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Uncertainty quantification of ion chemistry in lean and stoichiometric homogenous mixtures of methane, oxygen, and argon

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Abstract

Uncertainty quantification (UQ) methods are implemented to obtain a quantitative characterization of the evolution of electrons and ions during the ignition of methane–oxygen mixtures under lean and stoichiometric conditions. The GRI-Mech 3.0 mechanism is combined with an extensive set of ion chemistry pathways and the forward propagation of uncertainty from model parameters to observables is performed using response surfaces. The UQ analysis considers 22 uncertain rate parameters, which include both chemi-ionization, proton transfer, and electron attachment reactions as well as neutral reactions pertaining to the chemistry of the CH radical. The uncertainty ranges for each rate parameter are discussed. Our results indicate that the uncertainty in the time evolution of the electron number density is due mostly to the chemi-ionization reaction $\text{CH} + \text{O} \rightleftharpoons \text{HCO}^+ + \text{e}^-$ and to the main CH consumption reaction $\text{CH} + \text{O}_2 \rightleftharpoons \text{O} + \text{HCO}$. Similar conclusions hold

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for the hydronium ion H_3O^+ , since electrons and H_3O^+ account for more than 99% of the total negative and positive charge density, respectively. Surprisingly, the statistics of the number density of charged species show very little sensitivity to the uncertainty in the rate of the recombination reaction $\text{H}_3\text{O}^+ + \text{E}^- \rightarrow \text{products}$, until very late in the decay process, when the electron number density has fallen below 20% of its peak value. Finally, uncertainties in the secondary reactions within networks leading to the formation of minor ions (e.g., $\text{C}_2\text{H}_3\text{O}^+$, HCO^+ , OH^- , and O^-) do not play any role in controlling the mean and variance of electrons and H_3O^+ , but do affect the statistics of the minor ions significantly. The observed trends point to the role of key neutral reactions in controlling the mean and variance of the charged species number density in an indirect fashion. Furthermore, total sensitivity indices provide quantitative metrics to focus future efforts aiming at improving the rates of key reactions responsible for the formation of charges during hydrocarbon combustion.

Keywords: chemi-ionization; ion chemistry; electrons; ignition; methane combustion; uncertainty quantification; polynomial chaos; sparse-adaptive sampling

1. Introduction

Excluding secondary ionization of neutral molecules by high-energy electron impact during discharges, the chemi-ionization reaction $\text{CH} + \text{O} \rightleftharpoons \text{HCO}^+ + \text{E}^-$ [1] is the primary mechanism for the generation of ions and electrons in the reaction zone of hydrocarbon flames [2]. Following chemi-ionization, a multitude of cations and anions are formed as positive and negative charges are shuffled among neutral molecules, including reactants, radicals, stable intermediates, and combustion products [2–5]. Recombination reactions among

9 cations and electrons re-establish charge neutrality [6].

10 In the absence of discharges, ions and electrons are present in flames in
11 minute amounts, with typical mole fractions ranging from 10^{-9} to 10^{-7} [7].
12 Thus, non-intrusive, laser-based diagnostics are difficult to apply for the pur-
13 pose of measuring electron and ion concentrations in flames, and the quan-
14 titative characterization of charged species in flames often proceeds through
15 invasive methods, such as sampling followed by a mass-spectrometer analy-
16 sis [7, 8] or Langmuir probes [7, 9, 10].

17 Given the important limitations in the accuracy and completeness of ex-
18 perimental databases, numerical simulations are recognized as a valuable tool
19 to characterize the interplay of reactions, transport of neutral and charged
20 species, and electric fields. An increasing number of numerical studies has
21 been undertaken to simulate the distribution of charged species in flames [11,
22 12] and the effect of external voltages on flame properties and behavior [13–
23 15], and to calculate transport properties and collision rates of electrons in
24 combustion gases [16–18].

25 Early attempts to formulate a complete ion chemistry mechanism for
26 numerical simulations of ions in flames are due to Brown et al. [19–21]. Prager
27 et al. [11] assembled the most comprehensive and detailed mechanism for the
28 formation of ions and electrons in flames up to date. The mechanism includes
29 electrons, 4 cations, and 6 anions. It consists of 67 reactions and focuses on
30 ion chemistry pathways in lean methane-oxygen flames. In developing the
31 mechanism, Prager et al. [11] relied both on the previous mechanism and rate
32 parameters proposed by Brown et al. [19–21] as well as the comprehensive
33 analysis of ion pathways in methane-oxygen flames by Goodings et al. [4, 5].
34 The authors [11] then proceeded to update the reaction rate parameters
35 based on the most recent data available in the literature, largely from the

36 UMIST database for astrophysical chemistry [22], and they computed rate
37 parameters based on the average dipole orientation (ADO) theory [23], when
38 data were not available. Additional rate parameters were obtained from
39 Refs. [24–28].

40 The main goals of this work are *(i)* to advance the quantitative charac-
41 terization of ion chemistry during the oxidation of methane, exploring the
42 impact of the uncertainties in the rate parameters proposed recently [11],
43 and *(ii)* to exploit the metrics produced by uncertainty quantification (UQ)
44 techniques [29–32, 32–39] to quantify the most important chemical pathways
45 of charged species. Attention is specifically focused on ignition of lean and
46 stoichiometric methane-oxygen mixtures under isochoric and adiabatic con-
47 ditions.

48 Despite the simplicity of the canonical setting of zero-dimensional iso-
49 choric and adiabatic reactors, the problem of quantifying the impact of reac-
50 tion rate uncertainties remains quite challenging, because these lead to con-
51 siderable computational difficulties associated with severe stretching and,
52 in extreme cases, bifurcation of concentration trajectories during ignition.
53 In the case of the so-called intrusive methods [29–32], these phenomena may
54 lead to instabilities in the governing system and several approaches have been
55 developed to mitigate those issues. Those include adaptive basis representa-
56 tions [30, 31] and filtering [40] techniques. In the case of non-intrusive polyno-
57 mial chaos (PC) methods [32, 35–39] and response surface methods [33, 34],
58 the problem manifests itself in terms of increasing resolution requirements,
59 namely the need for a basis with rapidly growing dimension [30, 41]. This
60 issue compounds the well known challenges associated with the curse of di-
61 mensionality and has constrained most previous applications to a small or
62 moderate number of uncertain parameters.

63 In order to mitigate these effects and to enable efficient sampling of high-
 64 dimensional spaces of uncertain parameters, a recently developed adaptive
 65 pseudo-spectral algorithm (aPSP) [42, 43] is used in this work. The algorithm
 66 combines sparse grid concepts [44] and greedy anisotropic refinement [45]
 67 with a pseudo-spectral projection technique that enables the determination
 68 of a maximal basis without internal aliasing. The aPSP scheme has been
 69 applied with success to extreme-scale models involving a moderate number
 70 of stochastic dimensions [46] as well as to model problems with a large number
 71 of uncertain parameters [47].

72 The paper is organized as follows. Section 2 introduces the kinetic mecha-
 73 nism employed in this study, specifies ranges of uncertain parameters deemed
 74 most relevant to the evolution of electrons and ions, and provides a brief out-
 75 line of the UQ methods. In Section 3, results from the UQ analysis are pre-
 76 sented, focusing on quantitative metrics for key pathways to ion and electron
 77 formation in flames. Conclusions are presented in Section 4.

78 **2. Models and methods**

79 The UQ analysis is carried out for ignition in a zero-dimensional reactor
 80 under isochoric and adiabatic conditions. Thus, the combustion process con-
 81 sidered here is akin to that occurring in the quiescent combustible mixture
 82 behind the shock front in a shock tube facility. The set of ODEs describing
 83 the ignition of the reactive mixture are integrated via the **TChem** library [48].

84 In this section, the kinetic and thermodynamic data for neutral and
 85 charged species are presented first. We then discuss the quantities of interest
 86 that are central to the analysis and formulate the UQ problem. Finally, the
 87 mathematical aspects of the UQ methodology are briefly outlined.

2.1. Kinetic and thermodynamic data

The GRI-Mech 3.0 mechanism [49] is adopted to describe the oxidation chemistry of methane-oxygen mixtures under lean and stoichiometric conditions. It consists of 53 neutral species and 325 reactions. The GRI-Mech 3.0 mechanism is chosen because of its excellent prediction of the concentration of the CH radical against available experimental data in premixed low pressure flat flames [50, 51]. As it shall be explained, the CH radical is the most important neutral species in the chemi-ionization process.

