Kinetic Modeling and Sensitivity Analysis of Plasma-Assisted Oxidation in a H₂/O₂/Ar Mixture

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Abstract

A numerical scheme describing the oxidation process induced by single and multiple dielectric barrier discharges in a H₂/O₂/Ar mixture is developed. Path flux and sensitivity analyses are performed in order to identify important reaction paths. The analyses are conducted for an initial mixture of 2000 ppm H₂ and 3000 ppm O₂ balanced in Ar at a constant pressure of 1 atm and temperatures ranging from 474 K to 1008 K, covering both below and above the second explosion limit. Results with only one discharge as well as with repetitive discharges at rates between 1 kHz and 5 kHz are discussed. Three sets of reaction schemes leading to H₂O formation are identified: two short-time-scale schemes involving negative ions and O(¹D), respectively, and a long-time-scale scheme involving ground state radicals, which is responsible for the majority of the H₂O formation and driven by plasma dissociation of H₂ and O₂. At temperatures below the second explosion limit, the last scheme drives the straight chain propagation mechanism without causing exponential growth of radicals, where the reactions of HO₂ play important roles on the overall fuel oxidation. At temperatures above the second explosion limit, H and O atoms produced from the dissociation of reactants by deactivation of excited argon subsequently trigger ignition significantly reducing the ignition delay. The consumption of H₂ and O₂ which follows is governed by conventional high temperature chain branching kinetics and occurs at a rate equivalent to that of the purely thermal reaction. Increasing the pulse repetition rate of the discharge at low temperatures results in a shift of the rate-limiting steps from reactions of H atoms to those of the OH radical. Furthermore, the kinetics of metastable Ar^{*m}, HO₂, O₂(¹Δ_g), and O(¹D) are analyzed and their implications to other systems are discussed.

Keywords: Plasma assisted combustion; Nanosecond plasma discharge; Kinetic modeling; Sensitivity analysis

1 Introduction

One of the major challenges in developing a scramjet engine is dealing with the short flow residence time in the combustor. If the order of the characteristic chemical reaction time for combustion is longer than the flow residence time, the engine will simply not work [1]. Recently, the use of non-equilibrium plasma discharges to influence combustion processes has attracted interest as the means to overcome this issue [2–5]. The primary attraction of this technique, called plasma-assisted combustion (PAC), is that it enables volumetric energy injection into the internal degrees of freedom (DOF) of the gas molecules, which may efficiently accelerate the overall oxidation process of the fuel. This is a unique feature of PAC in that non-equilibrium plasmas have the potential of *in situ* production of reactive species at desirable times or spatial locations in the gas flow. Although many past studies have demonstrated the effectiveness of PAC, the understanding of the mechanism as to how exactly plasma discharges enhance combustion is still limited. One of the reasons is the vastly different kinetic pathways that plasma discharges introduce. In this regard, the reduced electric field E/N , which is the electric field divided by the gas number density, is an important parameter governing the behavior of plasma discharges. E/N is a scale of the energy that electrons gain from the electric field between collisions, and it characterizes how the electron energy is redistributed to heavy particles.

The value of E/N controls the partitions of the electron energy among the DOF of the constituent atoms and molecules of the system. At different values of E/N , the electron energy is lost to different DOF with progressively higher energy levels being excited as E/N increases [5]. These high-energy DOF may equilibrate with other DOF or among themselves relatively slowly, allowing for other kinetic processes to occur. In fact, vibrationally or electronically excited particles sometimes demonstrate chemical reaction rates significantly higher than their ground-state

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7 counterparts [5] due to their high energy. The kinetics governing PAC can be conceptually
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9 summarized into a three step process: (1) the creation of high-energy species by electron-impact
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11 processes, (2) reactions of the high-energy species with other species, and (3) their subsequent
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13 influences on the overall oxidation mechanism.
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16 The electron-impact processes themselves are relatively well understood, especially for
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18 common gases such as Ar, N₂, O₂, or H₂. For modeling purposes, databases of electron impact
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20 collision cross sections for a desired gas are readily available [6]. Using a Boltzmann equation
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22 solver (e.g., BOLSIG+ [7]), the electron energy distribution function (EEDF) can be obtained for a
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24 given temperature, mixture, and E/N . From the EEDF, the production rates of high-energy species
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26 can be determined. Such high-energy species may be roughly divided into four types: ground state
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28 radicals, electronically excited species, ions, and vibrationally excited species.
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32 The ground state radicals, which include reactant fragments such as O or H atoms, are
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34 already incorporated in conventional combustion reaction mechanisms. Thus, their roles in fuel
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36 oxidation have been studied rigorously, particularly at high temperatures ($T > 1000$ K) [8]. On the
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38 other hand, their role at lower temperatures has had less attention because the oxidation processes
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40 are too slow to make use of in practice due to low concentrations of active species and reaction
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42 barriers of tens of kcal/mol with typical hydrocarbons. However, PAC opens new possibilities to
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44 oxidize fuels at lower temperatures, and provides new motivation to study low temperature radical
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46 kinetics. An example of such work is that of Uddi et al. [9], where they performed optical
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48 measurements of the O atom density in a plasma and concluded that the consumption of O atoms
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50 was much faster in a fuel/air mixture than in air alone. Sun et al. [10] extended the analysis of O
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52 atom reactions even further, and identified that the reaction chain is extended to produce H and OH
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54 radicals, which subsequently initiates the low temperature oxidation chemistry of fuels.
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With regards to electronically-excited species, the combustion enhancement effects of the singlet delta oxygen molecule $O_2(a^1\Delta_g)$ have had significant study. The introduction of singlet delta oxygen to combustion systems has produced higher flame speeds and shorter ignition delays, both experimentally [11] and numerically [12–14]. For H_2/O_2 systems, the enhancement has been described to take place through the chain branching step [12,14]:

which proceeds faster than its ground state counterpart:

More recently, the influence of singlet oxygen atom $O(^1D)$ has been studied by Popov [15] and shown to influence oxidation through its reaction with fuel molecules by rapid production of radicals, particularly at low temperatures where the reactions of the ground state O atoms are slow.

The rates of ion reactions (i.e., ion-molecule, ion-ion, or ion-electron) have been compiled in several forms [16–20]. However, their significance in contributing to fuel oxidation is generally minimal due to their small concentrations in weakly ionized plasmas.

