1. Introduction

Recently there has been significant progress demonstrating the utility of non-equilibrium pulsed plasmas for augmentation of combustion phenomena, such as reduction of ignition delay time, as well as increase in flame stability and flammability limits [1]. Non-equilibrium pulsed discharges can be operated at high pressures (up to atmospheric pressure), high pulse repetition rates (1–100 kHz), and are characterized by their inherently high peak reduced electric fields, E/N, of several hundred Townsend (1 Td = 10^{-17} V cm^2). From a fundamental kinetics perspective, however, the mechanisms that dominate in these discharges are not well understood. At these high reduced electric fields, a considerable fraction of discharge power goes into population of excited states by electron impact, with their subsequent collisional quenching,
complicating the kinetic pathways. Fuel oxidation, in particular, offers a challenge to understanding due to the wide range of rates of electron impact, reactive quenching of excited species, and chemical branching reactions, along with temperature changes that may be observed. In many cases, reactions of atomic oxygen play a key role in the chemical oxidation kinetics of these systems.

Many experimental and modeling studies have been conducted with the goal of understanding the kinetic processes involved in plasma combustion. Most of these studies focused on the role of plasma-generated species on important combustion characteristics, such as ignition delay, flame stability, and flame speed. Using nanosecond pulsed discharges, Kosarev et al. [8] demonstrated ignition delay time reduction in hydrocarbon and oxygen mixtures by more than an order of magnitude. Pilla et al. [3] were able to stabilize flames in lean conditions using a nanosecond pulsed discharge with only 0.3% of the maximum power of the flame, while recent work by Lacoste et al. [4] provided insight into the temporal response of a lean-premixed flame to nanosecond pulse discharge excitation. Not only has work been done in understanding the effect of these plasma on ignition and flameholding, but a body of literature exists on chemical kinetic processes involved. Ombrello et al. [5] isolated the kinetic effects resulting from O atoms, O_2(a_1Δ_g), and O_3 from other species produced in the plasma. They found that even at low concentrations, on the order of parts per million, each of these species can significantly enhance flame speed. Kinetic modeling of this system exposed the need for further understanding of collisional quenching rates of excited species with hydrocarbons [6].

Of particular relevance to the work presented here, Sun et al. [7] have studied the effects of atomic oxygen production on the extinction limits of methane diffusion flames at low pressure conditions. Using Two Photon Absorption Laser Induced Fluorescence (TALIF) for the measurement of O atoms, they determined that both the atomic oxygen concentration and the oxidizer flow temperature had a significant effect on the extinction limit. Using kinetic modeling, they were able to determine the specific temperature and concentration range where significant kinetic enhancement is possible [7]. The same authors later expanded upon this study to look at the kinetics of CH_4 oxidation at low temperatures. Through a combination of TALIF, Fourier Transform Infrared (FTIR) absorption spectroscopy, and gas chromatography (GC) they characterized the product species generated in the CH_4/O_2 plasma. These results, combined with kinetic modeling, give critical insight into understanding the formation of atomic oxygen and its role in plasma enhancement of fuel oxidation. Specifically, atomic oxygen was produced by electron impact and during quenching of electronically excited species in collisions with O_2 [8]. Other recent studies include Stanca et al. [9] who measured time-resolved number densities of metastable nitrogen molecules N_2(A^3Σ) (by Cavity Ring-Down Spectroscopy, CRDS), N_2(B^3Π) and N_2(C^3Π) (by calibrated optical emission spectroscopy), and O atoms (by TALIF) in nanosecond pulse filament discharge at atmospheric pressure air, and Popov [10], who studied the effect of pulsed non-equilibrium excitation on ignition of hydrogen/oxygen mixtures. Finally, and of direct relevance to the work to be presented here, Uddi et al. [11] have recently reported absolute O atom number density TALIF measurements and in air, methane/air, and ethylene/air mixtures, and Zuzeek et al. have reported pure rotational CARS thermometry measurements in ethylene/air [12], and hydrogen/air [13] mixtures. Good agreement was found in all cases between the experimental temporal profiles and predictions of a plasma kinetic chemical oxidation model.

In the present paper, new experimental and modeling results are presented of the kinetics of heat release and atomic oxygen production and loss in low temperature, repetitively pulsed nanosecond discharges in H_2–O_2–Ar and C_2H_4–O_2–Ar mixtures. The work is motivated by the recognition that measurements of the temporal evolution of rotational/translational temperature and a key intermediate species, in this case atomic oxygen, provides insight both into kinetics of radical generation in the plasma and energy release during fuel oxidation. This also provides an additional test of kinetic modeling predictions. The primary emphasis of the work is three-fold. First, unlike previous measurements, this work is performed with argon as the diluent gas in place of nitrogen, to exercise the plasma chemistry kinetic model presented in [11] in an environment in which nitrogen chemistry has been eliminated. Specifically, TALIF and pure rotational CARS data is obtained in 20% O_2/Ar/H_2 and 20% O_2/Ar/C_2H_4 mixtures at a variety of equivalence ratios (ranging from stoichiometric to quite fuel lean) at P = 40 Torr. Second, this work presents data obtained in repetitive ‘bursts’ of between 10 and 450 discharge pulses, conditions in which atomic oxygen concentration rapidly builds up to values much higher than those reported in [11] and where heat release is significant. Finally, this work demonstrates the high sensitivity of pure rotational psec CARS for accurate thermometry measurements at low partial pressures of molecular oxygen (as low as ~8 Torr) in non-equilibrium discharges. This is a result of the insensitivity of pure rotational CARS to Stark shifting/broadening effects, which enables the use of high laser intensities.