The GRI-Mech 3.0 mechanism is augmented with free electrons, 10 ions, and 67 reactions from the ion chemistry mechanism assembled by Prager et al. [11]. The 4 cations are H_3O^+ , $\text{C}_2\text{H}_3\text{O}^+$, CH_5O^+ , and HCO^+ , while the 6 anions are OH^- , O^- , CHO_2^- , O_2^- , CO_3^- , and CHO_3^- . C_3H_3^+ is not included since its concentration is negligible in lean to stoichiometric mixtures [3]. In our model, the ions $\text{C}_2\text{H}_3\text{O}^+$ and CH_5O^+ possess the acetyl cationic [52] and the methoxymethyl cationic [53] structures, respectively. Two neutral species (CH_3CO and $\text{C}_2\text{H}_5\text{OH}$) are added to the set of species in GRI-Mech 3.0, since they appear as product species in selected ion chemistry reactions. The thermodynamic data is taken from GRI-Mech 3.0 [49] and complemented with data from Burcat [54] for all charged species.

2.2. Setup of the UQ problem

The relevant quantities of interest (QoIs) for the present analysis are the concentrations of electrons and of the most abundant ions. Consequently, the three most abundant cations, i.e., H_3O^+ , HCO^+ , and $\text{C}_2\text{H}_3\text{O}^+$, and the two most abundant anions OH^- and O^- are selected as QoIs together with electrons E^- . In addition to charged species, the number density of the CH radical is included in the set of QoIs as well, due to the key role played

114 by CH in the production of electrons and ions through the chemi-ionization
115 reaction.

116 The extended kinetic mechanism assembled comprises 55 neutrals, 11
117 charged species, and 392 elementary reactions involving more than a thou-
118 sand rate parameters. Because it is not feasible to include all parameters in
119 the UQ analysis, we conducted an initial screening to determine a reduced
120 set of elementary reactions that affect ion pathways significantly. To this
121 end, an heuristic approach was adopted, as summarized below.

122 The 67 reactions involving charged species were ordered according to a
123 relative measure of their peak net rate during ignition: $r = |w_k|/w_m$, where
124 $|w_k|$ is the absolute value of the peak net reaction rate of reaction k and
125 $w_m = \max_k |w_k|$ is the maximum of $|w_k|$ over all reactions. Then, reactions
126 with $r \geq 5\%$ are selected, noting that the order may differ slightly for different
127 initial conditions.

128 This selection process yielded 15 reactions: the chemi-ionization reaction,
129 8 reactions involving cations, and 6 reactions involving anions. Using the
130 same approach for all reactions involving the CH radical, 7 reactions are
131 selected from GRI-Mech 3.0 [49]. The reactions involving ions are listed in
132 Tab. 1. Those for the radical CH are in Tab. 2.

133 The network of the ion chemistry reactions considered is shown in Fig. 1.
134 For cations, the reactions considered are: 2 proton transfer reactions from
135 HCO^+ to H_3O^+ and from H_3O^+ to $\text{C}_2\text{H}_3\text{O}^+$ (I02 and I09), 2 charge transfer
136 reactions with rearrangement between HCO^+ and $\text{C}_2\text{H}_3\text{O}^+$ (I07 and I08), and
137 4 recombination reactions between H_3O^+ and E^- (I03, I04, I05, and I06).

138 For anions, only electron detachment reactions are selected, indicating
139 that one or more of those reactions must proceed in the opposite direction
140 to allow for the formation of anions. A detailed analysis (not shown) re-

Figure 1: Major pathways for ion chemistry during the ignition of lean to stoichiometric mixtures. Labels refer to the reactions in Tab. 1. A negative sign in front of the reaction label indicates that the reaction proceeds in the reverse direction throughout the combustion process.

141 veals that the reaction $\text{OH}^- + \text{O} \rightleftharpoons \text{HO}_2 + \text{E}^-$ (I10) proceeds in the reverse
 142 direction and accounts for the formation of OH^- in an electron attachment
 143 process. The anion O^- is formed by charge transfer with rearrangement
 144 $\text{OH}^- + \text{OH} \rightleftharpoons \text{O}^- + \text{H}_2\text{O}$ (-I13, here written in the reverse direction for the
 145 sake of clarity). The remaining 4 reactions are electron detachment processes.

146 Note that the most active kinetic pathways for anions during the ignition
 147 of a homogeneous, lean methane-oxygen mixture are somewhat different from
 148 those in premixed flames, where E^- attaches primarily to molecular oxygen
 149 to form O_2^- , which then transfers the negative charge to other ions [11].

150 In closing, it is worth noting that it is more difficult to measure accurately
 151 the concentration of negative ions in flames than for positive ions [55]. Thus,
 152 kinetic models for negative ions are more rudimentary and important path-
 153 ways may be missing and rate parameters inaccurate. The work by Hayhurst
 154 et al. [55] presents a detailed analysis of the complexities associated with mass

155 spectrometric sampling of ions in flames.

156 2.3. Uncertain rate parameters

157 The analysis above identifies 22 reactions that are deemed most important
158 for the evolution of the QoIs. This section discusses the selection of the ranges
159 of the uncertain rate parameters and provides the sources used to define these
160 ranges.

161 The uncertainty range of the parameters of the 15 ion chemistry reactions
162 are reported in Tab. 1. Table 2 provides the uncertainty ranges for the 7
163 neutral reactions involving the CH radical.

164 The chemi-ionization reaction $\text{CH} + \text{O} \rightleftharpoons \text{HCO}^+ + \text{E}^-$ has been the sub-
165 ject of numerous experimental studies [57–59] and the resulting reaction rates
166 obtained from each set of published parameters differ to within one order of
167 magnitude in the temperature range 1500 to 2000 K. In this work, we adopted
168 the parameter values recommended by Warnatz [56]. Those rate parameters
169 are accepted widely and have been used in the majority of simulations of
170 charged species’ distributions in flames [11, 13–15, 20, 21].

171 The UMIST database [22] is a well-maintained and easily accessible repos-
172 itory for rate parameters of ion-neutral reactions and constitutes the primary
173 source of rates for the mechanism developed by Prager et al. [11]. It is also
174 the primary source for the reactions considered in the present uncertainty
175 quantification analysis and shown in Tab. 1. Whenever available, the recom-
176 mended uncertainty range provided in the UMIST database was used. The
177 uncertainty ranges are reported as $\pm 25\%$ or $\pm 50\%$ and as a factor of 2 (indi-
178 cated as $2^\pm$) with respect to the nominal value. It is apparent that reactions
179 involving anions have a larger degree of uncertainty compared to reactions
180 with cations [11].