While outside of the scope of the present study, vibrationally excited H_2 molecules, $H_2(v)$, may play an important role for ignition and combustion phenomena [5]. For a few reactions such as

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H_2 molecules at vibrational quantum number $v = 1$ are known to have two to three orders of magnitude faster reaction rates than those at $v = 0$. However, their implications on the overall oxidation process have not been investigated thoroughly due to modeling complexities associated with their consideration. Incorporating vibrationally excited molecules in a chemical kinetics model is quite challenging because the data necessary to construct a reasonably-validated reaction

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7 mechanism involving vibrational excitations are limited, and in many cases not available. Still,
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9 despite the challenge, there have been several studies which have incorporated vibrationally excited
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11 species in models of H_2/O_2 systems [21–23], and all agree that $\text{H}_2(v)$ molecules are capable of
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13 accelerating the rate of radical generation and reducing ignition delays.
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16 It should be evident that the range of different types of species and reactions involved in
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18 PAC systems can make the system quite complex to understand. Any attempt at a detailed kinetic
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20 analysis almost certainly requires some level of modeling analysis. PAC modeling studies have
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22 incorporated both zero-dimensional [23–25] and one-dimensional [26] formulations. Of these works,
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24 the one by Nagaraja et al. [26] was unique not only because of the dimensionality, but also because
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26 they investigated the cumulative effects on ignition caused by multiple discharges. Although the
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28 ability to simulate the chemical kinetics in a multi-discharge system is desirable, the analysis
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30 becomes more difficult than single-pulse systems.
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34 In summary, investigations to gain systematic understanding of the chemical kinetics of
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36 PAC are limited, particularly compared to kinetic studies on high temperature hydrocarbon
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38 oxidation, and a greater effort is needed in order to develop the understanding necessary for
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40 optimized integration of PAC into practical systems. As part of these elementary efforts, this study
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42 presents modeling results of PAC in a nanosecond dielectric barrier discharge (DBD) plasma flow
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44 reactor (PFR) at various temperatures and atmospheric pressure. Also, implications of the results on
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46 the overall PAC process are discussed with the aid of a formal sensitivity analysis. Together with
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48 species profiles and reaction flux analysis, in-depth insight into the governing kinetics is presented,
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50 including rate-limiting steps, competing steps, and time scales of the different sub-categories of
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52 chemistry. The modeling efforts presented in this paper are based on the experimental conditions
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54 presented in Tsolas et al. [27], to which the readers are directed for comparisons between
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56 experimental and modeling results.
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2 Numerical Framework

2.1 Modeling Concept and Governing Equations

In this study, the chemical reactions in the PFR are simulated using a code with zero-dimensional formulations, assuming that species concentrations and E/N are only functions of time (time that a fluid particle experiences in the reactor, as described later). With this zero-dimensional treatment, the use of sensitivity analysis with a detailed chemical reaction mechanism on a system with multiple plasma discharges is enabled without a prohibitively high computational cost.

The model consists of a modified SENKIN module [28] from CHEMKIN III suite, coupled with ZDPlasKin [29] package that provides access to a Boltzmann equation solver, BOLSIG+ [7]. The governing equations are a system of ordinary differential equations (ODEs) describing mass (species), and electric charge conservation equations. This set of ODEs describes the time-dependent chemical kinetics in DBD plasma reactors as an initial value problem.

The mass conservation of the species i is written in terms of the mass fraction Y_i as:

$$\frac{dY_i}{dt} = \nu W_i \dot{\omega}_i \quad (1)$$

where ν is the specific volume of the mixture, $\dot{\omega}_i$ is the molar production rate of the species i , and W_i is the molecular weight of the species i . The production rates are calculated by the law of mass action, whereas the reverse rates are calculated using the forward reaction rate constants and equilibrium constants. The electric field inside the discharge gap E_{gap} is calculated by charge conservation (Kirchhoff's law) applied to the equivalent circuit of the DBD plasma system as shown in Fig. 1:

$$\frac{dV_{\text{gap}}(t)}{dt} = \left(1 + \frac{2l_d}{\varepsilon L}\right)^{-1} \left(\frac{dV_{\text{app}}(t)}{dt} - \frac{2l_d}{\varepsilon_0 \varepsilon} J_d(t) \right), \quad (2)$$

$$E_{\text{gap}}(t) = \frac{V_{\text{gap}}(t)}{L}. \quad (3)$$

Here, V_{gap} is the voltage across the discharge gap, V_{app} is the voltage applied to the electrodes, J_{d} is the discharge current density, L is the gap length, l_{d} is the thickness of the dielectric layer, ε is the relative permittivity of the dielectric material, and ε_0 is the vacuum permittivity. The relation described in Eqn. (3) is only an approximation that assumes quasi-neutrality everywhere across the discharge gap. While the bulk of the plasma can, in fact, be treated to be quasi-neutral, this approximation ignores the formation of the sheath near the cathode. However, analysis in Adamovich et al. [30] showed that a sheath acts like an extra layer of capacitor, and its effect on the energy coupling to the plasma is weak if its quasi-steady-state thickness l_s^∞ is much less than $2l_{\text{d}}/\varepsilon$. In this study, l_s^∞ was found to be one to two orders of magnitude less than $2l_{\text{d}}/\varepsilon$ across all the conditions considered. Thus, the error estimation in the coupled energy due to this approximation is no more than 10%.

The coupling between the system of ODEs and the Boltzmann equation is made by supplying BOLSIG+ with the temperature, the number density of each species, as well as the E/N value given by E_{gap} divided by the number density of the gas N ,

$$\frac{E}{N} = \frac{|E_{\text{gap}}|}{N}, \quad (4)$$

and then updating the parameters in the ODEs with the values provided by BOLSIG+. The feedback parameters are the reaction rate constants of the electron-impact reactions and the electron drift velocity v_{dr} , which is used to calculate the discharge current density J_{d} as:

$$J_{\text{d}} = en_{\text{e}}v_{\text{dr}} \quad (5)$$

where e is the elementary charge and n_{e} is the number density of the electrons. Note that v_{dr} has the same sign as E_{gap} . This formulation of the discharge current density neglects the contributions from

the drift of ions because ion motilities are much smaller than electron mobility. BOLSIG+ is called and the parameters are updated every time step.

The time integration of the ODEs is handled by the DASAC [31] solver, which is adopted directly from SENKIN. This solver is also used to solve the associated sensitivity analysis equations for the normalized sensitivity coefficients $\tilde{S}_{i,j}$:

$$\tilde{S}_{i,j} = \frac{k_j}{X_i} \frac{\partial X_i}{\partial k_j} = \frac{\partial \ln X_i}{\partial \ln k_j}. \quad (6)$$

Mathematically, these coefficients represent the fractional change in X_i , the mole fraction of the species i , caused by a fractional change of k_j , the rate coefficient of the reaction j . These coefficients can provide physical insight into the dynamics of the chemical system when coefficients are compared to one another. It is often informative to examine the sensitivity coefficients for the reaction products specifically, since their formation represents the progress of the overall reaction. When coefficients are compared in this manner, reactions with the highest sensitivities are considered to be the rate-limiting steps of the overall reaction [32,33].