2. Experimental

The discharge cell employed in this work is essentially the same as used in our previous plasma kinetics experiments in air and premixed fuel-air flows, initially at room temperature [11–14]. Briefly, the plasma is generated in a rectangular (inner cross section 22 mm × 10 mm) quartz channel 200 mm long, with wall thickness of 1.75 mm. Two rectangular copper electrodes, 14 mm × 65 mm, encased in acrylic plastic blocks, are placed on the top and the bottom of the channel, as illustrated in figure 1. The edges of the electrodes are rounded to reduce electric field non-uniformity. The gaps between the electrodes and the acrylic blocks are filled with self-adhesive silicon rubber compound, such that there is no direct contact between the electrodes and ambient air. This is done to prevent corona discharge outside of the test section. The quartz channel is attached to two MDC flanges to enable connection
is approximately ~1 m s⁻¹. This corresponds to flow residence is set to 700 sccm, such that the flow velocity in the channel flows were premixed approximately 2 m upstream of the cell. The fuel and oxidizer mixtures, at a pressure of 40 Torr and different equivalence ratios. Fuel and oxidizer flow rates through the test cell were metered by MKS mass flow controllers. The fuel and oxidizer used as an oxidizer, as well as in H₂–O₂–Ar and C₂H₄–O₂–Ar mixtures, at a pressure of 40 Torr and different equivalence ratios. Fuel and oxidizer flows through the test cell were metered by MKS mass flow controllers. The fuel and oxidizer fed through a 100 μm pinhole. The interaction length is measured by translating a glass plate (microscope cover slip) 100 μm thick along the length of the probe region and measuring the resulting non-resonant background signal. The CARS signal is generated over the interaction length, and is spatially filtered using irises, after re-collimation by a 500 mm lens. The signal is then focused by a 100 mm spherical lens into a 0.75 m spectrometer equipped with a 1200 line mm⁻¹ grating (Shamrock 750). The spectra are detected using a back-illuminated electron-multiplying CCD camera (EMCCD, Andor). The signal was accumulated over 200–400 laser shots (i.e. over 20–40 s).

To improve signal discrimination and reduce noise due to scattering of the probe beam, a polarization approach [22] is employed, previously used by Zuzeek [12] for pure rotational O₂ rotational temperature on the centerline of the discharge cell was measured by picosecond, broadband, pure rotational Anti-Stokes Raman scattering (CARS). The schematic of CARS optical diagnostics setup is shown in figure 3. The second harmonic output of a picosecond Nd:YAG, ~150 ps pulse duration, (Ekspla SL333) is divided into two beams, using a half wave-plate and a thin-film polarizer. The power ratio between the two beams can be adjusted by rotating the half-wave plate. The higher power beam, vertically polarized, pumps a broadband modeless dye laser [17–19]. The low-power beam, horizontally polarized, is used to produce the CARS probe pulse and passes through a second half-wave plate to rotate the polarization, such that it is orthogonal to the polarization of the pump pulse. In the present work, the probe beam has a horizontal polarization and pulse energy ranging from 1 to 5 mJ pulse⁻¹.

The broadband modeless dye laser is patterned after Roy [20]. The laser has no optical cavity or grating and generates broadband output, free of mode structure. The laser consists of a side-pumped oscillator, followed by a side-pumped pre-amplifier and an end-pumped final amplifier cells. A broadband high reflector is placed within 3 mm of the oscillator cell, allowing ~80% temporal overlap between the reflected amplified spontaneous emission from the oscillator cell and 532 nm pumping of the oscillator. A 600 mm plano-convex lens is placed after the final amplifier to pseudo-collimate the output beam. A solution of Rhodamine 597 in methanol is used to generate broadband output centered at ~573 nm, with FWHM of 6.8 nm and conversion efficiency of 16.8%. As shown in figure 3, the dye laser output is divided into two beams, pump and Stokes. A half-wave plate and a polarizing beam splitter cube are inserted into the pathway of each beam, such that the pump beam is vertically polarized and the Stokes beam is horizontally polarized. For each beam, pulse energy ranges from about 1.0–3.6 mJ pulse⁻¹.

As shown in figure 3, the pump, Stokes, and probe beams are focused into the test cell with a 500 mm spherical lens using a planar-BOXCARS phase matching configuration [21], producing a cylindrical probe region with diameter of less than 100 μm and interaction length of ~4 mm. The diameter of the probe region was estimated by passing the laser beams through a 100 μm pinhole. The interaction length is measured by translating a glass plate (microscope cover slip) 100 μm thick along the length of the probe region and measuring the resulting non-resonant background signal. The CARS signal is generated over the interaction length, and is spatially filtered using irises, after re-collimation by a 500 mm lens. The signal is then focused by a 100 mm spherical lens into a 0.75 m spectrometer equipped with a 1200 line mm⁻¹ grating (Shamrock 750). The spectra are detected using a back-illuminated electron-multiplying CCD camera (EMCCD, Andor). The signal was accumulated over 200–400 laser shots (i.e. over 20–40 s).

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CARS temperature measurements in H₂–air and C₂H₄–air plasmas. Briefly, since the signal and the probe beam have orthogonal polarizations, placing a high extinction thin-film polarizer (CVI) into the CARS signal path reduces the polarized stray light by more than a factor of 1000. CARS resonant and non-resonant signals, however, are reduced to a factor of 9/16 and 1/9, respectively, of the signals which would be obtained for parallel polarizations. This has the effect of reducing the influence of the non-resonant background. Time delay between the probe and the Stokes beam is controlled by rotating a prism mounted on a translation stage, placed into the beam path. By adjusting the time delay, the temporal overlap of all three beams was optimized by maximizing the non-resonant signal obtained from a microscope cover slip, and was held the same for the work present here.