181 Apart from the chemi-ionization reaction and 10 reactions from the UMIST

Index	Reaction	A	n	E	Ref.	Range
I01	$\text{CH} + \text{O} \rightleftharpoons \text{HCO}^+ + \text{E}^-$	2.51×10^{11}	0	1700	[56]	$\pm 50\%$
I02	$\text{HCO}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}$	1.51×10^{15}	0	0	[22]	$\pm 50\%$
I03	$\text{H}_3\text{O}^+ + \text{E}^- \rightleftharpoons \text{H}_2\text{O} + \text{H}$	2.29×10^{18}	-0.5	0	[22]	$\pm 25\%$
I04	$\text{H}_3\text{O}^+ + \text{E}^- \rightleftharpoons \text{OH} + \text{H} + \text{H}$	7.95×10^{21}	-1.37	0	[22]	$\pm 25\%$
I05	$\text{H}_3\text{O}^+ + \text{E}^- \rightleftharpoons \text{H}_2 + \text{OH}$	1.25×10^{19}	-0.5	0	[22]	$\pm 25\%$
I06	$\text{H}_3\text{O}^+ + \text{E}^- \rightleftharpoons \text{O} + \text{H}_2 + \text{H}$	6.00×10^{17}	-0.3	0	[22]	$\pm 25\%$
I07	$\text{HCO}^+ + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_3\text{O}^+ + \text{H}$	7.76×10^{14}	-0.006	0	[21]	$2^\pm$
I08	$\text{C}_2\text{H}_3\text{O}^+ + \text{O} \rightleftharpoons \text{HCO}^+ + \text{CH}_2\text{O}$	2.00×10^{14}	0	0	[11]	$\pm 50\%$
I09	$\text{H}_3\text{O}^+ + \text{CH}_2\text{CO} \rightleftharpoons \text{C}_2\text{H}_3\text{O}^+ + \text{H}_2\text{O}$	1.20×10^{15}	0	0	[22]	$\pm 25\%$
I10	$\text{OH}^- + \text{O} \rightleftharpoons \text{HO}_2 + \text{E}^-$	1.20×10^{14}	0	0	[5]	$\pm 50\%$
I11	$\text{OH}^- + \text{H} \rightleftharpoons \text{H}_2\text{O} + \text{E}^-$	1.08×10^{15}	0	0	[22]	$2^\pm$
I12	$\text{OH}^- + \text{CH}_3 \rightleftharpoons \text{CH}_3\text{OH} + \text{E}^-$	6.02×10^{14}	0	0	[22]	$2^\pm$
I13	$\text{O}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{OH}$	8.43×10^{14}	0	0	[24]	$2^\pm$
I14	$\text{O}^- + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{E}^-$	4.22×10^{14}	0	0	[22]	$2^\pm$
I15	$\text{O}^- + \text{CO} \rightleftharpoons \text{CO}_2 + \text{E}^-$	3.91×10^{14}	0	0	[22]	$2^\pm$

Table 1: Rate parameters for chemi-ionization, recombination, and ion/neutral reactions selected for the uncertainty quantification analysis. The rate constants are presented as $k = AT^n \exp(-E/RT)$ and the units for the reaction parameters are cm, mol, cal, K, and s.

Index	Reaction	A	n	E	Range
N01	$\text{CH} + \text{O}_2 \rightleftharpoons \text{O} + \text{HCO}$	6.17×10^{13}	0	0	$\pm 50\%$
N02	$\text{CH} + \text{H}_2 \rightleftharpoons \text{H} + \text{CH}_2$	1.08×10^{14}	0	3110	$\pm 50\%$
N03	$\text{OH} + \text{CH}_2 \rightleftharpoons \text{CH} + \text{H}_2\text{O}$	1.13×10^7	2.0	3000	$\pm 25\%$
N04	$\text{H} + \text{CH} \rightleftharpoons \text{C} + \text{H}_2$	1.65×10^{14}	0	0	$1.5^\pm$
N05	$\text{O} + \text{CH} \rightleftharpoons \text{H} + \text{CO}$	5.70×10^{13}	0	0	$\pm 25\%$
N06	$\text{OH} + \text{CH} \rightleftharpoons \text{H} + \text{HCO}$	3.00×10^{13}	0	0	$\pm 25\%$
N07	$\text{CH} + \text{H}_2\text{O} \rightleftharpoons \text{H} + \text{CH}_2\text{O}$	5.71×10^{12}	0	-755	$3^\pm$

Table 2: Rate parameters for chemical reactions involving the CH radical considered in the uncertainty quantification analysis. All reactions and parameters are taken from the GRI-Mech 3.0 mechanism [49]. The rate constants are presented as $k = AT^n \exp(-E/RT)$ and the units for the reaction parameters are cm, mol, cal, K, and s.

182 database, there are 4 additional ion/neutral reactions from various other
183 sources. Two of those reactions, I07 and I08 in Tab. 1, originate from the
184 application of the average dipole orientation (ADO) theory [23] and are taken
185 as computed in Refs. [21] and [11], respectively. In the case of I08, an uncer-
186 tainty of $\pm 50\%$ is used in line with the quoted accuracy of the ADO theory,
187 while for I07 a larger uncertainty of a factor of 2 is considered. The uncer-
188 tainty range for I10 is quoted from the original reference [5] and the range
189 for I13 is arbitrarily set to a factor of 2 in the absence of specific data in
190 Ref. [24].

191 The neutral reactions in Tab. 2 are taken from GRI-Mech 3.0 and their
192 uncertainty ranges are estimated based on the discussion in the original GRI-
193 Mech 3.0 references. Messing et al. [60] suggests a value of around 25% as the
194 uncertainty range of N05. The uncertainty range of N04 is given by Dean

et al. [61] from shock tube experiments with atomic resonance absorption spectroscopy. The shock tube experiments of Rohrig et al. [62] provide the uncertainty range for N01. The rate coefficients of a theoretical study [63] on N02 are in agreement with those from a photolysis/probe experiment [64]. The review of reaction kinetic data of Baulch et al. [65] includes N07, which is listed with an uncertainty factor of ≈ 3 . As we were unable to find any discussion on the uncertainty of reactions N03 and N06, 25% is selected as the uncertainty range.

2.4. Uncertainty quantification framework

We use a probabilistic framework to represent uncertain model inputs as well as the dependence of the solution on these uncertain inputs. Uncertain reaction rates are parametrized in terms of canonical random variables, ξ_i , $i = 1, \dots, d$, where d is the number of reaction rate parameters allowed to vary in the UQ analysis.

Since the main goal of this work is a forward propagation of uncertainty from model parameters to observables using response surfaces and no prior knowledge about correlations is known, we assume the rates to be independent. Thus, the ξ_i 's are assumed to be independent and uniformly distributed over the interval $[-1, 1]$ and the uncertain inputs are specified in terms of a d -dimensional germ, $\boldsymbol{\xi} = \{\xi_1, \dots, \xi_d\}$.

The uncertainty ranges in Tables 1 and 2 are given either as a fraction or as multiplicative factor of the nominal rate constant. Thus, two types of parameterization are needed to map the canonical random variables ξ_i to the reaction parameters. For the first type, the random rate constant k_i follows

$$\frac{k_i}{k_{i,0}} = 1 + d_r \xi_i, \quad (1)$$

where $k_{i,0}$ is the nominal value of the rate constant of reaction i and d_r is the

uncertainty fraction. For example, $d_r = 0.5$ for I01 in Tab. 1. The reaction rate constant k_i is now a random variable centered at $k_{i,0}$ and uniformly distributed on the range $[k_{i,0}(1 - d_r), k_{i,0}(1 + d_r)]$. For the second type, k_i takes the form

$$\frac{k_i}{k_{i,0}} = f^{\xi_i}, \quad (2)$$

where f is the uncertainty factor. The uncertainty range of k_i is from $k_{i,0}/f$ to $k_{i,0}f$ and $\log k_i$ is a uniform random variable centered at $\log k_{i,0}$. An example is I07 in Tab. 1, for which $f = 2$. For both types of parametrization, the random rate constant k_i takes the nominal value $k_{i,0}$ when $\xi_i = 0$.

It is worth noting that the selection of uniform distributions for the canonical variables is convenient as it ensures that the rate constants are bounded. Nonetheless, the rate constants do not follow a uniform distribution, namely when a multiplicative uncertainty factor is specified.

We rely on a polynomial chaos expansion [66–68] to express the dependence of the quantities of interest on ξ . This functional representation is generically expressed as:

$$U(\xi) \approx \sum_{j=0}^{P+1} U_j \Psi_j(\xi), \quad (3)$$

where the Ψ_j are multi-dimensional Legendre polynomials that are orthogonal with respect to the uniform measure defined over $[-1, 1]^d$.

The coefficients U_j (modes) appearing in Eq. (3) are determined using a non-intrusive spectral projection (NISP) [69]. This amounts to evaluating the quantities of interest (QoIs) for selected values of the germ ξ based on independent simulations of the ignition event. The corresponding discrete values of the QoIs are then used in conjunction with quadrature formulas to evaluate the U_j 's.