2.2 H₂/O₂/Ar Plasma Oxidation Reaction Mechanism

The chemical reaction mechanism employed within this work consists of 39 species and 424 reactions. The mechanism is derived from the HP-Mech/Plasma mechanism [34], which is an expansion of the basic H₂/O₂ mechanism originally developed by Burke et al. [35]. Additional reactions pertaining to ions and electronically excited species of Ar, O₂, and O are included. Vibrational excitations are neglected in the current version of the mechanism as the characteristic time of vibrational relaxation of H₂($v=1$) through VT collisions with Ar [36] is at least two orders of magnitude shorter than the characteristic times of reactions (R3) and (R4) [37] over the range of conditions considered in this study. The complete reaction set and associated rate constants are tabulated in Supplementary Material 1.

The model also includes the thermodynamic properties of all species to ensure consistent calculation of the reverse rate constants. The properties of most of the species in the present mechanism are taken from the database compiled by Burcat and Ruscic [38], while those of the electronically-excited species and ionic species not found in the database were estimated from the spectroscopic parameters using a statistical-mechanical approach outlined by Liu et al. [39]. The least square fit polynomial coefficients of the thermodynamic properties in CHEMKIN format are presented in Supplementary Material 2.

2.3 Simulation Conditions

The aforementioned numerical model is used to describe the physics and the chemistry of the PFR experiments conducted by Tsolas et al. [27], where the reactor assembly was placed inside an electric tube furnace that created a trapezoidal temperature profile along the reactor. The model only considers the 40-cm plateau (isothermal) region in the middle, of which the first 5 cm is the electrode assembly that generates the plasma. The temperature ramps on both sides of the plateau region are not included. When the furnace temperature is below the second explosion limit, the simulation results shown later suggest that the chemical reactions are almost frozen outside of the plasma region even in the isothermal region where the temperature is the highest, and by extension, the reaction rates in the temperature ramp region are even slower. The flow reactor is modeled as a plug flow reactor, where the assumption is that the time evolutions of the species in a fluid element that travels downstream with an average flow velocity U is simulated. The initial composition is fixed at 2000 ppm H_2 and 3000 ppm O_2 balanced in Ar, and multiple cases are considered with different initial temperatures between 474 K and 1008 K. As the mass flow rate of the gas is fixed for all cases, the average residence time of a fluid element within the reactor varies with the furnace temperature, T (in kelvin). The average residence time of a fluid element traveling through the 40-cm isothermal region is $409.5/T$ seconds, of which the first $56.7/T$ seconds corresponds to the 5-cm

plasma region where repetitive discharges are applied. The physical parameters of the reactor are set to be $L = 7$ mm, $l_d = 2.3$ mm, and $\varepsilon = 5.26$ (1.0 mm MACOR and 1.3 mm quartz). The voltage pulses applied to the electrodes are modeled as Gaussian pulses with a peak voltage of 10 kV and FWHM of 83 ns (Fig. 2). All the results presented here are from the simulations performed with isobaric and isothermal conditions, as the primary intention of this paper is to study the pure kinetics by decoupling them from exothermic (or endothermic) effects. Simulations with isobaric and adiabatic conditions (with the addition of the energy conservation equation) were performed for reference, however, and the temperature changes were found to be less than 35 K at all initial temperatures, owing to the use of a dilute mixture.

3 Results and Discussions

3.1 Single Discharge at Low Temperature

To simplify any forthcoming discussion, a single discharge system is first considered and analyzed. The conditions were set to replicate the experiments of Tsolas et al. [27], with the exception that only one high-voltage pulse is applied. The initial mixture of the gas is set at 668 K and 1 atm. This condition is well below the second explosion limit (878 K at 1 atm as determined from the model) and thus called “low temperature.”

Figure 3 shows the simulated behavior of the E/N value and the species evolution when a single Gaussian voltage pulse is applied to the initial mixture. The voltage pulse peaks at $t = 100$ ns while breakdown occurs a few ns prior. The maximum E/N before the breakdown is 110 Td. After the breakdown, electric charges are built up on the surfaces of the dielectric materials by the electric current in the plasma, and the gap electric field is rapidly reduced. A second peak of E/N follows with a maximum value of 3.2 Td (secondary discharge), which is caused by the change in the sign of the time derivative of the applied voltage. During this very short breakdown process, the electron

energies are transferred to atoms and molecules through collisions. The important electron-impact process on the species evolutions shown in Fig. 3 is the excitation of an Ar atom to its 4s metastable state Ar^{*m} :

This electronic excitation step of argon is the dominant path for electron energy losses for E/N above 10 Td. These metastable argon atoms are efficiently quenched through collisions with diatomic or polyatomic molecules in the gas, and such collisions with H_2 or O_2 molecules predominantly result in dissociation [40,41]. These dissociation processes are the major contributor of H and O atoms in the gas before $t = 10^{-6}$ s. In turn, these ground-state atoms subsequently drive the conventional reactions found in the H_2/O_2 mechanism, which contribute the most to the oxidation of the fuel on a timescale of ~ 0.1 ms and longer. The H atoms formed by H_2 dissociation start the fuel oxidation sequence with the production of HO_2 through

The majority of HO_2 formed by this reaction is then converted to OH either by O or H:

and finally, OH reacts with H_2 to produce H_2O , the final product:

The majority of the O atoms formed from O_2 dissociation are consumed through either the termination step (R7) or the branching step

H and OH radicals produced by reactions (R7) and (R10) then join the radical pool that drives reactions (R6), (R8), and (R9).

Detailed path flux analysis of the oxidation mechanism reveals that the reactions of HO₂ play a very important role on the kinetics of H, OH, and O radicals, and hence on the H₂ oxidation. The HO₂ consumption routes, integrated over a time period of 10⁻² s corresponding to an approximate lifetime of H, OH, and O radicals as seen in Fig. 3, consisted of the following reactions and percentages of total consumption:

Of these six reactions, (R8) is the only step that is chain propagating; all other reactions are chain terminating steps that lead to the depletion of H, OH, and O radicals. Thus, as the HO₂ concentration builds up, the rate of radical loss from the system is accelerated. The formation of H₂O₂ from reaction (R14), while being slower than other reactions, contributes to the eventual removal of HO₂ from the mixture after other radicals are depleted.

Examining the reactions from (R6) through (R14), it is interesting to point out that reaction (R13), which accounts for only 5% of the HO₂ consumption, is the only producer of O atoms through thermal reactions[†]. This is in sharp contrast with the large yield of OH from HO₂ by reactions (R7) and (R8), which subsequently react to form H and H₂O from reaction (R9). The small yield of O atoms in a low temperature system also results from the slow rate of their major producer usually found active in a high temperature H₂/O₂ system, i.e., the chain branching step

[†] The majority of O(¹D) is collisionally quenched to the ground state in the present system. See later discussions.

At low temperatures, this step is slow due to its endothermicity [42], making its participation in the overall oxidation process of minimal importance. It is in fact driven backwards by the superequilibrium concentrations of O and OH under the present condition. The low yield of O atoms from the thermal reactions essentially eliminates the exponential growth characteristics of the system that would otherwise facilitate reaction (R10) at high temperatures. This also makes competing reaction (R6) to become both a necessary and major consumer of H atoms, allowing the HO₂ chemistry to govern the H₂ oxidation mechanism in the low-temperature plasma system.

