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 $CH + O \rightleftharpoons HCO^+ + E^-$ and to the main CH consumption reaction $CH + O_2 \rightleftharpoons O + HCO$. Similar conclusions hold 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 $H_3O^+ + E^- \rightarrow$ 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., $C_2H_3O^+$, 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.

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1. Introduction

Excluding secondary ionization of neutral molecules by high-energy electron impact during discharges, the chemi-ionization reaction $CH + O \rightleftharpoons HCO^+ + E^-$ [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 cations and electrons re-establish charge neutrality [6].

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

Given the important limitations in the accuracy and completeness of experimental databases, numerical simulations are recognized as a valuable tool to characterize the interplay of reactions, transport of neutral and charged species, and electric fields.

An increasing number of numerical studies has been undertaken to simulate the distribution of charged species in flames [11,12] and the effect of external voltages on flame properties and behavior [13–15], and to calculate transport properties and collision rates of electrons in combustion gases [16–18].

Early attempts to formulate a complete ion chemistry mechanism for numerical simulations of ions in flames are due to Brown et al. [19–21]. Prager et al. [11] assembled the most comprehensive and detailed mechanism for the formation of ions and electrons in flames up to date. The mechanism includes electrons, 4 cations, and 6 anions. It consists of 67 reactions and focuses on ion chemistry pathways in lean methane-oxygen flames. In developing the mechanism, Prager et al. [11] relied both on the previous mechanism and rate parameters proposed by Brown et al. [19–21] as well as the comprehensive analysis of ion pathways in methane-oxygen flames by Goodings et al. [4,5]. The authors [11] then proceeded to update the reaction rate parameters based on the most recent data available in the literature, largely from the UMIST database for astrophysical chemistry [22], and they computed rate parameters based on the average dipole orientation (ADO) theory [23], when data were not available. Additional rate parameters were obtained from Refs. [24–28].

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

Despite the simplicity of the canonical setting of zero-dimensional isochoric and adiabatic reactors, the problem of quantifying the impact of reaction rate uncertainties remains quite challenging, because these lead to considerable computational difficulties associated with severe stretching and, in extreme cases, bifurcation of concentration trajectories during ignition. In the case of the so-called intrusive methods [29–32], these phenomena may lead to instabilities in the governing system and several approaches have been developed to mitigate those issues. Those include adaptive basis representations [30,31] and filtering [40] techniques. In the case of non-intrusive polynomial chaos (PC) methods [32,35–39] and response surface methods [33,34], the problem manifests itself in terms of increasing resolution requirements, namely the need for a basis with rapidly growing dimension [30,41]. This issue compounds the well known challenges associated with the curse of dimensionality and has constrained most previous applications to a small or moderate number of uncertain parameters.

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

The paper is organized as follows. Section 2 introduces the kinetic mechanism employed in this study, specifies ranges of uncertain parameters deemed most relevant to the evolution of electrons and ions, and provides a brief outline of the UQ methods. In Section 3, results from the UQ analysis are presented, focusing on quantitative metrics for key pathways to ion and electron formation in flames. Conclusions are presented in Section 4.

2. Models and methods

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

In this section, the kinetic and thermodynamic data for neutral and charged species are presented first. We then discuss the quantities of interest that are central to the analysis and formulate the UQ problem. Finally, the 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^+, $C_2H_3O^+$, 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 $C_2H_3O^+$ and CH_5O^+ possess the acetyl cationic [52] and the methoxymethyl cationic [53] structures, respectively. Two neutral species (CH_3CO and C_2H_5OH) 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 $C_2H_3O^+$, 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 by CH in the production of electrons and ions through the chemi-ionization reaction.

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

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

This selection process yielded 15 reactions: the chemi-ionization reaction, 8 reactions involving cations, and 6 reactions involving anions. Using the same approach for all reactions involving the