Case	T_0 (K)	Φ	X_{CH_4} (%)	X_{O_2} (%)	X_{Ar} (%)	τ_{ign} (μs)	$n_{e,\text{max}}$ (10^{10} cm^{-3})	$\tau_{\text{max}} - \tau_{\text{ign}}$ (μs)	$n_{\text{CH,max}}$ (10^{13} cm^{-3})
1	2250	0.5	0.75	3.0	96.25	45 (55)	9.0 (5.1)	6.7 (52)	1.5
2	2500	0.5	0.50	2.0	97.50	23 (26)	9.4 (5.5)	6.9 (41)	2.0
3	2750	0.5	0.20	0.8	99.00	17 (18)	7.3 (4.1)	8.8 (41)	2.2
4	2500	1	0.50	1.0	98.50	33	11.5	8.8	4.2

Table 3: Initial temperature (T_0), mixture equivalence ratio (Φ) and composition (% by volume), ignition delay times (τ_{ign}), maximum number densities of electrons ($n_{e,\text{max}}$) and CH ($n_{\text{CH,max}}$). The time between ignition and peak electron concentration, $\tau_{\text{max}} - \tau_{\text{ign}}$, is also shown. The initial pressure is atmospheric for all cases. The numbers in parentheses refer to the experimental data from Ref. [70].

243 To accommodate the high dimensionality of the germ efficiently, an adap-
 244 tive pseudo-spectral approach is utilized [42, 43, 46]. As outlined in Ref. [46],
 245 our implementation relies on a nested construction based on the 1D Gauss-
 246 Kronrod-Patterson quadrature and accommodates a general (non-isotropic)
 247 sparse grid refinement algorithm [45]. The adaptation is based on a greedy
 248 refinement algorithm, which uses variance surplus as an error indicator. The
 249 refinement is carried out until a minimum threshold is obtained. As discussed
 250 in Refs. [42, 43, 46], the pseudo-spectral construction offers the advantage
 251 that a maximal basis can be determined without internal aliasing. For addi-
 252 tional details regarding the algorithms, see Refs. [42, 43, 46].

3. Results

3.1. Preliminaries

Four cases comprising different initial temperatures and mixtures are considered. The details of each case are presented in Tab. 3 alongside with the ignition delay times and peak number densities of electrons and CH radicals. The cases feature lean ($\Phi = 0.5$ for cases 1-3) and stoichiometric ($\Phi = 1$ for case 4) mixtures of CH_4 and O_2 in Ar diluent. Case 1 has the lowest initial temperature (2250 K) and the mixture with the highest strength ($X_{\text{Ar}} = 0.9625$), while case 3 has the highest initial temperature (2750 K) and the most diluted mixture ($X_{\text{Ar}} = 0.99$). The initial pressure is atmospheric for all cases and the pressure rise due to ignition is minimal (see section 3.2).

The conditions above are selected according to three guiding principles. Firstly, the three cases featuring lean mixtures (cases 1-3) match the initial conditions for the shock tube experiments in Karasevich's work [70], which we plan to extend and improve upon at KAUST. The data reported in Ref. [70] are the most extensive set of electron density measurements in shock-heated methane-oxygen mixtures to date. Secondly, the ion chemistry mechanism adopted in our work [11] was developed for lean to stoichiometric conditions, so that the mixtures that may be simulated are limited to equivalence ratios below or equal to unity. Thirdly, the level of dilution is chosen in order to limit the pressure and temperature rise associated with ignition, yet allow for appreciable amounts of electrons, which may be readily measured by a microwave-interferometric (MWI) technique under development at KAUST [71]. The detection threshold for the MWI device is estimated to be $1 \times 10^{10} \text{ cm}^{-3}$.

The ignition delay time is defined here as the time interval between the start of the simulation and the instant when the peak number density of the

CH radical occurs. The ignition delay time decreases from 45 to 17 μs with increasing temperature. For all cases, the computed ignition delay times are very close to those reported in the experiments [70].

The computed peak electron number densities fall in the range 7×10^{10} to $12 \times 10^{10} \text{ cm}^{-3}$ and are between 60 to 80% higher than the reported experimental values [70]. Despite those differences, the overall trend is well captured, as case 2 displays the highest peak electron number density and case 3 the lowest among all $\Phi = 0.5$ cases for both experimental and numerical results. The stoichiometric mixture yields the highest peak electron number density.

A significant difference between the present data and the experimental results in Ref. [70] pertains to the time interval between ignition and the time when the electron number density reaches its maximum value. In Tab. 3, this quantity is indicated as $\tau_{\text{max}} - \tau_{\text{ign}}$ and may be interpreted as an induction time for ionization. It is apparent that the induction time observed experimentally is significantly larger than that obtained in the simulations and the two datasets differ by a factor between 4 and 8. As it shall be discussed in detail in Section 3.2, we relate this discrepancy to differences in the chemionization rate of reaction prescribed in this work and the ionization rates observed experimentally in Ref. [70], whereby the latter is significantly lower than the former.

3.2. Overview

Figure 2 shows the temporal evolution of selected neutral and charged species during the ignition of a lean ($\Phi = 0.5$) methane-oxygen mixture with 2500 K initial temperature, atmospheric pressure, and 97.5% Ar diluent (case 2 in Tab. 3). As apparent, ignition occurs at 23 μs and is accompanied by the disappearance of the methane fuel, a sharp rise and decay of the

Figure 2: Temporal evolution of selected species during ignition (case 2 in Tab. 3). (a) Methane (CH_4), water (H_2O), and the radicals CH (multiplied by 10^9) and O . (b) Electrons and H_3O^+ are shown alongside minor cations ($\text{C}_2\text{H}_3\text{O}^+$ and HCO^+) and anions (OH^- and O^-). With the exception of H_3O^+ , the concentration of the ions is multiplied by a factor of 20 for the sake of clarity.

307 concentration of CH radical, and an increase in the rate of formation of
 308 water and O radical. Because of the minute amounts of charged species,
 309 the concentrations of the neutral molecules are not affected by the details
 310 of the ion chemistry. In particular, the consumption of CH and O through
 311 chemi-ionization is negligible. Due to the significant dilution, the equilibrium
 312 temperature is only 50 K higher than the initial conditions and the pressure
 313 increases by 3% from 1 to 1.03 atm (not shown).

314 Electrons are the most abundant negative charges and their number den-
 315 sity peaks at $9 \times 10^{10} \text{ cm}^{-3}$. The number density of the hydronium ion H_3O^+ ,
 316 which accounts for $\approx 99\%$ of all positive charges, is nearly equal to that of
 317 the electrons. The temporal evolution of electron and H_3O^+ is characterized
 318 by a rapid rise followed by a slow decay, which continues after the mixture
 319 is fully reacted and the temperature has reached its equilibrium value. The
 320 first ions appear concurrently with the rise in the concentration of CH during
 321 ignition, while the peak concentration of electrons and H_3O^+ are attained af-
 322 ter the peak in CH at the time when the methane fuel is consumed entirely
 323 ($\approx 29 \mu\text{s}$). These general observations agree with the analysis presented in
 324 Ref. [70] and hold for all cases.

325 The difference between the number densities of electrons and hydronium
 326 ion (H_3O^+) is nearly zero, indicating that charge neutrality is attained by
 327 summing the concentrations of these two charged species alone. It is worth-
 328 while to point out that zero-dimensional reactors maintain net charge neu-
 329 trality by virtue of stoichiometrically balanced reactions, while this is not
 330 the case for spatially inhomogeneous systems such as flames, where thin re-
 331 gions near the reaction zone are not neutral due to the concomitant effects
 332 of electric field, transport, and reactions [11].

333 Figure 2 also shows the number densities of other minor ions. The cation

334 $\text{C}_2\text{H}_3\text{O}^+$ is the second most abundant ion with a peak number density that
 335 is less than 1% of that of H_3O^+ . $\text{C}_2\text{H}_3\text{O}^+$ forms during the ignition event
 336 prior to the peak in H_3O^+ and electron concentrations and its maximum
 337 concentration is attained when CH peaks also. As the number density of
 338 $\text{C}_2\text{H}_3\text{O}^+$ decreases, that of the hydronium ion increases. Similar trends have
 339 been reported in the region ahead of the reaction zone of methane-oxygen
 340 flames [4].

341 The cation HCO^+ is also a minor positive ion. In contrast to $\text{C}_2\text{H}_3\text{O}^+$,
 342 the time evolution of HCO^+ resembles more closely that of H_3O^+ as the two
 343 ions peak nearly at the same time and display a slow decay. Finally, other
 344 minor negative ions worth mentioning are the OH^- and O^- anions, for which
 345 the number density is less than 1% of that of the electron. The remaining
 346 ions included in the kinetic mechanism appear in minute concentrations and
 347 are not shown nor discussed for the sake of brevity.