The sensitivity analysis results agree with the aforementioned discussion. Figure 4 shows the time evolution of sensitivity coefficients for the mole fraction of the product species H₂O. The sensitivity plots reveal three different reaction schemes: two “short time scale” schemes that form a small quantity of H₂O rapidly and a “long time scale” scheme that forms the majority of H₂O more slowly. The first scheme involves the reactions of negative ions, O⁻, and O₂⁻. Shortly after the breakdown, the electrons produced during the breakdown facilitates the rapid formation of ~10⁻² ppm of H₂O between 10⁻⁷ s and 10⁻⁵ s either by

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before electrons are depleted through recombination with positive ions. While being rate-limited by formation steps of negative ions (i.e., reactions (R15) and (R17)), there are no other reactions that

compete with this scheme. The second scheme involves the reactions of $O(^1D)$ atoms that are predominantly produced through dissociation of O_2 molecules through collisions with Ar^{*m} .

Rapid formation of OH radicals before 10^{-6} s occurs through reaction (R20) and the amount of H_2O formation from this scheme is comparable to the negative ion scheme. This scheme has alternate paths for Ar^{*m} and $O(^1D)$ clearly seen in Fig. 4a, i.e.,

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competing with reactions (R19) and (R20), respectively. However, the impact of these two schemes is limited to “short time scales.” Although they form H_2O very rapidly, the quantity of formation is much lesser than the “long time scale” scheme consisting of reactions (R5) through (R10), which is driven by molecular dissociation and HO_2 chemistry as explained before. At time scales longer than 10^{-4} s in Fig. 4b, the large positive sensitivity coefficients are associated with reactions (R5), (R8), (R9), and (R10). The negative coefficients are associated with the HO_2 production step (R6) as well as the HO_2 consumption steps other than reaction (R8), i.e.,

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7 although the sensitivity coefficients of reactions (R13) and (R14) are omitted from the figure due to
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9 their small magnitudes. The sensitivity coefficient associated with reaction (R6) behaves rather
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11 interestingly, because of the mixed role of HO₂. Its value is positive initially because of the
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13 necessity of HO₂ production on fuel oxidation facilitated through reaction (R8). It then turns
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15 negative at 10⁻³ s when reactions (R7), (R11), and (R12), which are chain termination steps, become
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17 competitive with reaction (R8) for HO₂. Reaction (R8) is the “desired” HO₂ consumption path
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19 because it is the only chain propagation step.
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22 As discussed above, formation of Ar^{*m} via reaction (R5) is one of the steps to which the
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24 system is the most sensitive because Ar^{*m} produces H and O atoms efficiently by dissociation.
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26 However, interestingly, the dissociation steps themselves are not among those with the highest
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28 sensitivities, except for the competition between the production of the ground-state O atom via
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30 reaction (R21) and the excited-state O(¹D) atom via reaction (R19) during short time scales. There
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32 are two reasons behind this, and the first one is the absence of a process that can quench Ar^{*m} as
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34 efficiently as the dissociation processes involving reactants H₂ and O₂. Because of the dilute
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36 characteristics of the mixture with more than 99% Ar in the mixture, Ar is naturally the most
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38 probable collision partner in the system. However, collisional quenching of Ar^{*m} with ground state
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40 Ar is four orders of magnitude slower than that with H₂ or O₂ (see Supplementary Material 1 for
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42 rates). Therefore, collisions of Ar^{*m} with the initial reactant molecules of H₂ and O₂ are still the
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44 major consumption paths of Ar^{*m} even though their mole fractions are only of the order of 10³ ppm.
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46 The second reason is that dissociation processes of both H₂ and O₂ contribute to the oxidation
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48 process. Microscopically, they are competing with each other for the removal of Ar^{*m}, while
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50 macroscopically as far as the overall oxidation process is concerned, they both achieve almost the
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52 same result. The second argument pointed out here is expected to be a unique feature of an
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54 H₂/O₂/Ar system where H₂O is the only major product and the major molecular species in the
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system are both reactants. The product distribution from collisions of Ar^{*m} with other species is expected to carry much more importance in other systems, such as ones with more complex hydrocarbon fuels.

3.2 Repetitive Discharges at Low Temperature

In this section, the single discharge analysis is extended to the analysis of a multi-discharge system that reflects the experimental conditions of [27] more appropriately. Figure 5 shows the time evolution of species profiles simulated in the isothermal region of the reactor at $T = 668$ K when the repetitive voltage pulses are applied at a rate of 1 kHz. The maximum E/N remained nearly constant pulse to pulse. The oxidation of fuel proceeds almost linearly with time within the plasma region, which is the first 85 ms indicated by the gray region in the plots. This prediction is directly equivalent to the trends observed in the experiments, where the plasma discharge perturbations are applied at the beginning of the isothermal region. The simulations demonstrate that at this particular reactor temperature the extent of the reaction is confined to the plasma discharge region with little reaction continuing upon exiting. In Fig. 5b-d, the evolution of radical species are tracked through the plasma discharge. Here, it can be seen that these species are directly coupled to the plasma perturbations, continually being formed and consumed for every single discharge pulse. The slight change in behaviors of the radical species observed near 75 ms is caused by the reduction of E/N during the secondary discharges. This results from the progressive increase in electron drift velocity at values of E/N on the order of 0.1 Td and above as H_2O accumulates in the mixture, which was reported previously in air [43,44] and also verified with BOLSIG+ [7] calculations for the present results. The predicted profiles of both major and radical species indicate the lack of chain-branching chemistry, which is also supported by the reaction flux plots of H_2O and OH shown in Fig. 6. The dominant H_2O formation step is reaction (R9), which is also the dominant consumption step of OH. Hydroxyl radicals are formed by reactions (R8), (R7), and (R10), in the order of significance.

Figure 7 shows the normalized sensitivity coefficients for H₂O and OH in the plasma region. The sensitivity coefficient of the ionization step

risks and falls quite drastically. The close coupling of the sensitivity coefficient to the breakdown makes the effects of perturbing this reaction very complicated over multiple discharges, and the sensitivity coefficient represented by only a local first order derivative of mole fraction, without accounting for higher order effects, carries much less significance. A brute force sensitivity coefficient for reaction (R23) (which takes into account the higher order effects) shows negative values overall. One notable difference between the sensitivity coefficient plots for H₂O and OH is that the former are smooth while the latter oscillate. This is a result largely from the normalization process, Eqn. (6), where H₂O is a final product that builds up with time rather smoothly, while OH is an intermediate species whose mole fraction fluctuation with every discharge is significant compared to the OH absolute value. An interesting observation for the H₂O sensitivity coefficients is that the reactions with large absolute values of sensitivity coefficients in Fig. 7a are very similar to the ones of importance during the long time scale shown in Fig. 4. The OH mole fraction is sensitive to reactions similar to those found sensitive for H₂O, indicating a close coupling with the H₂O formation.