Background, caused mainly by scattering of the probe and pump beams, was subtracted from the experimental spectra by blocking the Stokes beam. After background subtraction, the spectra were normalized and corrected for the dye laser output distribution. For this, the spectra were divided by a reference non-resonant background spectrum, obtained before data collection by placing a 1 mm thick glass microscope slide into the CARS probe region. The reference spectrum also accounts for the convolution of the probe beam with the broadband dye laser. Finally, the square root of the spectrum was compared with synthetic CARS spectra generated using the Sandia CARSFIT code [23], using least squares fitting to the experimental data to infer the O₂ rotational temperature. For each set of experimental conditions, five CARS spectra were taken, each of them accumulated over 200–400 laser shots. For each experimental spectrum, the temperature was inferred from the best fit synthetic spectrum, and the average of the five temperature values was determined. The error bars reported in the present work represent the 95% confidence interval for the average temperature values inferred using this procedure. This corresponds to the precision of the temperature data.

Atomic oxygen concentration was measured by Two Photon Absorption Laser Induced Fluorescence (TALIF).
This technique, in which absorption of two photons (from the ground state to a higher excited state) results in single photon fluorescence to an intermediate state, is frequently used for measurements of atomic species concentrations. A schematic diagram of the apparatus used is shown in figure 4. This technique has been described in detail previously [11, 24] and is only summarized here. Briefly, the 532 nm output of an injection seeded, Q-switched Nd:YAG laser (Continuum Surelite III) pumped a tunable dye laser (Continuum ND6000) centered around 619 nm. This output was then mixed with the 355 nm output from the Nd:YAG laser to generate the 226 nm UV beam required for TALIF measurements. Mixing of the beams was controlled using an InRad autotracker device as the dye laser was scanned across the 2p 3P → 3p 3P two photon absorption transition. The UV beam was focused ~2 cm downstream of the measurement volume and its energy was kept below 750 µJ per pulse during the experiment, in order to minimize saturation effects. The 844 nm single photon fluorescence from the 3p 3P → 3s 3S transition passed through an 80 nm bandpass filter and 1:1 imaged onto a standard photomultiplier tube. Argon emission lines around 850 nm, measured in pure argon, were found to be very weak compared to the atomic oxygen signal, and were subtracted prior to data processing. The PMT signal was amplified by a factor of 25 and numerically integrated using a programmable digital oscilloscope. During the experiments, a photodiode was used to monitor scattered UV laser light, which was then used for normalization of the signal. To put the relative measurements on an absolute scale, the atomic oxygen signal was compared to that from a known concentration of xenon [25, 26]. This method of calibration is efficient since no change in optics or detectors is necessary for the two measurements. Uncertainty in absolute atomic oxygen concentration was estimated to be approximately 30–40%, primarily due to uncertainty in published O atom quenching rates [24]. Note that at the present conditions, fluorescence decay could not be resolved in time, such that the quenching rate could not be measured directly.

3. Kinetic modeling

To obtain insight into kinetics of plasmachemical radical generation / consumption and resultant heat release, we use a kinetic model developed in our previous work [11–14, 27–29]. The model incorporates nonequilibrium O2–Ar plasma chemistry, expanded to include hydrogen and ethylene dissociation processes in the plasma [10, 14]. The dominant radical species generation processes in H2–O2–Ar and C2H4–O2–Ar plasmas, incorporated into the model are listed in table 1. In the present work, kinetic processes involving low-energy metastable electronics states of oxygen, O2(a1Δ) and O2(b1Σ), are neglected since discharge energy fraction into electron impact excitation of these two states at high electric fields in ns pulse discharge is quite low, a few percent. The plasma chemistry model is coupled with one of two ‘conventional’ hydrogen–oxygen chemistry mechanisms developed by Popov [10], with the low-temperature rate coefficient of reaction O + OH → H + O2 corrected as discussed in [29], k = 2.4 · 10−11 exp(109/T) cm3 s−1, and by Konnov [30]. For kinetic modeling of reacting C2H4–O2–Ar mixtures, a hydrocarbon chemistry mechanism developed by Wang [31] was used. These chemistry mechanisms have been developed and validated for relatively high temperatures, significantly higher than in the present experiments, and may well be inaccurate at the present conditions. Assessing applicability of these mechanisms is one of the objectives of the present work.
electron density significantly. In the plane-to-plane geometry, attachment, and ion conversion processes do not affect the [27]. On the nanosecond time scales involved, recombination, which results in plasma self-shielding and limits ionization are (i) electron impact ionization, and (ii) charge separation control the electric field and the electron density in the plasma. However, in a nanosecond pulsed dielectric barrier discharge charge transfer and ion-molecule reactions (e.g. see) [35]. ion neutralization, electron attachment and detachment, and Penning ionization, electron–ion recombination and ion–electron reactions occur with the electric field, E/N, in the plasma. In general, predicting these parameters in the electric discharge requires solving Poisson’s equation for the electric field, coupled with the equations for the electron number density and ion number densities. In electronegative plasmas, this approach requires incorporating detailed charged species kinetics, including electron impact and Penning ionization, electron–ion recombination and ion–electron neutralization, electron attachment and detachment, and charge transfer and ion-molecule reactions (e.g. see) [35]. However, in a nanosecond pulsed dielectric barrier discharge in plane-to-plane geometry a simpler approach may be used. Basically, at these conditions, the two dominant processes that control the electric field and the electron density in the plasma are (i) electron impact ionization, and (ii) charge separation which results in plasma self-shielding and limits ionization [27]. On the nanosecond time scales involved, recombination, attachment, and ion conversion processes do not affect the electron density significantly. In the plane-to-plane geometry, real-time measured electron density, $n_e(t)$, and electric field in the plasma, $E(t)$, during the pulse are predicted by the analytic model of energy coupling in a ns pulse discharge [27], which incorporates key effects of pulsed breakdown and sheath development on ns time scale. The model also predicts pulse energy coupled to the plasma versus pulse voltage waveform, pressure, and discharge geometry. The accuracy of the analytic model was verified comparing its predictions to a numerical model where the Poisson equation and ionization kinetics in a repetitively pulsed nanosecond discharge in air were fully coupled with plasma chemistry [38]. In particular, the results of [38] show that for relatively long discharge burst durations (~10–100 pulses), the predicted O atom number density and temperature distributions between the electrodes are uniform over ~80–90% of the discharge gap, justifying the use of a 0D analytic model [27].