348 Figure 3 shows the time evolution of the rate of selected reactions among
 349 the 22 reactions included in the UQ analysis (see Section 3.3 for details).
 350 A reaction path diagram, detailing the most active pathways at the time of
 351 peak electron concentration (29 μs), is shown in Fig. 4.

352 As discussed earlier, the chemi-ionization reaction $\text{CH} + \text{O} \rightleftharpoons \text{HCO}^+ + \text{e}^-$
 353 (I01) is responsible for the production of charged species in flames [1] and has
 354 been the subject of numerous theoretical and experimental studies [57–59].
 355 Since this reaction involves both CH and O, it is clear that the maximum
 356 rate of chemi-ionization occurs after the peak in CH as the concentration of
 357 O increases monotonically towards its equilibrium value (see Fig. 2(a)).

358 From Fig. 3, the peak value of the chemi-ionization rate is $1.6 \times 10^{16} \text{ cm}^{-3}$
 359 s^{-1} and may be compared readily with the ionization rate inferred experi-
 360 mentally in Ref. [70]. At the temperature, pressure, and mixture conditions

Figure 3: Evolution of the rate of reaction for selected ion chemistry and neutral reactions during ignition (case 2 in Tab. 3). The reactions are grouped by magnitude in (a) and (b). Note that the rate of reactions N01 and N02 are divided by 10^4 . For consistency, the curve labeled I07-I08 reports the negative of the sum of the rate of reaction of $-\text{I07}$ (i.e., considered in the reverse direction) and I08, both of which are consumption channels for $\text{C}_2\text{H}_3\text{O}^+$ (see Fig. 1). In (a), the onset of ignition at $23 \mu\text{s}$ is indicated by a vertical line. In (a) and (b), the additional vertical line indicates the time when the pathway analysis (p.a.) is reported in Fig. 4, corresponding to the time of peak concentration of electrons and H_3O^+ ($29 \mu\text{s}$).

Figure 4: Pathway analysis at peak electron concentration ($29 \mu\text{s}$) for case 2. See Tab. 3 for details and Fig. 1 for reaction labels. The thickness of the arrows is proportional to the absolute value of the rate of reaction. Dotted shapes indicate that the charged species is in quasi-steady state (QSS). The percentages next to the arrows indicate the fraction of total loss or total gain for the species due to the pathway represented by the arrow. For example, 83% next to HCO^+ indicates that the reaction $\text{CH} + \text{O} \rightleftharpoons \text{HCO}^+ + \text{E}^-$ (I01) accounts for 83% of the total rate of production of HCO^+ , while the remaining 17% is due to reactions involving H, O, and $\text{C}_2\text{H}_3\text{O}^+$ (I07 and I08).

361 matching case 2 in this work (see Tab. 3), Karasevich reports a measured
 362 peak ionization rate equal to 1.7×10^{15} [70], which is approximately 10 times
 363 lower than the peak chemi-ionization rate from our simulation. Clearly, this
 364 is an important difference between experiments and simulations, which ex-
 365 plains the discrepancy in the ionization induction time ($\tau_{\max} - \tau_{\text{ign}}$) reported
 366 in Tab. 3. In this work, the rate coefficient for the chemi-ionization reaction
 367 (I01) is equal to $2.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at 2500 K. This value is in perfect agree-
 368 ment with the value obtained experimentally by Peeters and Christiaan [58],
 369 but a factor of two larger than the rate coefficient suggested by Karasevich
 370 ($1.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$) based on a zero-dimensional reactor analysis and best-
 371 fit to the shock tube data on electron number densities [70]. At this time,
 372 this difference between peak ionization rates in our study and Karasevich's
 373 work [70] is noted, but no further attempt at explaining its origin is made.

374 The newly produced ion HCO^+ is rapidly converted to H_3O^+ through the
 375 proton transfer reaction $\text{HCO}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}$ (I02). The production
 376 and consumption rates for HCO^+ are nearly identical and HCO^+ is in quasi-
 377 steady state (not shown). Recombination reactions between E^- and H_3O^+
 378 (I03, I04, I05, and I06) leading to various neutrals (H_2O , H , OH , O , and H_2)
 379 are active throughout the ignition event and become dominant late in the
 380 charged species decay phase from about $30 \mu\text{s}$ onwards.

381 In summary, the most important reactions involving charges species are
 382 chemi-ionization (I01), proton transfer (I02), and recombination (I03, I04,
 383 I05, and I06). This is clearly shown in Fig. 4, where the main pathways be-
 384 tween the charged species are shown schematically. While the pathways are
 385 shown when the concentration of electron and H_3O^+ is maximum ($29 \mu\text{s}$),
 386 similar considerations apply during the decay phase, even though recombi-
 387 nation reactions become more important. Furthermore, similar conclusions

388 apply for all four cases.

389 In Fig. 3(a), the neutral reactions responsible for most of the production
 390 and consumption of CH are shown also: $\text{H} + \text{CH}_2 \rightleftharpoons \text{CH} + \text{H}_2$ (-N02, here
 391 written in the reverse direction) and $\text{CH} + \text{O}_2 \rightleftharpoons \text{O} + \text{HCO}$ (N01). Notice
 392 that the rates for the two reactions are almost equal, indicating that the CH
 393 radical is in quasi-steady state, as confirmed by an additional analysis (not
 394 shown).

395 In addition to the main pathways involving ions and electrons described
 396 above, there exist a handful of reactions responsible for the formation and
 397 consumption of the minor ions $\text{C}_2\text{H}_3\text{O}^+$, OH^- , and O^- . The rates and path-
 398 ways of those reactions are shown in Fig. 3(b) and Fig. 4.

399 The proton transfer reaction $\text{H}_3\text{O}^+ + \text{CH}_2\text{CO} \rightleftharpoons \text{C}_2\text{H}_3\text{O}^+ + \text{H}_2\text{O}$ (I09) is
 400 thermodynamically favorable (i.e, CH_2CO has a higher *proton affinity* than
 401 H_2O) and is the main channel for the formation of $\text{C}_2\text{H}_3\text{O}^+$. Consumption
 402 occurs when $\text{C}_2\text{H}_3\text{O}^+$ combines with O and H to form HCO^+ and the neutral
 403 species CH_2O (I08) and CH_3 (I07), respectively. Together, those reactions
 404 also contribute to the production of HCO^+ , which is dominated by the chemi-
 405 ionization reaction (I01) nonetheless. The consumption channels for $\text{C}_2\text{H}_3\text{O}^+$
 406 become active only as the concentrations of O and H increase from ignition
 407 onwards and are inactive before, thereby explaining why $\text{C}_2\text{H}_3\text{O}^+$ displays
 408 an early peak compared to H_3O^+ .

409 Electrons make up more than 99% of the negative charges, while OH^-
 410 and O^- are present in minute amounts. Figure 4 illustrates that there ex-
 411 ist two sets of production and consumption channels that shuffle negative
 412 charges, which cascade from E^- to OH^- to O^- . The production channels
 413 involve the electron attachment $\text{HO}_2 + \text{E}^- \rightleftharpoons \text{OH}^- + \text{O}$ (-I10, here written
 414 in the reverse direction) and charge transfer $\text{OH} + \text{OH}^- \rightleftharpoons \text{O}^- + \text{H}_2$ (-I13,

Figure 5: Statistics from the UQ analysis of the time evolution of the number density of CH for all four cases (see Tab. 3). Mean μ (thick solid line), standard deviation σ (thick dashed line), and $1-\sigma$ range (gray shaded region). The coefficient of variation (COV) σ/μ (thin dashed line) is plotted on the right y axis.

here written in the reverse direction) reactions. Overall, electron attachment to HO_2 is responsible for 30% of the total electron consumption rate. In addition to chemi-ionization (66%), the electron production channels are electron detachment processes (I11, I12, I14, and I15), whereby the anions combine with a neutral species (CO , H_2 , and H) and release a free electron. Altogether, electron detachment reactions are responsible for approximately 30% of the total electron production.

3.3. Uncertainty Quantification

3.3.1. CH

The results of the uncertainty quantification analysis on the CH radical are shown in Fig. 5, where various statistical quantities are reported as a

function of time during the ignition event for cases 1 through 4 (see Tab. 3). Qualitatively, the mean of the CH number density follows the trends shown in Fig. 2, where CH was shown to grow rapidly and decay in correspondence of ignition.