Figure 8 shows the change in the normalized sensitivity coefficients for H₂O when the pulse repetition rate of the discharges is varied between 1 kHz, 3 kHz, and 5 kHz. As the pulse repetition rate increases, the magnitudes of the coefficients associated with reactions (R5), (R8), and (R6) decline more than the coefficients of other reactions. These three reactions are the steps responsible for production and consumption of H atoms. In contrast, the coefficients associated OH consumption steps, i.e., reactions (R2) and (R9), show an increase in magnitude with the pulse

repetition rate. These results suggest a shift in the rate-limiting process of the reaction chain from reactions of H atoms to those of OH.

3.3 Kinetics at High Temperature

At temperatures above the second explosion limit, the thermal chain branching factor is greater than unity, and the role of the plasma is presented here for a similar mixture composition and pressure, but a temperature of 921 K. Figure 9 shows the simulated behavior of E/N and the species evolution when a single Gaussian voltage pulse is applied to the initial mixture. The maximum E/N before the breakdown is 135 Td. Comparing Fig. 9 with Fig. 3, almost identical reaction profiles are predicted up to around 10^{-5} s, showing the amounts of O and H atom formation to be on the order of 1 ppm due to dissociation of the initial reactants. However, instead of the radical concentrations declining after this time, the reactions shift to overall chain-branching characterized by an exponential growth in the radical concentrations peaking around 10^{-2} s. The plasma discharge created sufficient radicals to initiate the explosive character almost immediately, and the need for any further thermal radical buildup is unnecessary. Just as in the low temperature case, molecular dissociation was found to be responsible for the onset of radical growth.

Figure 10 compares the reactant and product species profiles for simulations with no plasma application (thermal), one discharge at the beginning of the reaction, and multiple discharges during the reaction at a pulse repetition rate of 1 kHz. A drastic reduction in the ignition delay, by about 35 ms, is predicted even with one discharge compared to the thermal case, but applying multiple discharges only further reduced the ignition delay by about 1 ms from the single-discharge case. Since the curves of the profiles are similar to each other after its ignition delay period, thermal chain-branching reactions appear to dominate the oxidation process during fuel consumption, even when multiple plasma discharges are applied. The dominance of the chain-branching kinetics is confirmed by the sensitivity coefficients shown in Fig. 11, where the most

sensitive reactions and the sensitivity coefficient profiles are similar to those found for high temperature thermal chain branched chemistry (see, for example, Mueller et al. [45]).

3.4 Dependence of Kinetics on Temperature

In Ref. [27], the plasma flow reactor experiments were performed for a wide range of temperatures where the extent of reaction was monitored by measuring the H_2 and O_2 species concentrations at the reactor outlet for a fixed mass flow rate. The simulations of these experiments are presented in Fig. 12. The increase in reactor temperature produces a faster plasma assisted reaction and higher E/N in the plasma region, resulting in more oxidation which agrees with the trends observed in the experiments [27].

Figure 13 shows the temperature dependence of the normalized sensitivity coefficients of the H_2O mole fraction at the reactor exit. The sensitivity coefficients approach zero above the second explosion limit (878 K) because almost all the H_2 is oxidized upstream before reaching the exit. As a consequence, the reactions become microscopically balanced as equilibrium is approached, and the forward and backward rate constants of each reaction have equal importance. Focusing on the temperature dependence of the sensitivity coefficients, the coefficients associated with reaction (R7) and reaction (R2) are found to have positive values at some temperatures and negative values at others. Reaction (R7), a HO_2 consumption step, has positive sensitivity coefficients below ~ 550 K and negative coefficients above it. This behavior arises from its direct competition with reaction (R8) as they both form OH from HO_2 . At temperatures below ~ 550 K, despite its chain-terminating nature, reaction (R7) actually produces OH faster than reaction (R8), thus making its sensitivity coefficient positive. As temperature increases, the OH production rate by reaction (R8) overtakes that by reaction (R7) and the sensitivity coefficient for reaction (R7) becomes negative above ~ 550 K. The sensitivity coefficient of reaction (R2), on the other hand, change sign at ~ 720 K from negative at low temperatures to positive at high temperatures. This

change in coefficient sign is an interesting result because chain branching steps usually have the largest positive sensitivity coefficient in a conventional chain-branching system [45]. The negative values at low temperatures arise from the fact that the superequilibrium radical concentrations drive reaction (R2) backwards, effectively making it a chain-termination step.

3.5 Kinetics of $O_2(a^1\Delta_g)$ and $O(^1D)$

Despite being proposed to be important by many researchers, electronic excitation of O_2 by the plasma was not identified to play a significant role for the conditions of the present study. The ineffectiveness of $O_2(a^1\Delta_g)$ can be attributed to its small concentration ($[O_2(a^1\Delta_g)]/[O_2] \approx 10^{-5}$ to 10^{-4}) and the large concentration of HO_2 that quenches $O_2(a^1\Delta_g)$ to ground state O_2 at low temperatures. The former is likely a result of the abundance of Ar in the mixture, which makes Ar the most probable collision partner of electrons. If Ar is excited by an electron, the energy is high such that subsequent collisions with O_2 predominantly result in dissociation instead of excitation (the energy of $O_2(a^1\Delta_g)$ is 0.98 eV while the first excited state of Ar is 11.55 eV). $O_2(a^1\Delta_g)$ in the present system results from direct excitation by a small fraction of electrons, collisional quenching of the higher states, and the energy transfer from $O(^1D)$:

Together with the relative importance of molecular dissociations as a means of oxidation enhancement, the same conclusion drawn by Popov [14] can be made here regarding the difficulty to observe an influence of $O_2(a^1\Delta_g)$ when the plasma also produces atomic species by dissociation.

On the other hand, the reactions of $O(^1D)$ are shown to rapidly produce OH radicals during the time scale of 10^{-6} s, contributing to H_2 oxidation. Unlike $O_2(a^1\Delta_g)$ molecules, $O(^1D)$ atoms are produced rather effectively in a plasma in Ar-abundant mixtures because it is formed through collisions between Ar^{*m} and O_2 [46]. For the present conditions, the consumption steps of $O(^1D)$ are, in the order of significance:

More than 70% of $\text{O}(^1\text{D})$ atoms are quenched by Ar (R22), diminishing the branching effects of other paths that could have otherwise enhanced the overall H_2 oxidation. More flux of $\text{O}(^1\text{D})$ through reactions (R20), (R24), and (R25) in a less-dilute mixture could have made appreciable contributions at temperatures below the second explosion limit where, as discussed in the previous sections, the amount of radicals produced by the plasma is closely related to the oxidation rate. For example, using the current reaction rate expressions at $T = 668$ K, having about $[\text{Ar}]:[\text{H}_2] = 108:1$ will make the reaction flux of the branching reaction (R20) comparable to that of the electronic quenching reaction (R22). In contrast, those effects would have been minimal above the second explosion limit where the conventional ground state chain branching kinetics is responsible for the majority of the oxidation. Since the plasma already produces more than sufficient seed radicals to trigger the ignition without delay, producing even more radicals through $\text{O}(^1\text{D})$ reactions would not have made an appreciable difference.