In the present experiments, energy coupled to the plasma is measured using custom-made, high-bandwidth, calibrated voltage and current probes, as discussed in [39]. Briefly, a pair of identical voltage probes, and a pair of identical current probes have been used to measure voltage and current, respectively, to cancel common mode current and voltage produced during the discharge pulse. In [39], it was shown that coupled pulse energy is nearly independent of pulse repetition rate and remains nearly constant during the pulse burst as long as the temperature remains constant, after which it scales nearly proportionally to number density, in good agreement with the ns pulse discharge model predictions. In the present work, the electric field and electron density predicted by the ns pulse discharge model are used as inputs in the plasma chemistry model.

The species concentration equations used in the plasma chemistry model are coupled with the two-term expansion Boltzmann equation for plasma electrons. The model incorporates the energy equation for the temperature on the discharge centerline [27], with heat transfer to the walls being the dominant energy loss mechanism at the present conditions. The model was exercised to predict time-resolved temperature and species concentrations during a burst of multiple discharge pulses and in the afterglow. The modeling calculations become very time-consuming for long discharge bursts (~100–500 pulses), since the code needs to manage repetitive increase and reduction of time step, by ~6 orders of magnitude, to resolve every discharge pulse while minimizing the run time in the afterglow between the pulses. At these conditions, pulse-periodic discharge excitation during the burst was replaced by continuous excitation at a constant ‘effective’ reduced electric field, $(E/N)_{eff}$, and the same time-averaged discharge power. The effective $E/N$ value was determined by matching the results of pulsed-periodic and continuous excitation for a burst of 21 pulses in O$_2$–Ar, as discussed in section 4.

The present model has been validated using measurements of O atom concentration (TALIF) [11, 14], temperature (rotational CARS, LIF, vibrational CARS) [12, 13, 28, 29], and OH concentration (LIF) [29] in ns discharge in air, and mixtures of air with H$_2$, CH$_4$, C$_2$H$_4$, and C$_3$H$_8$.

### 4. Results and discussion

Figure 5 shows a series of broadband, single-shot ICCD camera images of repetitively pulsed nanosecond discharge plasma emission in a 20% O$_2$–Ar mixture at $P = 40$ Torr and discharge pulse repetition rate of 40 kHz. The images are taken both through the side wall and through the end window of the discharge cell, using a 5 µs camera gate. In both sets of images, the plasma appears diffuse and uniform during the entire burst (with the exception of pulse #1). Images taken in a H$_2$–O$_2$–Ar ($\phi = 0.5$) plasma, shown in figure 6, appear similar to the ones in the O$_2$–Ar mixture, although end window images exhibit some reduction of the plasma volume in the region between the electrodes. Side wall images taken in a C$_2$H$_4$–O$_2$–Ar ($\phi = 0.43$) plasma, shown in figure 7, demonstrate noticeable discharge filamentation, readily apparent late in the burst. Images taken through the end wall clearly show predominant plasma formation along the center plane and in the corners of the channel. Similar filamentary structures have been observed in

### Table 1. Dominant primary radical species generation processes in the plasma.

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate, cm$^3$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2 + e^- = O(3P) + O(3P,1D) + e^-$</td>
<td>$\sigma^a$ [32]</td>
</tr>
<tr>
<td>$Ar + e^- = Ar_e + e^-$</td>
<td>$\sigma^b$ [33]</td>
</tr>
<tr>
<td>$H_2 + e^- = H + H + e^-$</td>
<td>$\sigma^c$ [32]</td>
</tr>
<tr>
<td>$C_2H_2 + e^- = products + e^-$</td>
<td>$\sigma^d$ [34]</td>
</tr>
<tr>
<td>$O(3P) + Ar = O + Ar$</td>
<td>$5 \cdot 10^{-12}$ [35]</td>
</tr>
<tr>
<td>$O(3P) + O_2 = O + O_2$</td>
<td>$5 \cdot 10^{-11}$ [35]</td>
</tr>
<tr>
<td>$O(3P) + H_2 = H + OH$</td>
<td>$1.1 \cdot 10^{-10}$ [10]</td>
</tr>
<tr>
<td>$O(3P) + C_2H_2 = O + O + C_2H_2$</td>
<td>$4 \cdot 10^{-10}$ [36]</td>
</tr>
<tr>
<td>$Ar_m + O_2 = Ar + O + O$</td>
<td>$2.1 \cdot 10^{-10}$ [37]</td>
</tr>
<tr>
<td>$Ar_m + H_2 = Ar + H + H$</td>
<td>$6.6 \cdot 10^{-11}$ [37]</td>
</tr>
<tr>
<td>$Ar_m + C_2H_4 = Ar + C_2H_3 + H$</td>
<td>$5.4 \cdot 10^{-10}$ [37]</td>
</tr>
</tbody>
</table>

