K. Obi, Photochemical reaction dynamics of  $O(^1D)$  with saturated hydrocarbons,  $CH_4$ ,  $C_2H_6$ , and  $C_3H_8$ , under bulk conditions and in van der Waals complexes, *J. Phys. Chem. A* 102 (20) (1998) 3481–3491.
- [15] S.A. Carl, A highly sensitive method for time-resolved detection of  $O(^1D)$  applied to precise determination of absolute  $O(^1D)$  reaction rate constants and  $O(^3P)$  yields, *Phys. Chem. Chem. Phys.* 7 (24) (2005) 4051–4053.
- [16] Y. Girard, P. Chaquin, Addition reactions of  $1D$  and  $3P$  atomic oxygen with acetylene. potential energy surfaces and stability of the primary products. is oxirene only a triplet molecule? A theoretical study, *J. Phys. Chem. A* 107 (48) (2003) 10462–10470.
- [17] D. Nuñez-Reyes, K.M. Hickson, Rate constants and H-atom product yields for the reactions of  $O(^1D)$  atoms with ethane and acetylene from 50 to 296 K, *J. Phys. Chem. A* 122 (20) (2018) 4696–4703, doi:10.1021/acs.jpca.8b02267. PMID: 29715024
- [18] M.-W. Chen, B. Rotavera, W. Chao, J. Zádor, C.A. Taatjes, Direct measurement of OH and HO<sub>2</sub> formation in R+ O<sub>2</sub> reactions of cyclohexane and tetrahydropyran, *Phys. Chem. Chem. Phys.* 20 (16) (2018) 10815–10825.
- [19] J.D. DeSain, A.D. Ho, C.A. Taatjes, High-resolution diode laser absorption spectroscopy of the O–H stretch overtone band (2, 0, 0)(0, 0, 0) of the HO<sub>2</sub> radical, *J. Mol. Spectrosc.* 219 (1) (2003) 163–169.
- [20] T. Wallington, P. Dagaut, M. Kurylo, Uv absorption cross sections and reaction kinetics and mechanisms for peroxy radicals in the gas phase, *Chem. Rev.* 92 (4) (1992) 667–710.
- [21] D.E. Heard, M.J. Pilling, Measurement of OH and HO<sub>2</sub> in the troposphere, *Chem. Rev.* 103 (12) (2003) 5163–5198.
- [22] K. Clemitshaw, A review of instrumentation and measurement techniques for ground-based and airborne field studies of gas-phase tropospheric chemistry, *Crit. Rev. Environ. Sci. Technol.* 34 (1) (2004) 1–108.
- [23] J. Thiebaud, C. Fittschen, Near infrared cw-CRDS coupled to laser photolysis: spectroscopy and kinetics of the HO<sub>2</sub> radical, *Appl. Phys. B* 85 (2,3) (2006) 383–389.
- [24] J.D. DeSain, S.J. Klippenstein, J.A. Miller, C.A. Taatjes, Measurements, theory, and modeling of OH formation in ethyl+ O<sub>2</sub> and propyl+ O<sub>2</sub> reactions, *J. Phys. Chem. A* 107 (22) (2003) 4415–4427.
- [25] S.A. Nizkorodov, W.W. Harper, B.W. Blackmon, D.J. Nesbitt, Temperature dependent kinetics of the OH/HO<sub>2</sub>/O<sub>3</sub> chain reaction by time-resolved ir laser absorption spectroscopy, *J. Phys. Chem. A* 104 (17) (2000) 3964–3973.
- [26] C. Yan, S. Kocovska, L.N. Krasnoperov, Kinetics of the reaction of CH<sub>2</sub>O<sub>2</sub> radicals with OH studied over the 292–526 K temperature range, *J. Phys. Chem. A* 120 (31) (2016) 6111–6121.
- [27] B. Brumfield, W. Sun, Y. Ju, G. Wysocki, Direct in situ quantification of HO<sub>2</sub> from a flow reactor, *J. Phys. Chem. Lett.* 4 (6) (2013) 872–876.
- [28] B. Brumfield, G. Wysocki, Faraday rotation spectroscopy based on permanent magnets for sensitive detection of oxygen at atmospheric conditions, *Opt. Express* 20 (28) (2012) 29727–29742.
- [29] X. Shen, X. Yang, J.S. Santner, J. Sun, Y. Ju, Experimental and kinetic studies of acetylene flames at elevated pressures, 52nd Aerospace Sciences Meeting (2014), p. 0129.
- [30] H. Zhao, X. Yang, Y. Ju, Kinetic studies of ozone assisted low temperature oxidation of dimethyl ether in a flow reactor using molecular-beam mass spectrometry, *Combust. Flame* 173 (2016) 187–194.
- [31] S. Sander, D. Golden, M. Kurylo, G. Moortgat, P. Wine, A. Ravishankara, C. Kolb, M. Molina, B. Finlayson-Pitts, R. Huie, et al., Chemical kinetics and photochemical data for use in atmospheric studies evaluation number 15, Technical Report, Jet Propulsion Laboratory, National Aeronautics and Space Administration, Pasadena, CA, 2006.
- [32] J. Westberg, G. Wysocki, Cavity ring-down faraday rotation spectroscopy for oxygen detection, *Appl. Phys. B* 123 (5) (2017) 168.
- [33] A.C. Johansson, J. Westberg, G. Wysocki, A. Foltynowicz, Optical frequency comb faraday rotation spectroscopy, *Appl. Phys. B* 124 (5) (2018) 79.
- [34] C.C. Teng, C. Yan, H. Zhong, A. Rouso, T. Chen, J. Westberg, Y. Ju, G. Wysocki, HO<sub>2</sub> radical measurements in a photolysis reactor using line-locked faraday rotation spectroscopy, *Optics and Photonics for Energy and the Environment*, Optical Society of America (2018), pp. EW3A–6.
- [35] I.E. Gordon, L.S. Rothman, C. Hill, R.V. Kochanov, Y. Tan, P.F. Bernath, M. Birk, V. Boudon, A. Campargue, K. Chance, et al., The HITRAN2016 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transf.* 203 (2017) 3–69.
- [36] R. Kee, F. Rupley, J. Miller, M. Coltrin, J. Grcar, E. Meeks, H. Moffat, A. Lutz, G. Dixon-Lewis, M. Smooke, 2008, Chemkin-Pro.
- [37] C.R. Park, J.R. Wiesenfeld, Full characterization of OH product energetics in the reaction of  $O(^1D_2)$  with hydrocarbons, *The Journal of chemical physics* 95 (11) (1991) 8166–8177.
- [38] K.W. McKee, M.A. Blitz, P.A. Cleary, D.R. Glowacki, M.J. Pilling, P.W. Seakins, L. Wang, Experimental and master equation study of the kinetics of OH+ C<sub>2</sub>H<sub>2</sub>: Temperature dependence of the limiting high pressure and pressure dependent rate coefficients, *J. Phys. Chem. A* 111 (19) (2007) 4043–4055.
- [39] J.P. Senosiain, S.J. Klippenstein, J.A. Miller, The reaction of acetylene with hydroxyl radicals, *J. Phys. Chem. A* 109 (27) (2005) 6045–6055.
- [40] J. Lockhart, M.A. Blitz, D.E. Heard, P.W. Seakins, R.J. Shannon, Mechanism of the reaction of oh with alkynes in the presence of oxygen, *J. Phys. Chem. A* 117 (26) (2013) 5407–5418.