Comparing the four cases, one concludes that the mean number density is largest for the stoichiometric mixture (case 4, $\Phi = 1$) and smallest for the lean mixture at the lowest initial temperature (case 1, $\Phi = 0.5$). At ignition, the maximum of the mean number density in the two cases differ by a factor of two. The coefficient of variation (COV), i.e., the ratio σ/μ of the standard deviation to the mean, is also shown. The standard deviation is between 20 to 30% of the mean value at those times when there exists a non-negligible amount of CH. For all cases and mixtures, the COV reaches a local minimum in correspondence of ignition and is larger during the rise and decay phases. Among all mixtures, case 4 ($\Phi = 1$) displays the smallest COV ($\sigma/\mu \approx 0.17$) and case 1 ($\Phi = 0.5$) the highest ($\sigma/\mu \approx 0.26$).

Figure 6 illustrates the contribution of the uncertain parameters of selected reactions to the variance of the number density of CH. The total sensitivity index provides a global, variance-based measure of the contribution of the corresponding uncertain rate parameter to the selected QoI. Specifically, the total sensitivity index T_i [72, 73] accounts for both a direct contribution of the i -th component of the germ (arising from monomial terms in ξ_i), as well as an indirect contribution due to mixed terms involving ξ_i . As discussed in Ref. [74], the total sensitivity indices may be readily obtained from the PC coefficients of selected QoIs.

The most important contribution (contributing up to 100% and in excess of 50% at all times and for all cases) originates from the main consumption channel $\text{CH} + \text{O}_2 \rightleftharpoons \text{O} + \text{HCO}$ (N01). The second most important reaction,

Figure 6: Evolution of the total sensitivity indices for the number density of CH with respect to the rate parameters of the following reactions: $\text{CH} + \text{O}_2 \rightleftharpoons \text{O} + \text{HCO}$ (N01), $\text{CH} + \text{H}_2 \rightleftharpoons \text{H} + \text{CH}_2$ (N02), and $\text{H} + \text{CH} \rightleftharpoons \text{C} + \text{H}_2$ (N04). For each sensitivity index, all four cases are shown (see Tab. 3). Data for the sensitivity indices with respect to the parameters of reaction N04 are plotted on the right y axis for the sake of clarity.

453 contributing up to 50%, is the production channel $\text{H} + \text{CH}_2 \rightleftharpoons \text{CH} + \text{H}_2$
 454 ($-\text{N02}$, here written in the reverse direction). A second consumption chan-
 455 nel $\text{H} + \text{CH} \rightleftharpoons \text{C} + \text{H}_2$ (N04) accounts for less than 20% of the standard
 456 deviation.

457 From Fig. 6, it is apparent that the relative importance of each reaction
 458 does not change significantly during ignition and is only slightly affected
 459 by the mixture stoichiometry and initial conditions. All cases display the
 460 same trends, with the exception of very early and late times before and after
 461 ignition, when the number density of CH is minute and negligible. One
 462 notable exception is the reaction $\text{H} + \text{CH} \rightleftharpoons \text{C} + \text{H}_2$ (N04), for which the
 463 sensitivity index does vary among cases and is largest for case 4 ($\Phi = 1$).

464 From a practical perspective, we conclude that conducting experiments at
 465 stoichiometric conditions is most desirable since higher CH number densities
 466 are beneficial in order to maximize the signal to noise ratio. On the other
 467 hand, the relative importance of all reaction is unchanged and the analysis
 468 and results are applicable over a wide range of stoichiometries ($0.5 \leq \Phi \leq 1$)
 469 and conditions (e.g., dilution, temperature, etc.).

470 3.3.2. Electron and H_3O^+

471 As discussed in Section 3.2, electrons E^- and hydronium ions H_3O^+ are
 472 the most abundant charged species and account for close to 99% of the nega-
 473 tive and positive charges. Due to charge neutrality, their concentrations are
 474 nearly identical throughout ignition, as shown in Fig. 2. In the following, we
 475 shall comment on the results of the uncertainty quantification analysis for
 476 electrons only since identical results hold for H_3O^+ .

477 In Fig. 7, the time evolution of mean and standard deviation of the num-
 478 ber density of electrons is shown for all four cases. Due to the abundance
 479 of CH radicals, case 4 displays the largest peak value of the mean electron

Figure 7: Statistics from the UQ analysis of the time evolution of the number density of E^- for all four cases (see Tab. 3). Mean μ (thick solid line), standard deviation σ (thick dashed line), and 1- σ range (gray shaded region). The coefficient of variation (COV) σ/μ (thin dashed line) is plotted on the right y axis.

number density. Similarly to the results for CH, the mean electron number density is lowest for case 1. The standard deviation σ is maximum shortly after ignition in correspondence with the peak mean electron number density.

At peak electron concentration, the COV σ/μ is such that $0.2 \leq \sigma/\mu \leq 0.3$. From the time of ignition onwards, the ratio decreases monotonically and reaches an asymptotic value ≈ 0.1 late during the electron decay phase. In part, the trend of decreasing σ may reflect the lower uncertainty range for the recombination rates (I03-I06), set at 25%, compared to the chemi-ionization reaction (I01) and key CH reaction (N01), which are both set at 50% (see Tab. 1).

An important observation is that the $\mu + \sigma$ and $\mu - \sigma$ curves, which mark the range of number densities within the $1\text{-}\sigma$ limit, do not show a significant shift in timing, rather only a change in magnitude in response to the variation in the uncertain reaction parameters. This behavior may be due to two concomitant physical effects. On the one hand, we note that the temperature remains approximately constant throughout the ignition event due to the significant inert dilution. Consequently, the frequently observed [29, 75] amplification of the effect of reaction rate uncertainties due to large temperature variations may not occur in the present case. On the other hand, it is also likely that ions follow quasi-steady state dynamics closely. The fact that we have focused solely on rate uncertainties affecting ions' number densities, rather than including heat-releasing reactions, further contributes to the absence of variation in reaction timescales as a result of uncertainty. Further analysis of these mechanisms is ongoing and will be reported at a later date.

As shown in Fig. 8, the chemi-ionization reaction (I01) and the main consumption reaction for CH (N01) account for most of the variance in the time evolution of the electron number density and their importance per-

Figure 8: Evolution of the total sensitivity indices for the number density of E^- with respect to the rate parameters of the following reactions: $CH + O \rightleftharpoons HCO^+ + E^-$ (I01), $CH + O_2 \rightleftharpoons O + HCO$ (N01), and all recombination reactions $H_3O^+ + E^- \rightarrow \text{products}$ (I03-I06). In the case of the recombination reactions, the sensitivity indices are summed together. For each sensitivity index, all four cases are shown (see Tab. 3).

sists late into the decay phase. The total sensitivity index due to $\text{CH} + \text{O} \rightleftharpoons \text{HCO}^+ + \text{E}^-$ (I01) is highest (≈ 0.8) for the stoichiometric case (case 4) and it is lowest for case 1 (≈ 0.6). Conversely, the total sensitivity index for $\text{CH} + \text{O}_2 \rightleftharpoons \text{O} + \text{HCO}$ (N01) is lowest for case 4 and highest for case 1.

From a practical perspective, the trends shown in Fig. 8 are important, as they point to the role of key neutral reactions involving the CH radical in controlling the mean and variance of the electron number density in an indirect fashion. Moreover, it is shown that stoichiometric mixtures may be preferred over lean ones, as they mitigate the role of neutral chemistry in controlling ionization rates.

The sensitivity index related to recombination reactions does not increase above all others until late into the decay process, when the electron number density has dropped more than fourfold with respect to its peak value. Thus, the contribution of the uncertainty in the rate parameters of the recombination reactions is overshadowed by that of the chemi-ionization reaction until late into the electron decay phase. The sensitivity index due to recombination reactions is highest and grows the earliest for the stoichiometric case (case 4) compared to the lean mixtures (cases 1, 2, and 3), since the decay rate is more rapid for higher values of peak electron density. The details of the recombination process are key to explaining the observed trends and are discussed later in Section 3.3.4.