| $\sigma$ | Calculated by the Boltzmann solver from experimental cross sections. |
| $\sigma^a$ | Total cross section for excitation of argon metastable $^3P_0,2$. |
| $\sigma^b$ | Sum of electronic excitation cross sections ($b_1^\Sigma, b_2^\Sigma, c_1^\Pi, c_2^\Pi, c_3^\Pi, a_1^\Sigma, a_2^\Pi$). |
| $\sigma^c$ | Three dissociation channels into $C_2H_3 + H$, $C_2H_2 + H_2$, and $C_2H_2 + H + H$. |
our previous experiments in repetitively pulsed discharges in room temperature air, although at significantly higher pressures, \( P = 90–100 \) Torr [40]. At \( P = 60 \) Torr, adding even small amounts of ethylene (0.07–0.7% mole fraction) or nitric oxide (0.7% mole fraction) to otherwise stable and diffuse air plasma resulted in well-defined filament formation [40]. This behavior, as well as kinetic modeling which predicts accelerated heating rate in C2H4–air and NO–air plasmas (compared to air plasmas), suggests that filamentation is caused by ionization—heating instability [41]. Further evidence of this was obtained by adding helium to filamentary, stoichiometric ethylene–air plasmas (10–40% mole fraction), thus increasing the thermal conductivity of the mixture, which countered the instability and helped dissipate the filaments [40]. Finally, preheating of air, H2–air, and C2H4–air mixtures to \( T = 500 \) K, instead of helium addition, to increase the thermal conductivity, resulted in generation of diffuse, filament free, repetitive nanosecond discharge plasmas at much higher pressures, up to at least \( P = 100–200 \) Torr [28, 29]. Summarizing, adding ethylene to the baseline 20% O2–Ar oxidizer mixture results in significant plasma nonuniformity.

Figure 8 plots experimental positive polarity pulse waveforms (applied electric field and coupled / stored energy) in a 20% O2–Ar mixture, obtained using the high bandwidth voltage and current probes [39], shown as dashed lines. The applied electric field was calculated from the voltage as follows, \( E_p = U_p/(L + 2d/\varepsilon) \), where \( U_p \) is the pulse voltage, \( L = 10 \) mm is the distance between the quartz channel walls (the discharge gap), \( d = 1.75 \) mm is the wall thickness, and \( \varepsilon = 3.8 \) is the dielectric constant of quartz. It can be seen that peak applied field is approximately 18 kV cm\(^{-1}\) and peak energy stored in the capacitive load exceeds 1 mJ. However, almost all of the stored energy is reflected back to the pulse generator, such that net energy coupled to the plasma during the pulse is fairly low, approximately 0.10 mJ pulse\(^{-1}\). As discussed in [27], the low value of the coupled / peak energy fraction is primarily due to the relatively long pulse duration, ~75 ns FWHM. Basically, the slow voltage increase during the pulse results in breakdown and subsequent plasma shielding occurring at fairly low voltage, thus limiting the energy dissipated in the plasma. The results for the negative polarity pulse are close, and the coupled pulse energy remains nearly the same during the entire 400-pulse burst. Figure 8 also plots the nanosecond pulse discharge model predictions, shown as solid lines, using a linear combination Gaussian fit to the experimental voltage pulse. One can see that the time-dependent stored / coupled energy, as well as the asymptotic value of energy coupled to the plasma, predicted by the model, 0.12 mJ pulse\(^{-1}\), are in good agreement with the measurements, providing confidence in the energy coupling model. The electric field in the plasma, predicted by the model, illustrates that breakdown in the cell indeed occurs at low applied electric field, approximately 3 kV cm\(^{-1}\) (see figure 8). After breakdown, the field in the plasma remains fairly low, in spite of applied electric field being very high (up to 18 kV cm\(^{-1}\)), due to plasma self-shielding.

Figure 9 plots time-dependent reduced electric field and electron density in the plasma, at the conditions of

![Figure 5. ICCD images of the plasma, taken both from the side and from the end of the discharge cell during the discharge burst in a 20–80% O2–Ar mixture. P = 40 Torr, camera gate 5 μs. Pulse number in the burst is identified in the images. In an image taken from the end of the cell, approximate cross section of the quartz channel and the extent of the electrodes are indicated.](image)
figure 8. It can be seen that although breakdown begins at $E/N \approx 240 \text{Td}$, the electric field rapidly (within a few ns) decreases to $E/N \approx 40 \text{Td}$, as the electron density increases. Electric field reduction caused by charge separation essentially terminates electron impact ionization, such that electron density levels off at $n_e \approx 10^{12} \text{cm}^{-3}$ (see figure 9). After breakdown, the electric field in the plasma is proportional to the time derivative of the applied electric field \[27\]. From figure 9, it can be seen that nearly 80% of the pulse energy is coupled to the plasma when the reduced electric field is fairly high, above $E/N = 30 \text{Td}$, thus considerably reducing the discharge energy fraction into excitation of low-energy excited electronic states of oxygen, $O_2(a^1\Delta)$ and $O_2(b^1\Sigma)$ \[42\]. Specifically, measurements of discharge energy fraction into excitation of $O_2(a^1\Delta)$ in $O_2$–Ar mixtures versus reduced electric field in a 20% $O_2$–Ar mixture \[42\] have shown that this fraction peaks at $\approx 33\%$ at $E/N \approx 2 \text{Td}$ and falls to $\approx 10\%$ at $E/N \approx 7 \text{Td}$ (modeling calculations \[42\] predict a somewhat higher value of $\approx 12\%$ at $E/N \approx 10 \text{Td}$). Figure 9 also plots $O$ atom concentration during the pulse, predicted by the model. As expected, $O$ atoms are generated predominantly at high $E/N$ values, reaching a predicted number density of $[O] \approx 2 \cdot 10^{11} \text{cm}^{-3}$ at the end of the pulse. The net discharge pulse energy going into to oxygen dissociation, both by electron impact and by energy transfer from metastable argon atoms (the former being the dominant channel), is about 60%. Most of the remaining input energy is rapidly thermalized, resulting in temperature rise due to energy defect in $\text{Ar}_m$ and $O(^1\text{D})$ quenching reactions, $\text{Ar}_m + O \rightarrow \text{Ar} + O + O$, $O(^1\text{D}) + O_2 \rightarrow O + O_2$.