Comparison of the consumption steps of $\text{O}(^1\text{D})$ with those of ground state O poses a question on a possibly missing reaction with HO_2 . For the ground state O, reaction (R7) is in fact one of the major consumption paths below the second explosion limit. No such reaction is included in the mechanism for the excited state $\text{O}(^1\text{D})$, but if it actually exists, it could become an important radical termination step that competes with the existing reactions discussed above. No discussion about this reaction was found through an extensive literature survey, except p. 387 of Banks and Kockarts [47] mentions that experimental evidence does not rule out such a reaction which could have zero activation energy (similarly to reaction (R7)) and proceed at a rate similar to the reactions

of $O(^1D)$ with H_2 (R20) or O_3 . Although the existence of the reaction $O(^1D) + HO_2$ remains an open question, missing this reaction would not have made a difference to the predictions of the present system as the enhancement effect of $O(^1D)$ kinetics is already diminished by the abundance of Ar and the reaction in question is likely to only weaken it further.

4 Conclusions

A new numerical code and a reaction mechanism that simulates the chemical kinetics in nanosecond DBD plasma was developed. The code was equipped with sensitivity analysis capabilities, aiming to provide deeper insight into the chemical kinetics than analysis of species profiles or reaction fluxes can provide alone.

Simulations coupled with sensitivity analysis were conducted to study and analyze the kinetics of an $H_2/O_2/Ar$ system excited by non-equilibrium plasma discharges. The simulations were performed at atmospheric pressure for a temperature range that would cover the kinetics both below and above the second explosion limit. For all conditions, dissociation of H_2 and O_2 molecules through their collisions with metastable Ar^{*m} produce the radicals that initiate the oxidation process. At temperatures below the second explosion limit, the plasma discharges were found to drive the fuel oxidation through a straight-chain sequence of the ground-state reactions, driven by molecular dissociation. An important part of the straight-chain reaction sequence is the kinetics of HO_2 , an inevitable intermediate species below the second explosion limit. It was found that the amount of OH radicals produced from HO_2 affects the overall rate of H_2 oxidation significantly. However, the HO_2 chemistry itself has a chain terminating nature and depletes the radicals as HO_2 builds up. At temperatures above the second limit, the molecular dissociation by the plasma produced more than sufficient amounts of radicals to trigger the chain branching kinetics significantly reducing its ignition delay. Varying the pulse repetition rate of the plasma discharges between 1 and 5 kHz

changed the rate-limiting steps of the mechanism. As the pulse rate was increased, the rate-limiting steps shifted from reactions of H atoms to those of OH.

In addition, the findings are further analyzed to discuss the implications to other systems. It was suggested that in some systems, the fate of Ar^{*m} as well as the kinetics of $\text{O}_2(a^1\Delta_g)$ and $\text{O}(^1D)$ may carry much more importance.

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References

- [1] C. Segal, *The Scramjet Engine: Processes and Characteristics*, Cambridge University Press, Cambridge, New York, 2009.
- [2] A.Y. Starikovskii, Plasma supported combustion, *Proc. Combust. Inst.* 30 (2005) 2405–2417. doi:10.1016/j.proci.2004.08.272.
- [3] S.M. Starikovskaia, Plasma assisted ignition and combustion, *J. Phys. D: Appl. Phys.* 39 (2006) R265–R299. doi:10.1088/0022-3727/39/16/R01.
- [4] S.M. Starikovskaia, A.Y. Starikovskii, Plasma-Assisted Ignition and Combustion, in: M. Lackner, F. Winter, A.K. Agarwal (Eds.), *Handbook of Combustion*, Wiley-VCH Verlag GmbH & Co. KGaA, 2010. <http://dx.doi.org/10.1002/9783527628148.hoc075>.
- [5] A. Starikovskiy, N. Aleksandrov, Plasma-assisted ignition and combustion, *Prog. Energy Combust. Sci.* 39 (2013) 61–110. doi:10.1016/j.pecs.2012.05.003.
- [6] LXcat. <http://www.lxcat.net>.
- [7] G.J.M. Hagelaar, L.C. Pitchford, Solving the Boltzmann equation to obtain electron transport coefficients and rate coefficients for fluid models, *Plasma Sources Sci. Technol.* 14 (2005) 722–733. doi:10.1088/0963-0252/14/4/011.
- [8] I. Glassman, R.A. Yetter, *Combustion*, 4th edition, Academic Press, 2008.
- [9] M. Uddi, N. Jiang, E. Mintusov, I.V. Adamovich, W.R. Lempert, Atomic oxygen measurements in air and air/fuel nanosecond pulse discharges by two photon laser induced fluorescence, *Proc. Combust. Inst.* 32 (2009) 929–936. doi:10.1016/j.proci.2008.06.049.