Based on the data in Fig. 8, a final observation pertains to the absence of any reaction responsible for the production or consumption of $\text{C}_2\text{H}_3\text{O}^+$, OH^- , and O^- . As noted before in Section 3.2, the amounts of those ions are negligible and the sensitivity of the statistics of the electron and hydronium ion's number densities to those secondary reactions is negligible also.

Figure 9: Statistics from the UQ analysis of the time evolution of the number density of $\text{C}_2\text{H}_3\text{O}^+$ for all four cases (see Tab. 3). Mean μ (thick solid line), standard deviation σ (thick dashed line), and $1\text{-}\sigma$ range (gray shaded region). The coefficient of variation (COV) σ/μ (thin dashed line) is plotted on the right y axis.

3.3.3. Minor ions

The minor ions $\text{C}_2\text{H}_3\text{O}^+$, HCO^+ , OH^- , and O^- are in or near quasi-steady state (not shown) and their evolution is characterized by a balance between production and consumption channels (see Fig. 3). Furthermore, the reactions involving those ions appear to be secondary and driven mostly by the primary populations of electrons and H_3O^+ ions as shown by the pathway analysis in Fig. 4. Even though those ions play a minor role in controlling the charge evolution during ignition, their behavior is influenced by their quasi-steady state (QSS) dynamics and warrants a more careful analysis.

Figure 9 shows the mean, standard deviation, and $1\text{-}\sigma$ range for $\text{C}_2\text{H}_3\text{O}^+$. In agreement with the behavior portrayed in Fig. 2(b), the mean of $\text{C}_2\text{H}_3\text{O}^+$

Figure 10: Evolution of the total sensitivity indices for the number density of $\text{C}_2\text{H}_3\text{O}^+$ (case 4, see Tab. 3). Among others, the indices for the following reactions are shown: $\text{CH} + \text{O} \rightleftharpoons \text{HCO}^+ + \text{E}^-$ (I01), $\text{CH} + \text{O}_2 \rightleftharpoons \text{O} + \text{HCO}$ (N01), $\text{CH} + \text{H}_2 \rightleftharpoons \text{H} + \text{CH}_2$ (N02), $\text{HCO}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}$ (I02), and $\text{HCO}^+ + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_3\text{O}^+ + \text{H}$ (I07). In the case of the recombination reactions (I03-I06), the sensitivity indices are summed together.

544 peaks prior to ignition and well in advance of the electron and H_3O^+ means.
545 The mean is maximum for the stoichiometric case (case 4). A striking dif-
546 ference with respect to the time evolution of the electrons in Fig. 7 is the
547 relative large values of σ . Note that the COV σ/μ is well above 40% for all
548 cases. Similarly high σ/μ ratios occur for other QSS ions such as HCO^+ ,
549 OH^- , and O^- (not shown).

550 Figure 10 portrays the total sensitivity indices for the standard deviation
551 of $\text{C}_2\text{H}_3\text{O}^+$ and reveals that uncertainty in the number density of this ion is
552 largely due to the chemi-ionization reaction (I01) and the two key neutral CH
553 reactions (N01 and N02), which do not directly involve $\text{C}_2\text{H}_3\text{O}^+$. The sensi-

554 tivity index for the proton transfer reaction $\text{HCO}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}$
 555 (I02) peaks at $\approx 20\%$ early in the ignition process and decreases monotoni-
 556 cally. Among all reactions involving $\text{C}_2\text{H}_3\text{O}^+$, only the consumption reaction
 557 $\text{C}_2\text{H}_3\text{O}^+ + \text{H} \rightleftharpoons \text{HCO}^+ + \text{CH}_3$ (–I07, here written in the reverse direction)
 558 contributes to the variance.

559 We conclude that the uncertainty in the concentration of $\text{C}_2\text{H}_3\text{O}^+$ is in-
 560 direct and due to the effect of the rate parameters on the populations of
 561 electrons and hydronium ions. Similar considerations apply to the statistics
 562 of HCO^+ , with the exception of a strong sensitivity to the proton transfer
 563 reaction $\text{HCO}^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CO}$ (I02), which affects directly both
 564 H_3O^+ and HCO^+ (not shown).

565 In the case of the anions OH^- and O^- , there exists a heightened sensitivity
 566 to the internal production and consumption channels in addition to that
 567 related to the chemi-ionization and CH neutral reactions. The σ associated
 568 with the concentrations of both OH^- and O^- originates mostly from the
 569 main production and consumption channels for OH^- , respectively: $\text{HO}_2 +$
 570 $\text{E}^- \rightleftharpoons \text{OH}^- + \text{O}$ (–I10, here written in the reverse direction) and $\text{OH}^- +$
 571 $\text{H} \rightleftharpoons \text{H}_2\text{O} + \text{E}^-$ (I11) (not shown).

572 3.3.4. Peak number density and half time

573 In this section, we present total sensitivity indices for the peak number
 574 density and half time of electrons and all ions. The data pertain to case
 575 2, the lean ($\Phi = 0.5$) mixture with 97.5% Ar dilution. For each species of
 576 interest, the “half time” is defined as the time interval between the peak
 577 number density and the time when the number density drops to half of the
 578 peak value. In the remainder of this section, the peak number density and
 579 half time are given the symbols n_{max} and $\tau_{1/2}$, respectively.

580 From the perspective of maximizing the signal to noise ratio in experi-

Figure 11: Total sensitivity indices for the peak species concentration with respect to each reaction included in the UQ analysis. The data are based on case 2 (see Tab. 3). The diameter of the circle is proportional to the sensitivity index for the species/reaction pair. The largest (smallest) circle corresponds to a sensitivity index equal to 0.877 (resp. 8.5×10^{-5}). The smallest circles may not be visible.

581 ments, the maximum number density of electrons and ions is an ideal mea-
582 surable quantity of interest. Furthermore, the rate of decay of the electron
583 and hydronium concentrations is another sensible choice to characterize the
584 recombination process.

585 Figure 11 shows the total sensitivity indices for $n_{\max}$ for various species/reactions
586 pairs. For all charged species, the largest indices are those related to chemi-
587 ionization (I01) and the key consumption channel for CH (N01). A second
588 important contribution is the CH production channel (N02). Interestingly,
589 I01, N01, and to some extent N02 account for most of the variance for all
590 species. In addition to those indices, HCO^+ is affected by the proton transfer
591 (I02), $\text{C}_2\text{H}_3\text{O}^+$ is affected by its production (I09) and consumption channels

Figure 12: Total sensitivity indices for the decay time ($\tau_{1/2}$) of species' number density with respect to each reaction included in the UQ analysis. The data are based on case 2 (see Tab. 3). The diameter of the circle is proportional to the sensitivity index for the species/reaction pair. The largest (smallest) circle corresponds to a sensitivity index equal to 0.851 (resp. 1.4×10^{-4}). The smallest circles may not be visible.

592 (I07 and I08), and the anions OH^- and O^- are affected by the OH^- produc-
 593 tion (I10) and consumption (I11) reactions. Naturally, N01 and N02 account
 594 for the contributions to the variance of the peak CH number density entirely.

595 An important observation pertains to the role of the recombination reac-
 596 tions, for which the total sensitivity indices are negligibly small in Fig. 11.
 597 We conclude that the contribution of the recombination rates to the variance
 598 of the peak concentration of all charged species is negligibly small. This
 599 statement is in agreement with the time evolution of the total sensitivity
 600 indices for the electron number density shown in Fig. 7.

601 Figure 12 shows the total sensitivity indices for $\tau_{1/2}$ for various species/reactions
 602 pairs. Similarly to the data in Fig. 11, there exist large indices for I01, N01,

Figure 13: Statistics of the time evolution of the number density of E^- for case 2 (see Tab. 3). Inverse mean $1/\mu$ (thick solid line) and $1\text{-}\sigma$ range $1/(\mu \pm \sigma)$ (gray shaded region). The case with the unperturbed rate parameters is also shown (open circles).

and N02 for all species, even though indices related to other reactions are more prominent. Examples of minor reactions' indices are those related to the pathways for $\text{C}_2\text{H}_3\text{O}^+$ and the anions OH^- and O^- .