Figure 10 plots time-dependent $O$ atom concentration and temperature predicted by the model during a 21-pulse burst in a 20% $O_2$–Ar mixture. The modeling predictions in figure 10 are shown for two different approaches, (i) discrete, repetitively pulsed excitation of the mixture by the reduced electric field and $O$ atom density waveforms shown in figure 9 (solid lines), and (ii) continuous excitation at a constant `effective` value of the reduced electric field, $(E/N)_{\text{eff}}$, and the same time-averaged discharge power (dashed lines). Stepwise $[O]$ dependence on time, caused by rapid $O$ atom generation (on $\approx 100 \text{ns}$ time scale) during individual discharge pulses, is apparent in figure 10, and the $O$ atom number density at the end of the burst, predicted using the repetitively pulse excitation, is consistent with the experimental result. The effective reduced electric field value, $(E/N)_{\text{eff}} = 88 \text{Td}$, was chosen such that the $O$ atom number density at the end of the burst predicted during continuous excitation would match the result of more accurate repetitively pulsed excitation (see figure 10). As can be seen from figure 10, the use of this approach somewhat overpredicts the rate of temperature rise on the time scale of $\approx 0.5 \text{ms}$ (20-pulse burst). However, on the time scale of $\approx 10 \text{ms}$, which corresponds to a 400-pulse burst, the difference between the temperature rise predicted using these two approaches is only about $\approx 10\%$ (see figure 11). This comparison justifies the use of the simplified continuous excitation approach.
for modeling of long discharge bursts. In general, the use of the ‘effective’ E/N, compared to E/N pulse waveform, is adequate when the metric used for comparison of these two approaches represents a kinetic process responsible for a significant net fraction of input energy (at the present conditions, oxygen dissociation).

From figure 11, comparing the measured and the predicted decay of O atoms after the burst, it can be seen that the experimental O atom number density is approximately a factor of two higher compared to the model predictions at the end of the burst. This difference is not very sensitive to the choice of O2 electron impact dissociation cross sections [32, 43]. Note that since the coupled discharge pulse energy predicted by the 1D discharge model is close to the experimental value (see figure 8), and since the model predicts about 60% discharge energy input into O2 dissociation, matching the experimental data points would require significantly higher specific energy loading per molecule than measured in the experiment (see figure 8). The reason for this discrepancy, also detected in the repetitive nanosecond pulse discharge in air [12], is not understood. While it is possible that coupled energy distribution across the horizontal centerplane of the plasma, especially in the spanwise direction, may be non-uniform and peak along the centerline, this does not appear to be consistent with plasma emission intensity distribution (see figure 5).

Figure 12 shows typical experimental and synthetic ‘best fit’ rotational CARS spectra, at two different conditions, (a) at relatively low temperature, in 20% O2–Ar mixture after 101 discharge pulses, and (b) at relatively high temperature, in C2H4–O2–Ar mixture at the equivalence ratio of $\phi = 0.5$, after 351 discharge pulses. The synthetic spectra were generated by a computer code CARSFIT [23], and
the ‘best fit’ rotational temperature, $T = 325 \pm 2 \text{K}$ and $T = 543 \pm 30 \text{K}$, respectively, were determined by least squares fitting. From figure 12, it can be seen that the experimental and the synthetic spectra match each other closely. Note that pure rotational CARS has the inherent advantage, compared to vibrational Q-branch CARS, that high pump/Stokes beam intensities can be employed without distortion of the spectra caused by Stark broadening/shifting effects. This is due to the basic spectroscopy in which the individual rotational transitions in O$_2$ molecule are separated by $8B$, where $B \approx 1.45 \text{cm}^{-1}$ is the rotational constant. The fact that even rotational levels are absent in the ground electronic state of O$_2$, due to quantum mechanical symmetry requirements for the total wave function, enables the individual rotational transitions to be completely resolved even with modest spectral resolution. At this resolution, the line shape is completely determined by the instrument function of the spectrometer and as such is independent of Stark effects.