- [10] W. Sun, M. Uddi, S.H. Won, T. Ombrello, C. Carter, Y. Ju, Kinetic effects of non-equilibrium plasma-assisted methane oxidation on diffusion flame extinction limits, *Combust. Flame.* 159 (2012) 221–229. doi:10.1016/j.combustflame.2011.07.008.
- [11] T. Ombrello, S.H. Won, Y. Ju, S. Williams, Flame propagation enhancement by plasma excitation of oxygen. Part II: Effects of $O_2(a^1\Delta_g)$, *Combust. Flame.* 157 (2010) 1916–1928. doi:10.1016/j.combustflame.2010.02.004.
- [12] A.M. Starik, V.E. Kozlov, N.S. Titova, On mechanisms of a flame velocity increase upon activation of O_2 molecules in electrical discharge, *J. Phys. D: Appl. Phys.* 41 (2008) 125206. doi:10.1088/0022-3727/41/12/125206.
- [13] A.M. Starik, V.E. Kozlov, N.S. Titova, On the influence of singlet oxygen molecules on the speed of flame propagation in methane–air mixture, *Combust. Flame.* 157 (2010) 313–327. doi:10.1016/j.combustflame.2009.11.008.
- [14] N.A. Popov, Effect of singlet oxygen $O_2(a^1\Delta_g)$ molecules produced in a gas discharge plasma on the ignition of hydrogen–oxygen mixtures, *Plasma Sources Sci. Technol.* 20 (2011) 045002. doi:10.1088/0963-0252/20/4/045002.
- [15] N.A. Popov, Plasma assisted ignition of combustible mixtures. Effect of electronically excited $O(^1D)$ atoms and vibrationally excited molecules, in: 53rd AIAA Aerospace Sciences Meeting, AIAA 2015-0410, Kissimmee, Florida, 2015. doi:10.2514/6.2015-0410.
- [16] F.E. Niles, Survey of Two-Body and Three-Body Reaction-Rate Coefficients for the Ionized Stratosphere and Mesosphere, AD776950, BRL1702, Ballistic Research Laboratories, Aberdeen Proving Ground, MD, 1974.
- [17] M.H. Bortner, T. Baurer, eds., Defense Nuclear Agency Reaction Rate Handbook, Second Edition, Revision No. 9, DNA-1948H-Rev 9, 1983.
- [18] Y. Ikezoe, S. Matsuoka, M. Takebe, A. Viggiano, Gas Phase Ion-Molecule Reaction Rate Constants Through 1986, Ion Reaction Research Group of the Mass Spectroscopy Society of Japan, Tokyo, Japan, 1987.
- [19] V.G. Anicich, Evaluated Bimolecular Ion-Molecule Gas Phase Kinetics of Positive Ions for Use in Modeling Planetary Atmospheres, Cometary Comae, and Interstellar Clouds, *J. Phys. Chem. Ref. Data.* 22 (1993) 1469–1569. doi:10.1063/1.555940.
- [20] D. McElroy, C. Walsh, A.J. Markwick, M.A. Cordiner, K. Smith, T.J. Millar, The UMIST database for astrochemistry 2012, *Astron. Astrophys.* 550 (2013) A36. doi:10.1051/0004-6361/201220465.
- [21] N.G. Dautov, A.M. Starik, Investigation of the Effect of Vibrational Excitation of Molecules on the Kinetics of Combustion of an $H_2 + O_2$ Mixture, *High Temp.* 32 (1994) 210–217.
- [22] A.M. Starik, N.G. Dautov, On a Possibility of Promotion of Combustion for H_2 - O_2 Mixture by Excitation of Molecular Vibrational Degrees of Freedom, *Phys. Dokl.* 39 (1994) 424–429.
- [23] S.M. Starikovskaia, A.Y. Starikovskii, D.V. Zatsepin, Hydrogen oxidation in a stoichiometric hydrogen-air mixture in the fast ionization wave, *Combust. Theory Model.* 5 (2001) 97–129. doi:10.1088/1364-7830/5/1/306.
- [24] N.L. Aleksandrov, S.V. Kindysheva, I.N. Kosarev, S.M. Starikovskaia, A.Y. Starikovskii, Mechanism of ignition by non-equilibrium plasma, *Proc. Combust. Inst.* 32 (2009) 205–212. doi:10.1016/j.proci.2008.06.124.
- [25] I.V. Adamovich, I. Choi, N. Jiang, J.-H. Kim, S. Keshav, W.R. Lempert, et al., Plasma assisted ignition and high-speed flow control: non-thermal and thermal effects, *Plasma Sources Sci. Technol.* 18 (2009) 034018. doi:10.1088/0963-0252/18/3/034018.
- [26] S. Nagaraja, V. Yang, Z. Yin, I. Adamovich, Ignition of hydrogen–air mixtures using pulsed nanosecond dielectric barrier plasma discharges in plane-to-plane geometry, *Combust. Flame.* 161 (2014) 1026–1037. doi:10.1016/j.combustflame.2013.10.007.

- [27] N. Tsolas, K. Togai, Z. Yin, K. Frederickson, R.A. Yetter, W.R. Lempert, et al., Plasma Flow Reactor Studies of $H_2/O_2/Ar$ Kinetics, *Combust. Flame*. Accepted.
- [28] A.E. Lutz, R.J. Kee, J.A. Miller, Senkin: A Fortran Program for Predicting Homogenous Gas Phase Chemical Kinetics with Sensitivity Analysis, SAND87-8248, Sandia National Laboratories, Livermore, CA, 1988.
- [29] S. Pancheshnyi, B. Eismann, G.J.M. Hagelaar, L.C. Pitchford, Computer Code ZDPlasKin, University of Toulouse, LAPLACE, CNRS-UPS-INP, Toulouse, France, 2008. <http://www.zdplaskin.laplace.univ-tlse.fr>.
- [30] I.V. Adamovich, M. Nishihara, I. Choi, M. Uddi, W.R. Lempert, Energy coupling to the plasma in repetitive nanosecond pulse discharges, *Phys. Plasmas*. 16 (2009) 113505. doi:10.1063/1.3264740.
- [31] M. Caracotsios, W.E. Stewart, Sensitivity analysis of initial value problems with mixed odes and algebraic equations, *Comp. Chem. Eng.* 9 (1985) 359–365. doi:10.1016/0098-1354(85)85014-6.
- [32] U. Nowak, J. Warnatz, Sensitivity Analysis in Aliphatic Hydrocarbon Combustion, in: A.L. Kuhl, J.R. Bowen, J.-C. Leyer, A. Borisov (Eds.), *Dynamics of Reactive Systems Part I: Flames; Part II: Heterogeneous Combustion and Applications*, American Institute of Aeronautics and Astronautics, Washington, D.C., 1988: pp. 87–103. <http://dx.doi.org/10.2514/5.9781600865879.0087.0103>.
- [33] T. Turányi, Applications of sensitivity analysis to combustion chemistry, *Reliability Eng. Sys. Safety*, 57 (1997) 41–48. doi:10.1016/S0951-8320(97)00016-1.
- [34] X. Yang, K. Togai, R.A. Yetter, Y. Ju, Preliminary validation of HP-Mech/plasma for $H_2/O_2/NO$ and methane/ O_3 reaction systems, (In preparation).
- [35] M.P. Burke, M. Chaos, Y. Ju, F.L. Dryer, S.J. Klippenstein, Comprehensive H_2/O_2 kinetic model for high-pressure combustion, *Int. J. Chem. Kinet.* 44 (2012) 444–474. doi:10.1002/kin.20603.
- [36] J.E. Dove, H. Teitelbaum, The vibrational relaxation of H_2 . I. Experimental measurements of the rate of relaxation by H_2 , He, Ne, Ar, and Kr, *Chem. Phys.* 6 (1974) 431–444. doi:10.1016/0301-0104(74)85027-5.
- [37] M. Agúndez, J.R. Goicoechea, J. Cernicharo, A. Faure, E. Roueff, The chemistry of vibrationally excited H_2 in the interstellar medium, *Astrophys. J.* 713 (2010) 662–670. doi:10.1088/0004-637X/713/1/662.
- [38] A. Burcat, B. Ruscic, Third Millenium Ideal Gas and Condensed Phase Thermochemical Database for Combustion (with Update from Active Thermochemical Tables), ANL-05/20 and TAE 960, Technion-IIT and Argonne National Laboratory, 2005. <http://dx.doi.org/10.2172/925269>.
- [39] Y. Liu, F. Shakib, M. Vinokur, A comparison of internal energy calculation methods for diatomic molecules, *Phys. Fluids A*. 2 (1990) 1884–1902. doi:10.1063/1.857663.
- [40] J. Balamuta, M.F. Golde, Quenching of metastable Ar, Kr, and Xe atoms by oxygen-containing compounds: A resonance fluorescence study of reaction products, *J. Chem. Phys.* 76 (1982) 2430–2440. doi:10.1063/1.443272.
- [41] J. Balamuta, M.F. Golde, Y.-S. Ho, Product distributions in the reactions of excited noble-gas atoms with hydrogen-containing compounds, *J. Chem. Phys.* 79 (1983) 2822–2830. doi:10.1063/1.446103.
- [42] C.K. Law, *Combustion Physics*, Cambridge University Press, Cambridge, New York, 2010.
- [43] H. Ryzko, Drift velocity of electrons and ions in dry and humid air and in water vapour, *Proc. Phys. Soc.* 85 (1965) 1283. doi:10.1088/0370-1328/85/6/327.