The most noticeable characteristic of the total sensitivity indices in Fig. 12 is that the indices related to the recombination reactions (I03-I06) are relatively small, albeit larger than those for the peak number density (see Fig. 11). Conversely, the total sensitivity index related to the chemi-ionization reaction is even larger for $\tau_{1/2}$ than for n_{max} . At first, this is surprising, considering that $\tau_{1/2}$ may seem an obvious quantity of interest with important sensitivities to recombination reactions.

In an effort to explain the observed behavior, we consider a simplified model for the evolution of the electron number density during the decay

phase. Recombination reactions between electrons and hydronium ions (I03-I06) are second-order reactions. Under the assumption of charge neutrality, one may assume that $n_{\text{E}^-} = n_{\text{H}_3\text{O}^+}$. If other reactions are negligible and k is the rate of recombination, the number density of electrons obeys the following ODE:

$$\dot{n} = -kn^2, \quad (4)$$

which may be easily integrated with initial conditions $n(0) = n_0$ to yield

$$n(t) = \frac{n_0}{1 + t/\theta}, \quad (5)$$

where $\theta = 1/(kn_0)$ is a time constant. It is apparent that, since $n(\theta)/n_0 = 1/2$, θ represents the time taken for the number density to decrease to half of the initial value n_0 .

We hasten to note that, in Eq. (5), $t = 0$ indicates the initial time when the number density is n_0 . Thus, $t = 0$ does not correspond to the initial time in the ignition process, rather to an arbitrary time when the model in Eq. (4) becomes applicable. In the remainder of the discussion, one may interpret $t = 0$ as corresponding to a time shortly after the peak electron concentration is attained.

The behavior implied by Eq. (5) is shown in Fig. 13, where $1/n_{\text{E}^-}$ and $1/\mu$ (μ is the mean electron number density) are shown for case 2. From Fig. 13, it is apparent that from about 15 μs after ignition onwards, the rate of change of the electron number density is consistent with the simple model in Eq. (4). Furthermore, the time evolution obtained with the unperturbed rate parameters is equal to the mean number density.

The time constant θ is a function of the number density of electrons n_0 at time $t = 0$, which corresponds approximately to the onset of the decay phase. The simple model in Eq. (5) suggests that due to the second-order

639 nature of the recombination reaction, the electrons' half time is a strong
 640 function of the electron number density. Since the variance of the electron
 641 number density is most sensitive to the chemi-ionization reaction (I01), this
 642 heightened sensitivity carries over to the half time $\tau_{1/2}$.

643 This observation has important implications for experiments. If one aims
 644 at improving the rate coefficients of the recombination reactions, measuring
 645 the decay rate from peak to 50% of peak electron number density may not be
 646 quite helpful due to the small sensitivity indices associated with the recom-
 647 bination reactions of interest. Careful inspection of Fig. 7 reveals that one
 648 needs to wait late into the decay process ($t \geq \tau_{\text{ign}} + 40 \mu\text{s}$) prior to the sen-
 649 sitivity to the recombination reactions becoming the dominant contribution
 650 to the electron number density variance. By that time, the number density
 651 of electrons may have decreased to less than 20% of the peak value. Accurate
 652 measurements may be difficult to accomplish late in the electron decay phase
 653 as the signal to noise ratio degrades rapidly with decreasing electron number
 654 density.

655 4. Conclusions

656 This paper presented the implementation of UQ methods towards the
 657 quantitative characterization of ion chemistry reactions during the oxida-
 658 tion of methane, and thus gain insight into the evolution of charged species.
 659 Attention was specifically focused on the ignition of dilute lean and stoichio-
 660 metric methane-oxygen mixtures under isochoric and adiabatic conditions.

661 To describe the oxidation and ionization processes adequately, the present
 662 analysis relied on the GRI-Mech 3.0 mechanism [49], which was augmented
 663 with the ion chemistry assembled by Prager et al. [11]. We employed the TChem li-
 664 brary [48] to integrate the stiff system of ODEs describing the evolution of

665 the system.

666 The UQ analysis focused on the impact of uncertain rate parameters on
667 the prediction of the concentrations of the charged species. In order to ren-
668 der the uncertainty quantification analysis manageable, a first screening was
669 conducted to determine a reduced set of elementary reactions that affect ion
670 formation and recombination significantly. To this end, a heuristic reaction
671 analysis approach was used, leading to the selection of 15 ion chemistry re-
672 actions and 7 reactions involving neutrals. We adopted the chemi-ionization
673 rate recommended by Warnatz [56], and whenever possible relied on the
674 UMIST database [22] to determine suitable ranges for the uncertain rate
675 parameters. A sparse adaptive pseudo-spectral sampling technique was then
676 applied in order to efficiently sample the resulting 22-dimensional probability
677 space used to parametrize the uncertain rates of reactions.

678 The UQ study considered four cases comprising different initial temper-
679 atures and mixtures of CH_4 and O_2 in Ar diluent. These match the initial
680 conditions in shock-tube experiments [70] available in the literature and fea-
681 ture three cases with lean mixtures ($\Phi = 0.5$) of various strengths and a
682 stoichiometric case (case 4). The analysis of the computations revealed that:

- 683 1. The most important contribution to the number density of CH origi-
684 nates from the main consumption channel $\text{CH} + \text{O}_2 \rightleftharpoons \text{O} + \text{HCO}$, fol-
685 lowed by the production channel $\text{H} + \text{CH}_2 \rightleftharpoons \text{CH} + \text{H}_2$. The relative
686 importance of these two reaction does not change significantly during
687 ignition, and is only slightly affected by the mixture stoichiometry and
688 initial conditions. From a practical perspective, the predictions sug-
689 gest that conducting experiments at stoichiometric conditions is most
690 desirable because higher CH number densities are beneficial from the
691 perspective of maximizing signal to noise ratio.

- 692 2. Electrons E^- and hydronium ions H_3O^+ are the most abundant charged
693 species and account for close to 99% of the charge. In zero-dimensional
694 reactors, the mixture is characterized by charge neutrality, so that the
695 concentrations of E^- and H_3O^+ are nearly identical throughout igni-
696 tion. Due to the abundance of CH radicals, the stoichiometric case
697 displays the largest peak value of electrons. The standard deviation σ
698 is maximum shortly after ignition in correspondence with peak electron
699 concentration, when the coefficient of variation σ/μ ranges between 0.2
700 and 0.3. From the time of ignition onwards, the σ/μ ratio decreases
701 monotonically and reaches an asymptotic value ≈ 0.1 late during the
702 electron decay phase.
- 703 3. The chemi-ionization reaction and the main consumption reaction for
704 CH account for most of the variance in the time evolution of the elec-
705 tron number density. This trend persists until late into the decay pro-
706 cess. For the case of the stoichiometric mixture, the total sensitivity
707 index due to $CH + O \rightleftharpoons HCO^+ + E^-$ is highest (≈ 0.8) and it is
708 lowest for case 1 (≈ 0.6). Conversely, the total sensitivity index for
709 $CH + O_2 \rightleftharpoons O + HCO$ is lowest for case 4 and highest for case 1.
710 From a practical perspective, the observed trends point to the role of
711 key neutral reactions involving CH in controlling the mean and vari-
712 ance of the electron number density in an indirect fashion, and that
713 stoichiometric mixtures are preferred over lean ones, as they mitigate
714 the role of neutral chemistry in controlling electron concentrations.
- 715 4. The sensitivity index of the electron number density due to the recom-
716 bination reactions does not increase above all others until late into the
717 decay process, when the electron number density has dropped more
718 than fourfold with respect to its peak value. Thus, the contribution

of the uncertainty in the recombination reactions is overshadowed by that of the chemi-ionization reaction until late into the electron decay phase. The sensitivity index due to recombination is highest and grows sooner for the stoichiometric case.

5. The contribution of the recombination rates to the variance of the peak concentration of all charged species is negligibly small. The total sensitivities of the decay timescale due to recombination reactions are also small. These observations have important implications from an experimental perspective. If one aims at improving the rate parameters of the recombination reactions, measuring the electron decay rate from peak to 50% of the peak value may not be quite helpful due to the small sensitivity indices of this quantity of interest to the recombination reactions. Furthermore, these trends indicate that one needs to wait late into the decay process before the recombination reactions become the dominant contributors to the statistics of the number density of E^- . By then, the number density of electrons may have decreased to less than 20% of the peak value and accurate measurements may be difficult to accomplish.

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