Figures 13 and 14 compare experimental rotational temperatures, inferred from CARS spectra, and absolute O atom concentrations, obtained from calibrated TALIF measurements, in H$_2$–O$_2$–Ar mixtures, with kinetic model predictions. The modeling calculations in figures 13 and 14 are done using the H$_2$–O$_2$ chemistry mechanism developed by Popov [10]. It can be seen that temperature measured in the O$_2$–Ar mixture increases approximately linearly with time, from room temperature to $T \approx 350 \text{K}$ after 400 pulses, consistent with the discharge pulse energy being approximately the same throughout the burst [39]. This trend is well reproduced by the kinetic model, although the model slightly overpredicts the heating rate in O$_2$–Ar. As expected, adding hydrogen to the oxidizer (O$_2$–Ar mixture) results in more rapid heating, caused by energy release in hydrogen oxidation reactions, since the coupled pulse energy in O$_2$–Ar and H$_2$–O$_2$–Ar mixtures is nearly the same. Although this trend is predicted by the kinetic model fairly well, the model overpredicts the heating rate in the lean H$_2$–O$_2$–Ar mixture (at $\phi = 0.1$). Basically, the model predicts the heating rate to be weakly dependent on the equivalence ratio, since at low temperatures, in the absence of chain branching, the rate of energy release in plasmachemical hydrogen oxidation reactions is limited by the amount of radicals generated in the plasma rather than by the amount of fuel. In the experiment, however, the heating rate in the lean H$_2$–O$_2$–Ar mixture, at $\phi = 0.1$,
is lower compared to the results obtained at $\phi = 0.5$ and $\phi = 1.0$ (see figure 13).

The results of O atom TALIF measurements, plotted in figure 14, demonstrate that in the O$_2$–Ar mixture, O atoms rapidly accumulate over first ~50 pulses, and then continue to increase more gradually, up to $[O] \approx 3 \cdot 10^{15} \text{ cm}^{-3}$, when their generation rate in the plasma (both by direct electron impact and by energy transfer from metastable
Ar atoms, see table 1) becomes nearly balanced by ozone production,
\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}, \quad (1) \]
\[ \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \quad (2) \]

Although the model underpredicts the rate of O atom production during the first ~100 pulses, up to a factor of 2, its predictions converge with the experimental results for longer burst durations. Adding hydrogen to the mixture results in significantly more rapid O atom loss. Analysis of dominant O atom generation and removal channels [13, 44] shows that this occurs via the reduced mechanism,
\[ \text{O}^{(\text{D})} + \text{H}_2 \rightarrow \text{H} + \text{OH}, \quad (3) \]

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}, \quad (4) \]
\[ \text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2, \quad (5) \]
\[ \text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}, \quad (6) \]
\[ \text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2, \quad (7) \]
\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2, \quad (8) \]
\[ \text{H} + \text{OH} \rightarrow \text{O} + \text{H}_2, \quad (9) \]
\[ \text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}, \quad (10) \]
\[ \text{H} + \text{HO}_2 \rightarrow \text{OH} + \text{OH}, \quad (11) \]
with reactions of equations (3)–(8) being dominant at the present conditions (near room temperature and high O atom number densities). The entire oxidation process at these conditions occurs essentially in the absence of chain branching. Chain branching, primarily in reverse reactions (7,9), begins only when the temperature increases up to $T = 500–600$ K [13]. This suggests that energy release in low-temperature reacting H$_2$–O$_2$–Ar mixtures, in addition to Joule heating, is mainly due to radical recombination and is limited by the amount of radicals (primarily O(3P) and O(1D) atoms) generated in the plasma. Although in the presence of hydrogen the rate of O atom generation in the plasma somewhat decreases, the enhanced rate of O atom removal due to hydrogen oxidation is the dominant effect. Thus, adding 3.8% of H$_2$ to the baseline O$_2$–Ar mixture (equivalence ratio $\phi = 0.1$) results in O atom number density reduction by almost an order of magnitude, from $[O] \approx 3 \cdot 10^{15}$ cm$^{-3}$ to $[O] \approx (3 – 4) \cdot 10^{14}$ cm$^{-3}$. The kinetic model reproduces this trend rather well (see figure 14).

To assess sensitivity of the present kinetic model to the choice of H$_2$–O$_2$ chemical kinetics mechanism, the modeling calculations were repeated at the conditions of figures 13 and 14, using the chemistry mechanism developed by Konnov [30]. The modeling results are compared with the experimental data in figures 15 and 16. It can be seen that in this case the temperature rise predicted by the model in O$_2$–Ar is in somewhat better agreement with the data (see figure 15), since the rates of O atom recombination in this mechanism, O + O + M $\rightarrow$ O$_2$ + M, (M = Ar, O$_2$) are slower, such that the quasi-steady-state
O atom number density in O₂–Ar predicted by the model using this mechanism is somewhat higher (see figure 16). However, the net rate of O atom removal in H₂–O₂–Ar mixtures is overpredicted, almost entirely due to the higher rate coefficient of reaction \( \text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2 \), \( k_T = 300 \text{K} = 1.8 \cdot 10^{-10} \text{cm}^3 \text{s}^{-1} \) (compared to \( k_T = 300 \text{K} = 3.45 \cdot 10^{-11} \text{cm}^3 \text{s}^{-1} \) in the corrected Popov’s mechanism). Because of this, the model now underpredicts the quasi-steady-state O atom number density, by up to a factor of 2 (see figure 16).