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3
4
5
6
7 [44] W.T. Wyatt Jr., Computed Electron Drift Velocity in Moist Air, Technical Report 1890, U.S.
8 Army Engineer Research and Development Laboratories, Fort Belvoir, VA, 1967.
9 [45] M.A. Mueller, T.J. Kim, R.A. Yetter, F.L. Dryer, Flow reactor studies and kinetic modeling of
10 the H_2/O_2 reaction, *Int. J. Chem. Kinet.* 31 (1999) 113–125. doi:10.1002/(SICI)1097-
11 4601(1999)31:2<113::AID-KIN5>3.0.CO;2-0.
12 [46] J.T. Gudmundsson, E.G. Thorsteinsson, Oxygen discharges diluted with argon: dissociation
13 processes, *Plasma Sources Sci. Technol.* 16 (2007) 399. doi:10.1088/0963-0252/16/2/025.
14 [47] P.M. Banks, G. Kockarts, *Aeronomy, Part A*, Academic Press, New York, 1973.
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Figure 1. Equivalent circuit of the DBD system.

Figure 2. Measured and modeled voltage pulse profile applied to the electrodes.

Figure 3. Time evolution of the reduced electric field and species mole fractions for a single discharge pulse with a peak voltage of 10 kV. The initial mixture composition is 2000 ppm H₂, 3000 ppm O₂, with the balance Ar. The temperature and pressure are $T = 668$ K and $P = 1$ atm, respectively.

Figure 4. Normalized sensitivity coefficients for the H_2O mole fraction for a single discharge pulse with a peak voltage of 10 kV for reactions of significance during (a) short time scales and (b) long time scales. The initial mixture composition is 2000 ppm H_2 , 3000 ppm O_2 , with the balance Ar. The temperature and pressure are $T = 668$ K and $P = 1$ atm, respectively.

Figure 5. Time evolution of the (a) major species and (b)-(d) minor species in the isothermal region of the plasma flow reactor described in Ref. [27]. The gray region corresponds to the residence time in the plasma region where the pulse repetition rate of the plasma discharge is 1 kHz and the pulse peak voltage is 10 kV. The initial mixture composition is 2000 ppm H_2 , 3000 ppm O_2 , with the balance Ar. The temperature and pressure are $T = 668$ K and $P = 1$ atm, respectively.

Figure 6. Time evolution of the reaction flux for the most significant reactions leading to the formation and consumption of (a) H₂O and (b) OH in the plasma region where the pulse repetition rate of the plasma discharge is 1 kHz and the pulse peak voltage is 10 kV. The initial mixture composition is 2000 ppm H₂, 3000 ppm O₂, with the balance Ar. The temperature and pressure are $T = 668$ K and $P = 1$ atm, respectively.

Figure 7. Normalized sensitivity coefficients for (a) the H₂O mole fraction and (b) the OH mole fraction in the plasma region where the pulse repetition rate of the plasma discharge is 1 kHz and the pulse peak voltage is 10 kV. The initial mixture composition is 2000 ppm H₂, 3000 ppm O₂, with the balance Ar. The temperature and pressure are $T = 668$ K and $P = 1$ atm, respectively.

Figure 8. Dependence of the normalized H_2O mole fraction sensitivity coefficients on the pulse repetition rate of the plasma discharge where the pulse peak voltage is 10 kV. The solid line (—) denotes a pulse repetition rate of 1 kHz, the dash-dot line (— · —), a pulse repetition rate of 3 kHz, and the broken line (— — —), a pulse repetition rate of 5 kHz. The initial mixture composition is 2000 ppm H_2 , 3000 ppm O_2 , with the balance Ar. The temperature and pressure are $T = 668$ K and $P = 1$ atm, respectively.

Figure 9. Time evolution of the reduced electric field and species mole fractions for a single discharge pulse with a peak voltage of 10 kV. The initial mixture composition is 2000 ppm H_2 , 3000 ppm O_2 , with the balance Ar. The temperature and pressure are $T = 921$ K and $P = 1$ atm, respectively.

Figure 10. Time evolution of the major species for a $H_2/O_2/Ar$ mixture reacting at conditions above the second explosion limit. The broken line (---) denotes the thermal reaction, the dash-dot line (—·—) denotes the single discharge pulse, and the solid line (—) denotes the case with 62 pulses corresponding to a pulse repetition rate of 1 kHz. The pulse peak voltage is 10 kV where applied. The initial mixture composition is 2000 ppm H_2 , 3000 ppm O_2 , with the balance Ar. The temperature and pressure are $T = 921$ K and $P = 1$ atm, respectively.

Figure 11. Normalized sensitivity coefficients for H_2O when the pulse repetition rate of the discharge is 1 kHz and the pulse peak voltage is 10 kV. The initial mixture composition is 2000 ppm H_2 , 3000 ppm O_2 , with the balance Ar. The temperature and pressure are $T = 921$ K and $P = 1$ atm, respectively.

Figure 12. Mixture composition in mole fractions at the exit of the plasma flow reactor for various reactor temperatures. The initial mixture composition is 2000 ppm H_2 , 3000 ppm O_2 , with the balance Ar. The pressure is $P = 1$ atm. The plasma pulse repetition rate is 1 kHz and the pulse peak voltage is 10 kV.

Figure 13. Normalized sensitivity coefficients of the H_2O mole fraction at the plasma flow reactor exit for various reactor temperatures. The initial mixture composition is 2000 ppm H_2 , 3000 ppm O_2 , with the balance Ar. The pressure is $P = 1$ atm. The plasma pulse repetition rate is 1 kHz and the pulse peak voltage is 10 kV.

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Figure 12. Mixture composition in mole fractions at the exit of the plasma flow reactor for various reactor temperatures. The initial mixture composition is 2000 ppm H₂, 3000 ppm O₂, with the balance Ar. The pressure is $P = 1$ atm. The plasma pulse repetition rate is 1 kHz and the pulse peak voltage is 10 kV.

Figure 13. Normalized sensitivity coefficients of the H₂O mole fraction at the plasma flow reactor exit for various reactor temperatures. The initial mixture composition is 2000 ppm H₂, 3000 ppm O₂, with the balance Ar. The pressure is $P = 1$ atm. The plasma pulse repetition rate is 1 kHz and the pulse peak voltage is 10 kV.