For both H₂–O₂ chemistry mechanisms used, the number density of water vapor in H₂–O₂–Ar mixtures predicted at the end of the burst is close to the number density of O atoms generated in the baseline O₂–Ar mixture at the end of the burst, [H₂O] \( \approx 4 \cdot 10^{15} \text{cm}^{-3} \) for the Popov mechanism and [H₂O] \( \approx 5 \cdot 10^{15} \text{cm}^{-3} \) for the Konnov mechanism at \( \phi = 1.0 \). This demonstrates that, as expected, hydrogen oxidation is basically limited by the amount of O atoms generated in the plasma without fuel (O atom mole fraction \( \sim 0.2\% \), [O]/[O₂] \( \sim 1\% \)), and that almost no radical chain branching occurs at these low temperatures. At these conditions, additional temperature rise caused by plasmachemical hydrogen oxidation can be estimated as the difference between net oxidation reaction enthalpy, \( \text{O} + \text{H}_2 \rightarrow \text{H}_2\text{O} \), \( \Delta h_R \approx 5.1 \text{eV} \), and O atom formation enthalpy, \( h_\text{O} \approx 2.6 \text{eV} \), times O atom mole fraction generated in the O₂–Ar mixture, \( \gamma_0 = n_\text{O} / N \approx 3 \cdot 10^{15} \text{cm}^{-3} / 1.3 \cdot 10^{18} \text{cm}^{-3} \approx 2.3 \cdot 10^{-3} \), \( \Delta T_{\text{max}} \approx (\Delta h_R - h_0) \cdot \gamma_0 / c_p \approx 25 \text{K} \). This estimate is somewhat lower than the experimental result and is close to the kinetic model predictions (see figures 13 and 15).

Figures 17 and 18 compare experimental rotational temperatures and O atom number density measurements in C₂H₄–O₂–Ar mixtures with kinetic model predictions using the hydrocarbon–oxygen chemistry mechanism developed by Wang [31]. Again, it can be seen that temperature and O atom number density predicted in O₂–Ar mixtures are in rather good agreement with
the measurement results. However, in the presence of ethylene the model considerably underestimates both the temperature rise (by up to a factor of 2 at $\phi = 0.5$) and the O atom number density, especially in lean mixtures (by up to a factor of 6 at $\phi = 0.08$, $C_2H_4$ mole fraction 0.5%). The results predicted using a different hydrocarbon chemistry mechanism, GRI Mech 3.0 [45], are similar to the ones shown in figures 17 and 18. Note that the present model accurately predicted O atom generation and decay in room-temperature and ethylene-air mixtures excited by a single-pulse nanosecond discharge [11] and by a burst of nanosecond pulses [12], where the pathways and rates of dominant reactions of O atom removal, $C_2H_4 + O \rightarrow CH_3 + HCO$ and $C_2H_4 + O \rightarrow CH_2 + CH_2O$ [31], are known well.

The fact that the model underpredicts both the O atom number density and the temperature rise, while predicting the coupled pulse energy correctly, strongly suggest that energy loading per molecule in the discharge is considerably higher compared to the quasi-one-dimensional model used [27]. The most likely reason for this is discharge nonuniformity, such that the effective time-averaged volume occupied by the plasma at these conditions becomes smaller and the energy loading per molecule is higher. This would result in considerably higher O atom concentration and more rapid heating due to heat release in plasmachemical reactions of ethylene oxidation. Qualitative evidence of this is apparent from $C_2H_4$–$O_2$–Ar plasma images, especially the ones taken through the window at the end of the cell (see figure 7). This behavior is consistent with our previous results on ignition of mildly preheated ($T = 100–200^\circ C$) $H_2$–air and $C_2H_4$–air mixtures, excited by repetitive nanosecond pulse discharge [46], which demonstrated nearly uniform large-volume ignition of hydrogen and distinctly non-uniform ignition of ethylene. Preheating the discharge cell is expected to reduce the effect of plasma nonuniformity considerably, such that more accurate measurement results can be obtained in hydrocarbon–oxygen–argon mixtures.

5. Summary

The paper presents results of time-resolved rotational temperature, by pure rotational Coherent Anti-Stokes Raman Spectroscopy (CARS) and absolute O atom number measurements, by Two-Photon Absorption Laser Induced Fluorescence (TALIF). The experiments were conducted in nanosecond pulse discharges in $H_2$–$O_2$–Ar and $C_2H_4$–$O_2$–Ar mixtures, initially at room temperature, operated at a high pulse repetition rate of 40 kHz, in plane-to-plane double dielectric barrier geometry at a pressure of 40 Torr. ICCD images show that $O_2$–Ar and $H_2$–$O_2$–Ar plasmas remain diffuse and volume-filling during the entire burst (with the exception of pulse #1). Images taken in $C_2H_4$–$O_2$–Ar plasma demonstrate significant discharge filamentation and constricttion along the center plane and in the corners of the test section. The experimental results demonstrate high accuracy of pure rotational psec CARS for thermometry measurements at low partial pressures of oxygen in nonequilibrium plasmas. The results are compared with kinetic modeling calculations, using two different $H_2$–$O_2$ chemistry and $C_2H_4$–$O_2$ chemistry mechanisms. In $H_2$–$O_2$–Ar mixtures, the kinetic modeling predictions, using the chemistry mechanism suggested by Popov, are in fairly good agreement with the data, predicting temperature rise and O atom accumulation in long discharge bursts, up to 450 pulses. The results show that adding hydrogen to the mixture results in additional temperature rise, due to its partial oxidation by radicals generated in the plasma, essentially without chain branching. In $C_2H_4$–$O_2$–Ar mixtures, the model consistently underpredicts both temperature and O atom number density. The most likely reason for difference between the experimental data and the model predictions is discharge non-uniformity developing when ethylene is added to the mixture, at fairly low temperatures involved. To reduce the effect of plasma nonuniformity, future measurements will be conducted in mildly preheated hydrocarbon-oxygen-argon mixtures, such as has been done in our recent work [29]. This will also allow studying kinetics of O atom decay and energy release in plasmachemical reactions at the conditions when chain branching plays a significant role.

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